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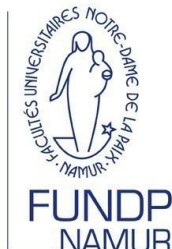
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**SYNTHESIS, SELF-ASSEMBLY AND OPTOELECTRONIC
PROPERTIES OF HETEROAROMATIC CHROMOPHORES**

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*"O frati," dissi, "che per cento milia
perigli siete giunti a l'occidente,
a questa tanto picciola vigilia*

*d'i nostri sensi ch'è del rimanente,
non vogliate negar l'esperienza,
di retro al sol, del mondo senza gente.*

*Considerate la vostra semenza:
fatti non foste a viver come bruti,
ma per seguir virtute e canoscenza".*

(Dante Alighieri, Divina Commedia, Inferno canto XXVI, 116-120)

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List of Abbreviations

HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
HLG	Homo-Lumo Gap
PIB	“a particle in a box”
BLA	Bond Length Alternation
PITN	Polyisothianaphthene
ECL	Effective Conjugated Length
PEDOS	Poly(3,4-ethylenedioxy-selenophene)
PEDOT	Poly(3,4-ethylenedioxythiophene)
NLO	Non-Linear Optics
ICT	Internal Charge Transfer
TEE	Tetraethynylethene
TCNE	Tetracyanoethene
CEE	Cyanoethynylethenes
WOLEDs	White Organic Light Emitting Diodes
PDT	Photodynamic Therapy
OFET	Organic Field Effect Transistor
AFM	Atomic Force Microscopy
STM	Scanning Tunneling Microscopy
HOPG	Highly Oriented Pyrolytic Graphite
PMMA	Poly(methyl methacrylate)
((	Microwave Irradiation
HMQC	Heteronuclear Multiple Quantum Correlation
LDOS	Local Density of States
ML	Mono Layer
DCTB	<i>trans</i> -2-[3-(4- <i>t</i> -butylphenyl)-2-methyl-2-propenylidene]malonitrile
PCBM	phenyl-C61-butyric acid methyl ester
TEM	Transmission Electron Microscopy
ITO	Indium Tin Oxide
EDC	1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
EDX	Energy Dispersive X-Ray Analysis
HBTU	O-Benzotriazole- <i>N,N,N',N'</i> -tetramethyl-uronium-hexafluoro-phosphate
P3HT-Py	Poly(3-hexylthiophene)-pyrene
SNOM	Scanning Near-field Optical Microscopy
EQE	External Quantum Efficiency

Abstract

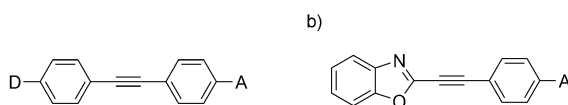
Conjugated molecules constitute the elemental bricks of molecular materials that have given rise to considerable research efforts in basic and applied material science to develop new materials for information, communication and lighting technologies. The interest around highly conjugated molecules has been fueled by advances in synthetic methodology, such as the development of metal-catalyzed cross-coupling reactions, and by advances in analytical techniques that now allow an accurate characterization.

The ambitions of the present work consisted to have a detailed understanding on the relationships between properties and the structure of π -conjugated skeleton. To do this end, different classes of π -conjugated organic compounds were investigated delving into their synthetic processes and chimico-physical features.

In *Chapter 1*, a short account on the relationships between the structure of conjugated molecules and the Highest Occupied Molecular Orbital (HOMO) Lowest Unoccupied Molecular Orbital (LUMO) gap is given to the reader. This chapter also reports a brief outline of the manuscript.

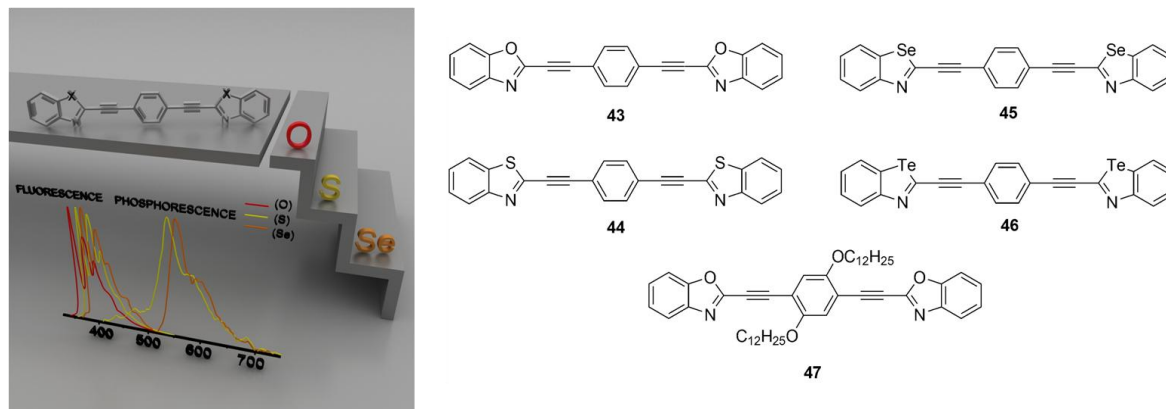
The first part of the present doctoral work is described in *Chapter 2* where organic π -conjugated molecules were investigated as wavelength shifters for an important medical imaging technique, the Positron Emission Tomography. Specifically, two approaches were considered to achieve the wavelength conversion, the push-pull approach and the heteroatom effect. Within the push-pull approach, the synthesis of linear π -conjugated systems based on diphenylacetylene backbone, **34-42**, is reported. All compounds were prepared exploiting *Sonogashira*-type cross-coupling reactions. Evidences for the successful synthesis of compounds **34-42** were obtained by ^1H - and ^{13}C -NMR spectroscopy and high resolution mass spectrometric (HR-MS) experiments. In collaboration with *Dr. Andrea Barbieri (CNR, ISOF, Bologna)* the photophysical properties of these dyes were investigated in solution and in polymeric matrices (PMMA) as wavelength converters to be incorporated onto a new concept of Positron Emission Tomography (PET) scanner. All compounds revealed to be highly luminescent in condensed media from ICT excited states with large Stokes shifts. In general terms, most of the studied luminescent molecules showed a neat increase of the quantum yield when embedded in a rigid environment with respect to solution, in some cases remarkably higher than one order of magnitude (**38**), and mono-exponential luminescence decays with excited state lifetimes shorter than 3 ns.

In the same chapter, a different π -conjugated system was also developed. In particular, a series of organic chromophoric compounds characterized by benzazole-based groups were synthesized, **43-45** and **47**. In order to study the effect of the heteroatom on the photophysical properties and on the solid state arrangement, synthetic procedures have been properly designed and in some cases adapted in order to insert in the benzazole-based structures, elements belonging to the sixth group of the periodic table, namely O, S, Se and Te. The successful synthesis of compounds **43-45** was proved by ^1H -, ^{13}C -NMR and 2D-NMR spectroscopy and HR-MS experiments. These dyes were, then, photophysically analyzed by the collaborators from *CNR in Bologna* to evaluate the effect of the heavy-atom on the



Compound	D	A
a) <i>Diphenylacetylenes</i>		
34	-H	-H
35	-N(C ₆ H ₁₃) ₂	-N(C ₆ H ₁₃) ₂
36	-NO ₂	-NO ₂
37	-N(C ₆ H ₁₃) ₂	-NO ₂
38	-N(C ₆ H ₁₃) ₂	-CN
39	-N(C ₆ H ₁₃) ₂	-CF ₃
40	-N(C ₆ H ₁₃) ₂	-(F) ₅
b) <i>Benzoxazoles</i>		
41	-	-NO ₂
42	-	-CF ₃

photophysical properties. Specifically, a pronounced fluorescence decrease was observed in solution in the series going from **43** to **45**. In the meantime phosphorescent emissions were detected for the sulfur derivative **44** and more intense for its selenium analogue, **45**, corroborating the occurring heavy atom effect in the series. The presence of high atomic number elements favors spin-orbit coupling phenomena, namely a transition from the singlet excited state to the triplet state provoking a triplet emission characteristic of a phosphorescence signal.



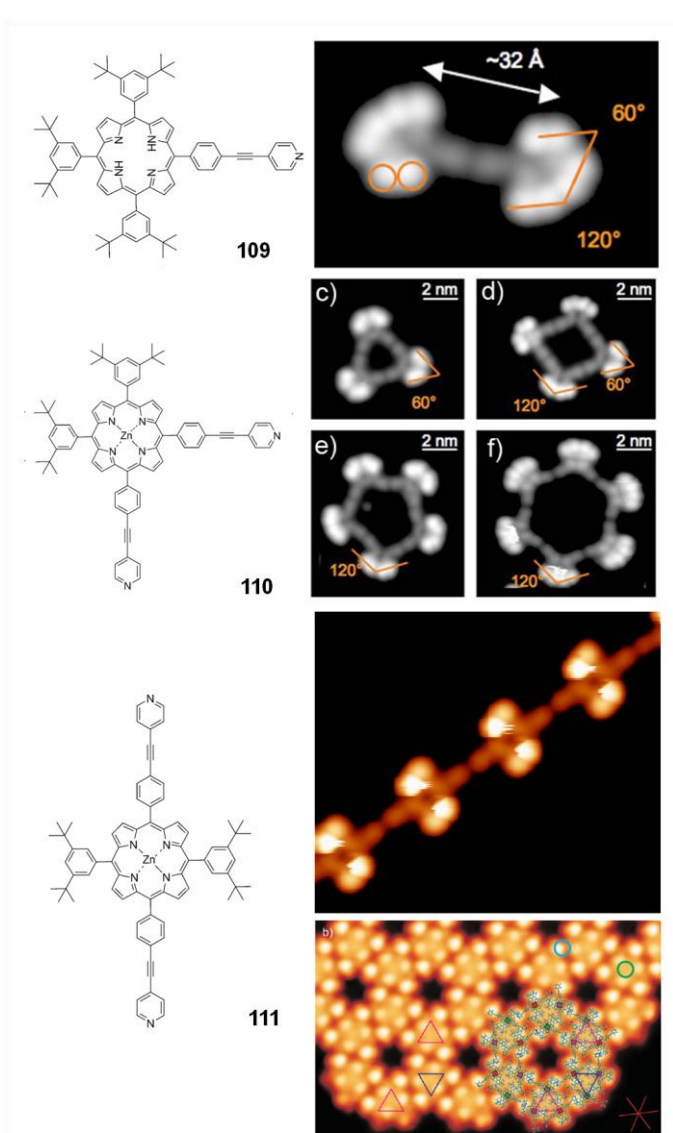
To investigate the solid state arrangements of bisbenzazoles **43-45**, crystals suitable for X-Ray characterization were grown. These clearly displayed the effect of the progressively heavier atom especially on the π - π stacking and offset distances. In order to explain the results obtained with the crystallized dyes, theoretical calculations were carried out to predict the geometry and to evaluate specific structural parameters for each dye. In general, a good overlap was found between experimental and theoretical data.

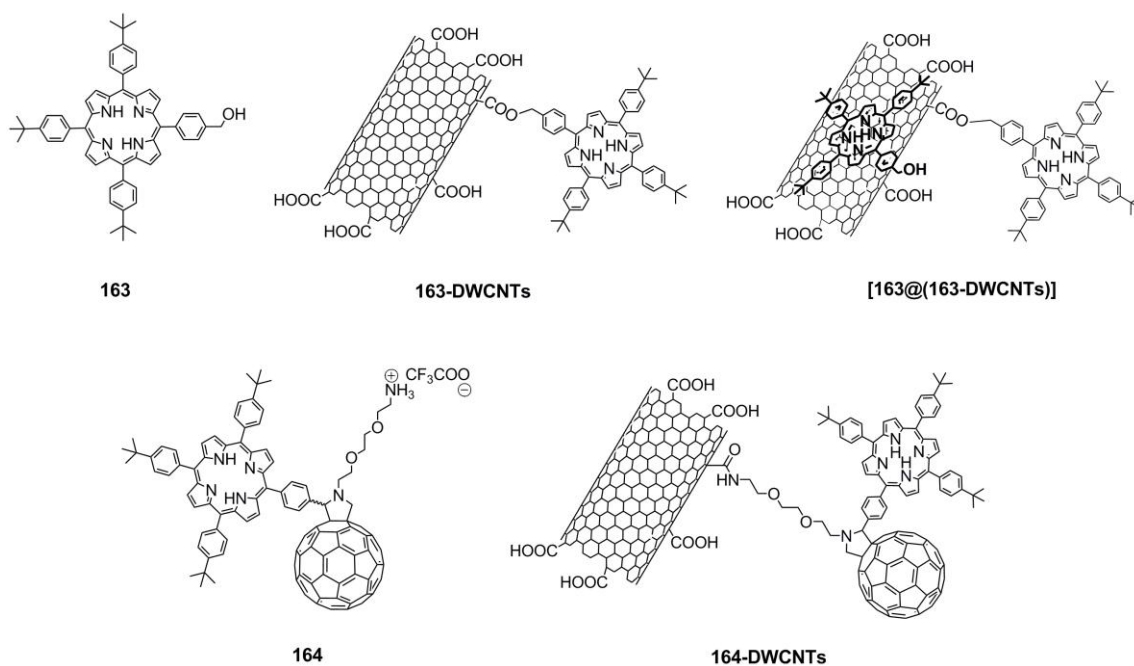
Chapter 3 addresses instead a different category of π -conjugates, namely the extended π -conjugated porphyrin macrocycle. Porphyrins were here exploited to study their interactions with metallic surfaces and their ability to form patterned surface based on unprecedented two-dimensional addressable supramolecular assemblies. Specifically, in view of studying the self-assembly processes formed through metal-ligand non-covalent interactions, monosubstituted **109** and disubstituted pyridyl porphyrins **110-111**, in *cis*-like and *trans*-like conformations, were synthesized. In collaboration with the group of Prof. Johannes Barth (Physical University of Munich, TUM), the dyes were successively deposited onto Cu(111) surfaces and investigated by means of Scanning Tunneling Microscopy (STM) technique under Ultra High Vacuum (UHV) conditions. The self-assembly of both mono **109** and *trans*-like **111** porphyrin results in distinct supramolecular dimers and chains, respectively. In contrast, the molecular symmetry in combination with the molecular flexibility and surface interactions explains the diversity of the assemblies formed by the *cis* species, expressed in three- to six-membered cyclic assemblies. Furthermore, upon combination of the different ditopic porphyrin building blocks, bicomponent cyclic supramolecules of unprecedented extended size could be engineered. The first sections of this chapter reports also the formation of extended and highly regular homochiral nanoporous networks on Ag(111) metal substrate, through a three-level hierarchical chiral self-assembly process, which is based on a flexible porphyrin derivative **111** adopting a chiral conformation upon surface confinement. The porosity observed in the networks might be useful for patterning and guest accommodation including chiroselective molecular recognition and catalytic centers for activating organic reactions.

This chapter also addresses the synthesis of a series of tetrasubstituted pyridyl porphyrins, **117-119**, with the aim of building infinite porous networks onto Cu(111) surface by exploiting the same metal-ligand coordinative interactions observed with the *cis*-like and *trans*-like parent compounds. However, the UHV-STM deposition of these modules onto Cu(111) led to probable degradation phenomena. The deposition of modules **117** and **118** afforded on surface species of different shapes and sizes, not referable to single porphyrin molecules. Module **119** featuring methyl groups in the 2- and 5-position of the *meso*-linked phenyl moieties, was the only porphyrin observed on the Cu(111) substrate. Though, the large majority of molecules **119** decomposed impeding the formation of any ordered assembled patterns.

The last sections of *Chapter 3* focused on the preparation and physical characterization of diverse porphyrin-derived Double-Walled Carbon Nanotubes (DWCNTs) conjugates with the aim of get insights on the structural and electronic properties of these materials. In particular,

COOH-derived DWCNTs, produced by means of a three-step oxidative protocol, were covalently linked and physically adsorbed to porphyrin molecules producing **163-DWCNTs**, **163@(163-DWCNTs)** and **163@DWCNTs** conjugates. The structural properties of all porphyrin-DWCNTs derivatives were comprehensively investigated via Thermogravimetric Analysis (TGA), Energy Dispersive X-ray Spectroscopy (EDX), X-Ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Dynamic Light Scattering (DLS) experiments. In collaboration with the group of Dr. Nicola Armaroli (CNR, ISOF, Bologna) the photophysical properties of the porphyrin-CNTs derivatives were investigated through absorption and emission spectroscopies both in solution and in polymeric matrices. Definitive experimental evidences could not be obtained for supporting photo-induced electron and/or energy transfer processes involving the porphyrin chromophores and the CNTs' wall. The synthesized DWCNTs-conjugates were then implemented in multilayered-type devices, fabricated with the aim of investigating the interaction of the porphyrin-derived CNTs with polymeric poly(3-hexylthiophene)-pyrene containing small amounts of [60]PCBM. In particular, asymmetric current density-voltage (*J-V*) characteristics for both forward and reverse bias displayed a strong rectification effect corroborating state-of-the-art devices.





Further investigations in this field will be developed onto novel systems characterized by porphyrin-C₆₀ functionalized DWCNTs. The synthesis of porphyrin-fullerene DWCNTs derivative **164** is thus reported in the last part of this dissertation. However, the future coupling reactions with carbon nanotubes and the corresponding photophysical characterization will be reported elsewhere. The photophysical properties of such materials will be necessary to assess the role of the fullerene moieties.

Riassunto

Le molecole coniugate costituiscono gli elementi fondamentali dei cosiddetti materiali molecolari avendo dato luogo a un notevole sforzo della ricerca scientifica di base e applicata per sviluppare nuovi materiali per l'informazione, per la comunicazione e per l'illuminazione. L'interesse dietro le molecole coniugate è aumentato anche grazie allo sviluppo di metodologie sintetiche avanzate, come le reazioni di *cross-coupling* catalizzate da metalli di transizione, e di nuove tecniche di analisi che permettono un'accurata caratterizzazione di ciascuna molecola.

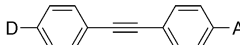
Le ambizioni di questo lavoro sono state quelle di fornire un'analisi dettagliata del rapporto che esiste fra le proprietà e la struttura di molecole coniugate. Per questo obiettivo, sono state prese in considerazione diverse classi di composti organici π -coniugati, approfondendo i loro aspetti sintetici e le loro caratteristiche chimico-fisiche.

Il *Capitolo 1* presenta al lettore una breve introduzione sul rapporto esistente fra la struttura di molecole organiche π -coniugate e la differenza di energia fra gli orbitali HOMO e LUMO, detto anche il *bandgap* della molecola. Questo capitolo riporta, nell'ultima sezione, anche i punti essenziali dell'intero manoscritto.

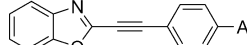
La prima parte del lavoro svolto in questo dottorato di ricerca è presentato nelle prime sezioni del *Capitolo 2*. In questa parte sono presentate molecole organiche π -coniugate per ideare convertitori di lunghezza d'onda, per un'importante tecnica medica d'*imaging*, la Tomografia ad Emissione di Positroni (acronimo: PET). In particolare, sono stati considerati due diversi approcci per produrre i suddetti convertitori, l'approccio donatore-accettore (o *push-pull*) e quello che sfrutta l'effetto dell'inserzione di un eteroatomo. Per quanto riguarda il primo approccio, sistemi lineari π -coniugati caratterizzati da una struttura tipo difenil acetilene, **34-42**, sono stati sintetizzati attraverso reazioni di *Sonogashira*. Questi composti sono stati poi caratterizzati attraverso spettroscopia NMR e spettrometria di massa ad alta risoluzione (HR-MS). Grazie alla collaborazione del *Dr. Andrea Barbieri (CNR, ISOF, Bologna)* sono state poi studiate le proprietà foto fisiche delle molecole **34-42** sia in soluzione sia in una matrice polimerica (PMMA), per valutare una loro applicazione come convertitori di lunghezza d'onda per la tecnica PET. Tutti i composti analizzati si sono rivelati essere molto luminescenti nella matrice polimerica dallo stato eccitato di *charge transfer* (ICT) e con ampi shift di *Stokes*. In generale, la maggior parte delle molecole studiate ha mostrato un netto aumento della resa quantica di fluorescenza nel polimero, che in alcuni casi ha raggiunto un aumento di un ordine di grandezza (**38**); a questo si aggiungono decadimenti di luminescenza mono-esponenziali con bassi tempi di vita dello stato eccitato (minori di 3 ns).

Nell'ambito dei convertitori di lunghezza d'onda, è stato poi studiato un diverso sistema organico π -coniugato, caratterizzato da gruppi benzazolici separati da uno spaziatore del tipo 1,4-dietinil benzene, **43-45** e **47**. Questi sistemi, presentando nella struttura elementi quali O, S, e Se, sono stati anche studiati per esaminare l'effetto dell'eteroatomo sulle loro proprietà chimico-fisiche. Dal punto di vista sintetico, questi sono stati preparati sfruttando diverse metodologie, in alcuni casi innovative. Sono stati caratterizzati sfruttando le comuni tecniche NMR, avvalendosi anche della spettroscopia NMR bidimensionale, e la spettrometria di massa. Le molecole in esame sono state in seguito analizzate dal punto di vista fotofisico in collaborazione

a)

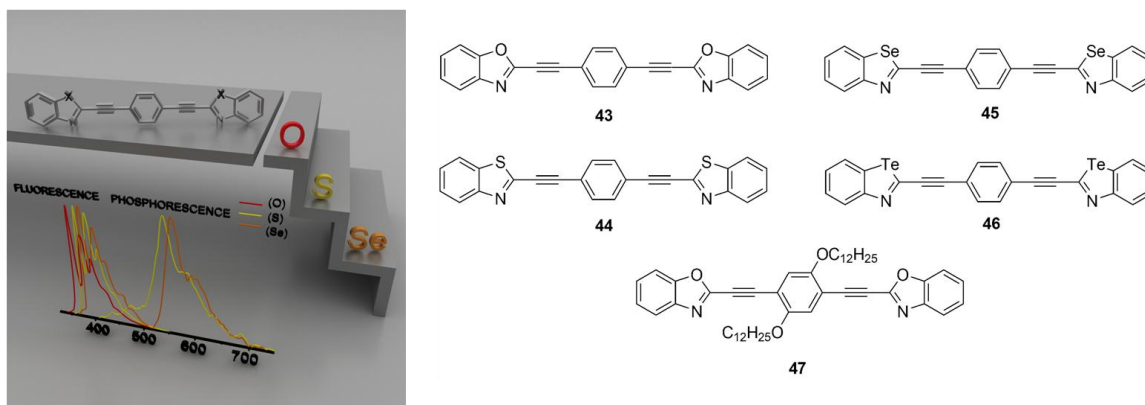


b)



Compound	D	A
a) <i>Diphenylacetylenes</i>		
34	-H	-H
35	-N(C ₆ H ₁₃) ₂	-N(C ₆ H ₁₃) ₂
36	-NO ₂	-NO ₂
37	-N(C ₆ H ₁₃) ₂	-NO ₂
38	-N(C ₆ H ₁₃) ₂	-CN
39	-N(C ₆ H ₁₃) ₂	-CF ₃
40	-N(C ₆ H ₁₃) ₂	(-F) ₅
b) <i>Benzoxazoles</i>		
41	-	-NO ₂
42	-	-CF ₃

con il gruppo del *CNR, ISOF*, per studiare l'effetto dell'atomo pesante sulle caratteristiche fotofisiche. In generale, partendo dal derivato con l'O (**43**) fino a quello con il Se (**45**), è stata osservata una marcata diminuzione della fluorescenza in soluzione. Parallelamente, è stato registrato un segnale di fosforescenza per il derivato con lo S, **44**, e più preponderante per la molecola con il Se, **45**, confermando il verificarsi dell'effetto dell'atomo pesante sulle proprietà di queste molecole. La presenza di un atomo pesante favorisce fenomeni di accoppiamento spin-orbita, e quindi una transizione di tipo *intersystem crossing* dallo stato eccitato di singoletto a quello eccitato di tripletto producendo un'emissione dallo stato di tripletto e quindi un segnale di fosforescenza.



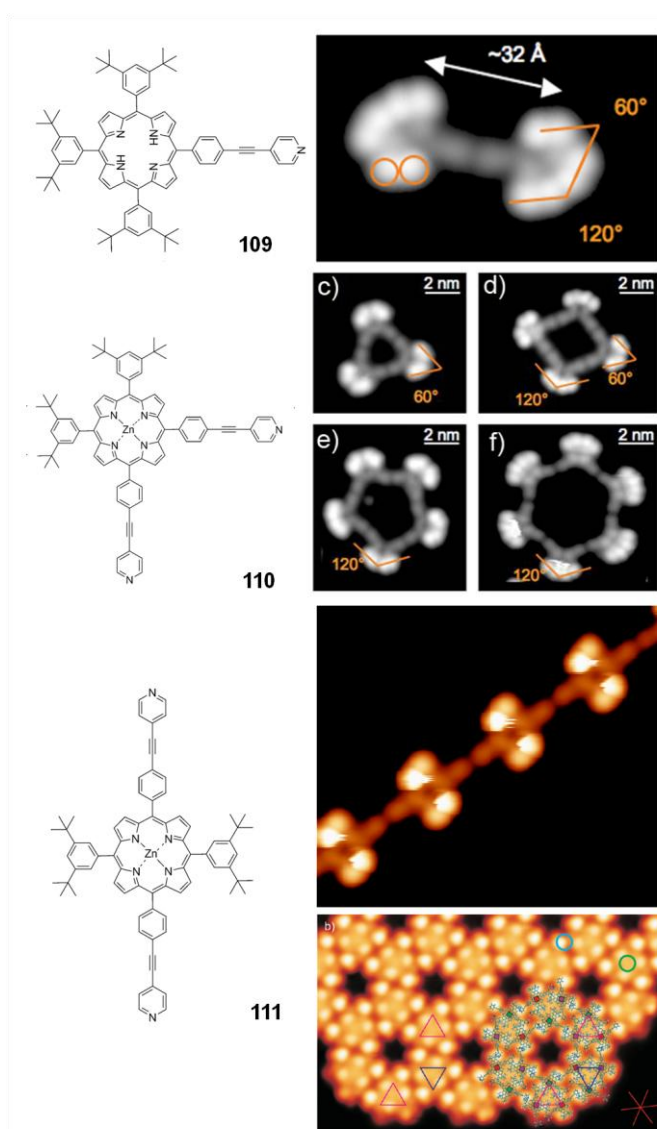
Questi sistemi sono anche stati studiati allo stato solido attraverso un'analisi cristallografica a raggi-X dei loro cristalli. L'analisi ha mostrato un marcato effetto dell'eteroatomo anche sulle proprietà d'impaccamento della molecola. Questo è stato riscontrato in particolare nelle interazioni di tipo π - π stacking e nelle distanze di offset fra due molecole sovrapposte. Per spiegare i risultati ottenuti attraverso gli studi cristallografici, la situazione osservata allo stato solido è stata simulata per ciascun composto attraverso calcoli teorici.

Il Capitolo 3 affronta una diversa classe di composti organici π -coniugati, le porfirine. Queste sono state studiate nell'ambito delle loro interazioni con superfici metalliche approfondendo le loro abilità di auto-assemblaggio bidimensionale (2D) per formare superfici con molecole organizzate che interagiscono attraverso interazioni supramolecolari. In particolare, per formare superfici di porfirine ordinate sfruttando un'interazione di tipo metallo-ligando, sono stati sintetizzati e studiati tre derivati caratterizzati da gruppi tipo fenil-etinil-piridina sostituiti nelle posizioni *meso* del macrociclo: una porfirina mono-sostituita, **109**, e due porfirine di-sostituite, **110-111**, rispettivamente con i gruppi fenil-etinil-piridina in configurazione tipo *cis* e tipo *trans*. Grazie alla collaborazione del gruppo del Prof. Johannes Barth (*Physical University of Munich, TUM*), le tre porfirine sono state depositate su superfici di Cu(111) e studiate con la tecnica *Scanning Tunneling Microscopy* (STM) in condizioni di ultra alto vuoto (UHV). L'auto-assemblaggio della porfirina **109** e dell'isomero di tipo *trans* **111** ha prodotto rispettivamente dimeri e lunghe catene formate attraverso interazioni supramolecolari. In maniera diversa, la simmetria molecolare insieme alla flessibilità dell'isomero di tipo *cis*, **110**, spiega la presenza di supramolecole cicliche, formate da tre a sei derivati porfirinici. In aggiunta, supramolecole cicliche con una cavità maggiore sono state generate su Cu(111) dalla combinazione delle molecole **110** e **111**. Le successive sezioni di questo capitolo affrontano anche la formazione di estesi *network* porosi altamente regolari su superfici di Ag(111), attraverso un processo di auto-assemblaggio chirale della porfirina **111**, la quale adotta una conformazione chirale una volta che ha interagito con la superficie metallica. I pori formati possono essere utilizzati in maniera tale da introdurre molecole ospiti e poter agire in futuro come centri catalitici attivando reazioni organiche enantioselettive.

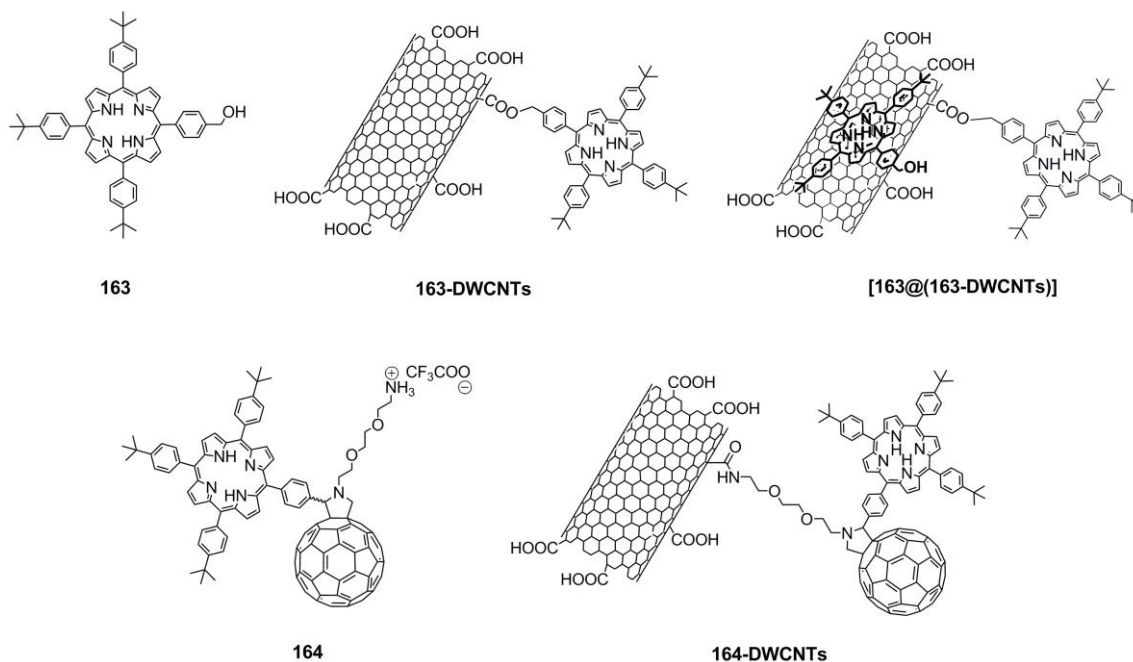
Con l'obiettivo di formare *network* porosi infiniti su superfici di Cu(111) attraverso interazioni supramolecolari di tipo metallo-ligando, questo capitolo presenta anche una nuova serie di porfirine tetra-sostituite con gruppi fenil-etinil-piridina nelle quattro posizioni *meso*, **117-119**. Queste molecole sono state depositate sulla superficie in condizioni di ultra alto vuoto e analizzate con la tecnica STM. Dalla deposizione delle molecole **117** e **118** sono stati osservati solamente frammenti di molecola, nessuno di questi riconducibile a singole molecole. La porfirina **119**, caratterizzata da gruppi 2,5-dimetil fenile direttamente legati alle posizioni *meso* della molecola, è stata invece la sola tetra-porfirina ad essere stata depositata sulla superficie di Cu(111). Sebbene sia stata l'unica porfirina osservata su Cu(111), la maggior parte delle molecole **119** si sono decomposte prima di raggiungere il substrato metallico, impedendo la formazione di alcuna struttura supramolecolare.

Le ultime sezioni del *Capitolo 3* hanno riguardato la preparazione e la caratterizzazione fotofisica di diversi coniugati porfirina-Nanotubi di Carbonio di tipo *double-wall* (DWCNTs) con l'obiettivo di

approfondire le relazioni struttura-proprietà di questi materiali. In particolare, DWCNTs ossidati, prodotti attraverso tre passaggi sintetici, sono stati covalentemente uniti, **163-DWCNTs**, e adsorbiti, **163@DWCNTs** ad un derivato porfirinico, **163**. In aggiunta, è stato prodotto un ultimo derivato ibrido in cui la porfirina è stata parzialmente legata ai nanotubi in maniera covalente e in parte solamente adsorbita, **163-(163@DWCNTs)**. La caratterizzazione strutturale di ciascun materiale è stata eseguita attraverso tecniche quali Analisi Termogravimetrica (TGA), Spettroscopia a Dispersione a Raggi-X (EDX), Spettroscopia Fotoelettronica a Raggi-X (XPS), Microscopia a Trasmissione Elettronica (TEM), Microscopia a Forza Atomica (AFM) e Scattering di Luce Dinamico (DLS). Grazie alla collaborazione del gruppo di ricerca del Dr. Nicola Armaroli (CNR, ISOF, Bologna) i suddetti materiali sono stati studiati dal punto di vista fotofisico attraverso spettroscopie di assorbimento ed emissione, in soluzione ed in matrici polimeriche. Non è stato possibile trovare evidenze sperimentali che supportino un trasferimento di elettrone e/o energia fotoindotto fra le molecole di porfirina ed i nanotubi. I materiali prodotti sono stati poi introdotti in un prototipo elettronico di tipo multistrato, fabbricato con lo scopo di studiare le interazioni fra i coniugati porfirina-nanotubi e la matrice polimerica con la quale sono stati mescolati per l'implementazione nel *device*, il polimero poli(3-esiltiofene)-pirene contenente anche piccole quantità di [60]PCBM. Ciascun coniugato ha presentato curve



asimmetriche di tipo densità di corrente-voltaggio (J - V) con un andamento di forte rettificazione confermando i risultati presenti in letteratura di questo tipo di *device* elettronico.



In un ampliamento di questo argomento, saranno effettuati nuovi studi su sistemi del tipo porfirina- C_{60} funzionalizzati covalentemente su DWCNTs. Sebbene nelle ultime sezioni di questa tesi di dottorato la sintesi di derivati porfirina-fullerene, **164**, sia presentata, le future reazioni necessarie a connettere questi derivati con i nanotubi e la loro successiva caratterizzazione saranno riportate in seguito. In particolare, gli studi fotofisici saranno necessari per stabilire il ruolo dei gruppi fullerenici nei processi di trasferimento fotoindotto di elettrone e/o di energia.

Résumé

Les molécules conjuguées constituent les briques élémentaires des matériaux moléculaires qui ont entraîné de considérables efforts de recherche dans la science des matériaux basique et appliquée, afin de développer de nouveaux matériaux pour les technologies d'information, de communication et d'éclairage. L'intérêt des molécules conjuguées a été alimenté par les avancées dans la méthodologie synthétique, tel que le développement des réactions de couplages croisés catalysées par des métaux, et par les avancées dans les techniques analytiques qui permettent maintenant de réaliser des caractérisations précises.

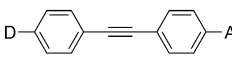
Les ambitions de ce présent travail permettent d'acquérir une compréhension détaillée des relations qui existent entre les propriétés et la structure du squelette π -conjugué. À cette fin, différentes classes de composés organiques π -conjugués ont été investiguées en se concentrant sur leurs procédés de synthèse et leurs caractéristiques chimico-physiques.

Dans le *Chapitre 1*, une brève description des relations entre la structure des molécules conjuguées et le *gap* entre les plus Hautes Orbitales Moléculaires Occupées (HOMO) et les plus Basses Orbitales Moléculaires Vacantes (LUMO) est introduite au lecteur. Ce chapitre expose également les grandes lignes du manuscrit.

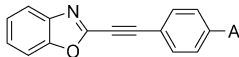
La première partie du travail de ce doctorat est décrite dans le *Chapitre 2*, dans lequel les molécules organiques π -conjuguées sont examinées en tant que convertisseurs de longueur d'onde pour une technique d'imagerie médicale importante, la Tomographie par Emission de Positrons. Deux approches permettent de réaliser des conversions de longueur d'onde : l'approche *push-pull* et l'effet hétéroatomique. La synthèse des systèmes linéaires π -conjugués basés sur une ossature diphenylacétylénique, **34-42**, est décrite pour l'approche *push-pull*. Tous les composés ont été préparés en exploitant des réactions de couplages croisés de type *Sonogashira*. Des indications manifestant la formation des composés désirés **34-42** ont été obtenues par spectroscopie RMN ^1H et ^{13}C , ainsi que par des expériences de spectrométrie de masse à haute résolution (HR-MS). En collaboration avec le Dr. Andrea Barbieri (CNR, ISOF, Bologne), les propriétés photophysiques de ces chromophores ont été investiguées en solution et dans des matrices polymériques (PMMA) en tant que convertisseurs de longueur d'onde, dans le but d'être incorporés dans un nouveau concept de scanner pour la technique de Tomographie par Emission de Positron (PET). Nous avons observé que tous les composés étudiés présentaient une très forte luminescence dans des milieux condensés, à partir des états excités ICT avec de larges déplacement de Stokes. D'une façon générale, la plupart des molécules luminescentes étudiées ont montré une nette augmentation du rendement quantique lorsqu'elles étaient implantées dans un environnement rigide, par rapport aux solutions ; dans certains cas remarquablement plus élevés qu'un ordre de magnitude (**38**), et présentant des décroissances mono-exponentielles de la luminescence avec une durée de vie des états excités plus courte que 3 ns.

Dans le même chapitre, un système π -conjugué différent a aussi été développé. En particulier, une série de composés organiques chromophoriques caractérisés par des groupements à base de benzazole ont été synthétisés, **43-45** et **47**. Afin d'étudier l'effet de l'hétéroatome sur les propriétés physiques et sur l'arrangement à l'état solide, des procédés

a)

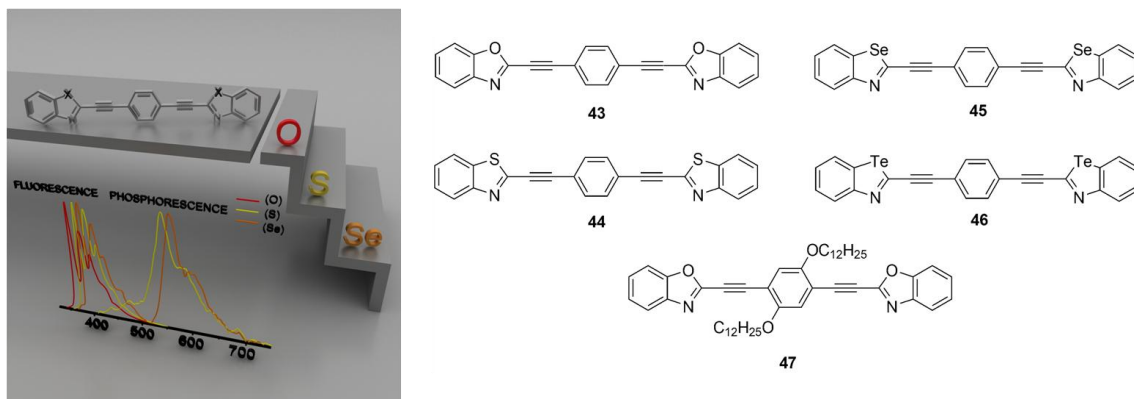


b)



	Compound	D	A
a)	<i>Diphenylacetylenes</i>		
	34	-H	-H
	35	-N(C ₆ H ₁₃) ₂	-N(C ₆ H ₁₃) ₂
	36	-NO ₂	-NO ₂
	37	-N(C ₆ H ₁₃) ₂	-NO ₂
	38	-N(C ₆ H ₁₃) ₂	-CN
	39	-N(C ₆ H ₁₃) ₂	-CF ₃
	40	-N(C ₆ H ₁₃) ₂	(-F) ₅
b)	<i>Benzoxazoles</i>		
	41	-	-NO ₂
	42	-	-CF ₃

synthétiques ont soigneusement été élaborés et dans certains cas adaptés afin d'insérer dans les structures à base de benzazole, des éléments provenant du sixième groupe du tableau périodique, c-à-d O, S Se et Te. Les synthèses des composés **43-45** réalisées avec succès ont été authentifiées par spectroscopie RMN ^1H , ^{13}C et 2D, ainsi que par des expériences HR-MS.



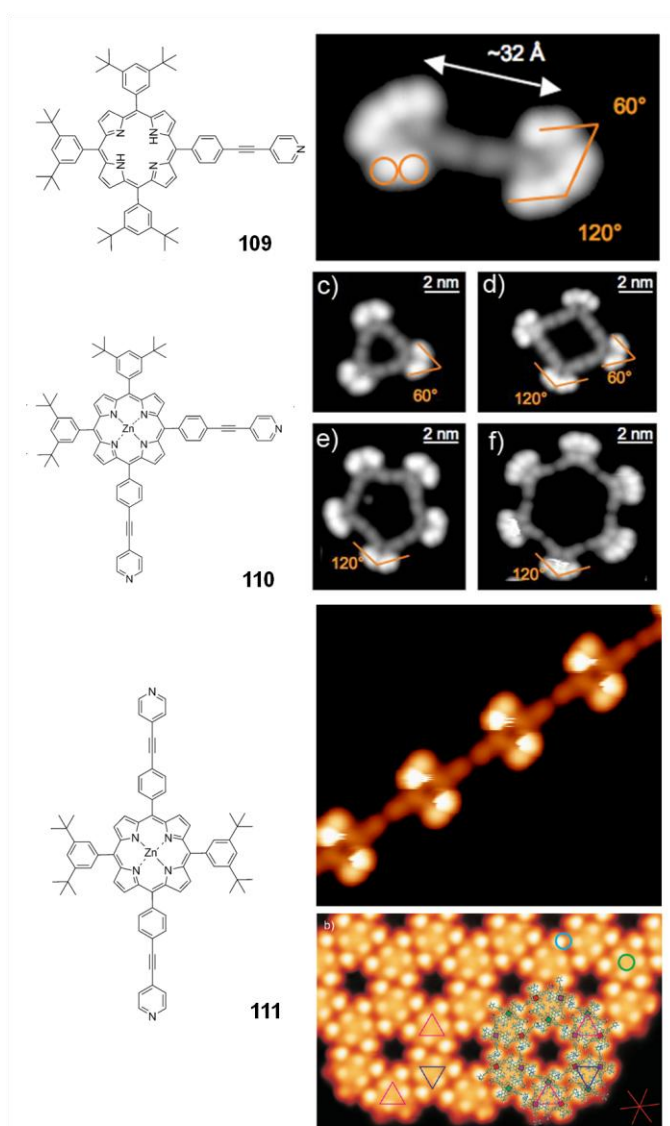
Ces chromophores furent ensuite analysés d'une façon photophysique par les collaborateurs du CNR à Bologne, afin d'évaluer l'effet des atomes lourds sur les propriétés photophysiques. Une diminution prononcée de la fluorescence a particulièrement été observée en solution pour les séries allant de **43** à **45**. En parallèle, les émissions phosphorescentes ont été détectées pour le dérivé à base de soufre **44** et une émission encore plus intense a été observée pour son analogue à base de sélénium, **45**, confirmant l'effet des atomes lourds dans la série. La présence d'éléments à numéro atomique élevé favorise le phénomène de couplage *spin-orbit*, à savoir la transition de l'état excité singulet à l'état triplet, provoquant l'émission à partir de l'état triplet, caractéristique du signal phosphorescent.

Afin d'examiner les arrangements à l'état solide des bisbenzazoles **43-45**, des cristaux adéquats aux caractérisations par Rayon-X ont été obtenus, montrant très distinctement l'effet des atomes de plus en plus lourds, en particulier sur les distances π - π stacking et les distances *offset*.

Afin d'expliquer les résultats obtenus avec les chromophores cristallisés, des calculs théoriques ont été réalisés pour prédire la géométrie et évaluer les paramètres structuraux spécifiques pour chaque chromophore. En général, une bonne corrélation a été trouvée entre les données expérimentales et théoriques.

Le Chapitre 3 aborde quant à lui une catégorie différente de π -conjugués, à savoir des macrocycles porphyrine π -conjugués étendus. Les porphyrines ont été exploitées afin d'étudier leurs interactions avec des surfaces métalliques et leur capacité à former des surfaces à motifs, basé sur des assemblages supramoléculaires sans précédents à deux dimensions. En particulier, en vue d'étudier les procédés d'auto-assemblage formés par des interactions non-covalentes métal-ligand, les porphyrines monosubstituée **109** et disubstituées **110-111**, par un groupement pyridyle, dans des conformations pseudo-cis et pseudo-trans, ont été synthétisées. Les chromophores ont ensuite été déposés à tour de rôle sur des surfaces de Cu(111) et ont été examinés *via* Microscopie à Effet Tunnel (STM) sous des conditions d'Ultra Haut Vide (UHV), en collaboration avec le groupe du Prof. Johannes Barth (Université Physique de Munich, TUM). L'auto-assemblage des porphyrines monosubstituées, **109**, et de type *trans*, **111**, résulte respectivement en des dimères et en des chaînes supramoléculaires distinctes. Cependant, la symétrie moléculaire ainsi que la flexibilité moléculaire et les interactions avec la surface, expliquent la diversité des assemblages formés par les espèces pseudo-cis, représentés par des assemblages cycliques de trois- à six-membres. En outre, en combinant les différents *building blocks* ditopiques porphyriniques, nous avons pu concevoir des supramolécules cycliques à deux composants et de taille étendue. Les premières sections de ce chapitre exposent également la

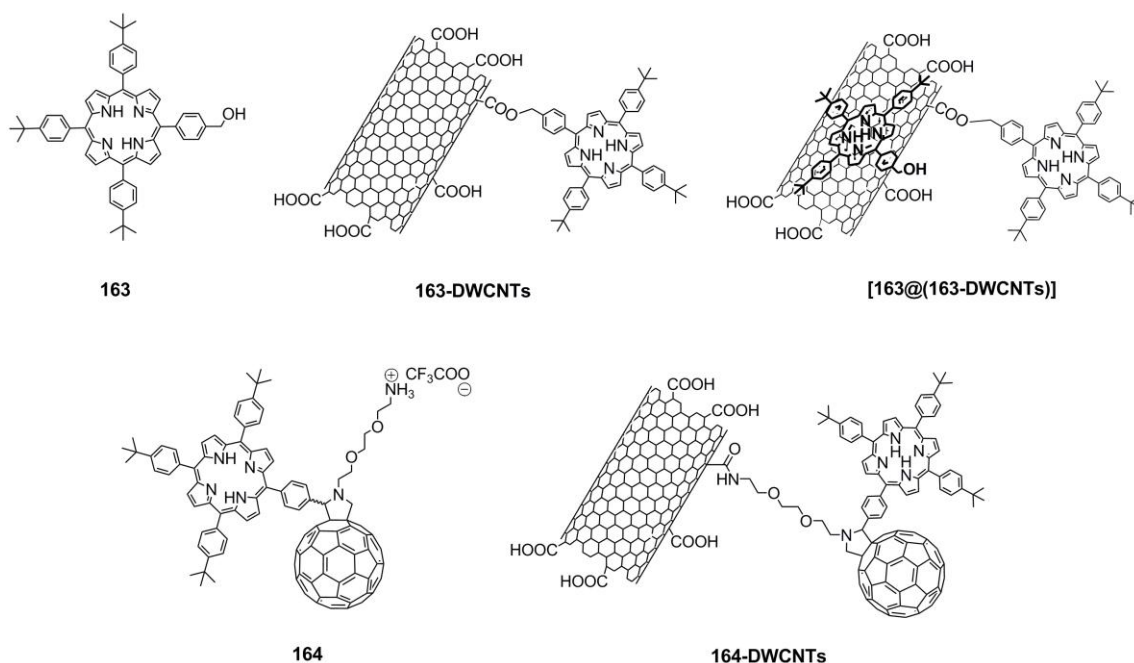
formation de réseaux nanoporeux homochiraux étendus et hautement réguliers sur des substrats de métaux Ag(111), via un procédé d'auto-assemblage chiral hiérarchique à trois niveaux, basé sur un dérivé de porphyrine **111** flexible, adoptant une conformation chirale lors du confinement sur surface. La porosité observée des réseaux peut être utile pour la formation de motifs et le logement de *guests*, incluant de la reconnaissance moléculaire chirale et des centres catalytiques pour l'activation de réactions organiques. Ce chapitre présente également la synthèse d'une série de porphyrines tétrasubstituées par des groupements pyridyle, **117-119**, dans le but de construire des réseaux poreux infinis sur des surfaces de Cu(111) en exploitant les mêmes interactions de coordination métal-ligand, observées avec les composés parents pseudo-cis et pseudo-trans. Cependant, il semble que la déposition UHV-STM de ces modules sur le Cu(111) a mené à des phénomènes de dégradation. La déposition sur surface des modules **117** et **118** a fourni des espèces de différentes formes et tailles, ne correspondant pas à des molécules individuelles de porphyrines. Le



module **119** présentant en *méso* des groupements 2,5-diméthylphényle, fut la seule porphyrine observée sur le substrat de Cu(111). Malgré tout, la grande majorité des molécules **119** se sont décomposées, gênant ainsi la formation d'un quelconque *pattern* assemblé et ordonné.

Les dernières sections du *Chapitre 3* se concentrent sur la préparation et la caractérisation physique de différents conjugués de Nanotubes de Carbone à Double Paroi (DWCNTs) avec des porphyrines, dans le but d'obtenir un aperçu des propriétés structurales et électroniques de ces matériaux. En particulier, des dérivés DWCNTs-COOH, produits via un procédé oxydatif à trois étapes, ont été liés d'une manière covalente et adsorbés physiquement à des molécules de porphyrine, générant les conjugués **163-DWCNTs**, **163@(163-DWCNTs)** et **163@DWCNTs**. Les propriétés structurales de tous les dérivés porphyrines-DWCNTs ont été extensivement investiguées par des Analyses Thermogravimétriques (TGA), par Spectroscopie Dispersive en Energie par Rayonnement X (EDX), par Spectroscopie de Photoélectrons induits par Rayons X (XPS), par Microscopie Electronique en Transmission (TEM), par Microscopie à Force Atomique (AFM), et par des expériences de Diffusion Dynamique de la Lumière (DLS). En collaboration avec le groupe du *Dr. Nicola Armaroli (CNR, ISOF, Bologna)*, les propriétés photophysiques des dérivés porphyrine-CNTs ont été examinées par spectroscopies d'absorption et d'émission, à la fois en solution et dans des matrices polymériques. Cela dit, nous n'avons pas réussi à obtenir des preuves expérimentales définitives

permettant de confirmer les procédés photo-induits de transfert d'électrons et/ou d'énergie impliquant les chromophores porphyriniques et les murs des CNTs. Les conjugués DWCNTs synthétisés ont ensuite été implantés dans des dispositifs de type multicouches, tels que les systèmes photovoltaïques, fabriqués dans le but d'étudier l'interaction du dérivé porphyrine-CNTs avec le pyrène poly(3-hexylthiophène) polymérique contenant de faibles quantités de [60]PCBM. En particulier, les graphes des tendances asymétriques densité de courant/voltage (J - V) présentaient un effet de rectification fort, corroborant avec les appareillages à l'état de l'art.



De plus amples investigations seront développées pour de nouveaux systèmes caractérisés par des DWCNTs fonctionnalisés par des porphyrines-C₆₀. La synthèse des dérivés porphyrine-fullerène DWCNTs **164** est ainsi décrite dans la dernière partie de cette dissertation doctorale. Cependant, les réactions de couplage à venir avec les nanotubes de carbone, ainsi que les caractérisations photophysiques correspondantes, seront décrites ailleurs. Les propriétés photophysiques de tels matériaux seront nécessaires pour évaluer le rôle des fullerènes.

1. Introduction

The aim of this doctoral thesis was to gain knowledge on the chemistry and the properties of π -conjugated organic molecules. In particular the intention was to investigate the relationships that exist between structure and properties. To do that, different classes of organic compounds were investigated delving into their synthetic processes and chimico-physical features.

Conjugated molecules constitute the elemental bricks of molecular materials that have given rise to considerable research efforts in basic and applied material science to develop new materials for information, communication and lighting technologies.^[1-3] The ambitions of the present work consisted to investigate the dependence of the macroscopic properties from the π -conjugated skeleton of the molecule. On the other hand, the chemical and physical properties of an organic compound are related to the energy levels of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO), which is commonly addressed as the HOMO-LUMO gap (HLG) or bandgap energy of the molecule. The tuning of the bandgap of a molecule can be achieved in numerous ways.^[2, 4] The aim of this chapter is, then, to provide an overview on the elements that affect the energy bandgap of organic π -conjugated molecules by means of key examples reported in literature.

One of the common ways to tune the bandgap of a π -conjugated molecule is related to the chain length. A theoretical model is used to explain the relationship between the π -chain and the HLG: “a particle in a box” (PIB).^[5] The PIB model treats π -electrons in the conjugated chain as particles, with mass m , contained within a “box” with a defined length L . Assuming that the electrons do not interact, the potential energy inside the box is zero and infinite at the edges, thus forcing the π -electrons to reside somewhere along the chain. The behavior of a particle in a box can be described mathematically by the *Schrödinger* wave equation. The general solution is a quantized energy that is dependent on the principle quantum number (n), the *Planck*’s constant (h), the mass of the particle (m), and box length (L):

$$E_n = \frac{h^2 n^2}{8mL^2} \quad (\text{eq. 1})$$

During an energetic transition, an electron residing in the HOMO is promoted to the LUMO. Therefore, the energy difference between the two states for a given system can be constructed by coupling eq. 1 and the Pauli Exclusion Principle:

$$\Delta E = \frac{h^2}{8mL^2} (n_{final}^2 - n_{initial}^2) \quad (\text{eq. 2})$$

Conjugated dyes are desirable systems to study using the PIB model because the box length (L) can be defined as the length of the conjugated carbon chain, while the particles inside the box are the π -electrons in the conjugated system. According to equation 2, an increase or decrease in the length of the chain will directly impact the energy of the HLG. In particular, the extension of the chain often results in a decreased energy bandgap.

A precise control over the energy of the HLG is desirable in order to generate useful and predictive structure-properties relationships. Beside the chain length, the energy of the HLG in π -conjugated molecules can be influenced by several other structural factors, such as the Bond Length Alternation (BLA), the planarity of the conjugated path, the insertion of electron donor and acceptor substituents or of heteroaromatic moieties.

1.1. Mind the Gap: General Strategies for the Bandgap Control in π -Conjugated Organic Oligomers

For many years, synthetic chemists have demonstrated their interest in constructing molecules capable of fulfilling many different requirements, such as mechanical, physical and chemical properties. On this regard, one of the most important aspects that gathered considerable attention involved the development of synthetic strategies directed to tune the energy of the HLG. One of the most investigated classes of organic molecules, which structure has been modified to tune the energy of the HLG, includes the π -conjugated organic oligomers.

The interest along these compounds was actually derived from a progenitor class, the π -conjugated organic polymers. These systems have started to be investigated in the late 1970s as advanced materials for electronic and photonic applications. The main advantages offered by π -conjugated organic polymers reside in their synthetic flexibility, and high versatility of properties tuning by structural modifications. These systems have thus found, during the years, many different fields of application, such as laser dyes,^[6] scintillators,^[6] light-emitting diodes,^[7] and are investigated for optical data storage,^[8] as well as non linear optical applications.^[9] However, despite the increased number of envisioned applications, their intrinsic limitations, such as low solubility with high molecular chains, made complicated the developing of industrial scale utilizations. To fight this obstacle, the research has subsequently directed the attentions towards parent structures exhibiting lower molecular weight and improved solubility such as the π -conjugated organic oligomers. The investigation of these systems as model compounds may have crucial role in understanding specific information concerning electronic, thermal and morphological properties of the corresponding polymeric materials. Moreover, a systematic study of π -conjugated oligomers enables the development of general rules to understand the relationship between structural modifications and molecular properties.

The unique properties of π -conjugated organic oligomers originate from their extended π -conjugated systems delocalized over the recurrent monomer units. The simplest model of this class of materials consists of alternating single and double carbon-carbon bonds. To assess the values of the bandgap energy of such systems, two main techniques are available: the electronic absorption, establishing the position of the low-energy absorption band, and the Cyclic Voltammetry (CV), through the measurements in solution of oxidation and reduction potentials.

The most common way to tune the HOMO and LUMO energy levels of a π -electron system involves the substitution of electron-releasing and electron-withdrawing groups. This approach is commonly called the push-pull effect and will be deeply tackled in the next chapter (section 2.2.1). The influence of the push-pull substitution on the energy of the HLG of a π -conjugate structure can be expressed as E^{sub} . One of the main features that bears down on the value of the HLG is explained by the *Peierls* instability, which depends on the degree of BLA in the conjugated path.^[10] Specifically, this parameter is related to the difference between single and double bond lengths and it usually represents the major contribution to the HLG with a term $E^{\delta r}$. Especially in the case of oligo aromatic species, other aspects have to be considered for a correct analysis of the bandgap of a conjugated molecule. The planarity in a molecule, defined by the term E^{θ} , where θ is the twist angle which two cycles generate around a carbon-carbon bond, can affect the overlap between the orbitals and thus the position of the HOMO and LUMO. For instance, a departure of the coplanarity can result in an increase of the energy bandgap. This is the reason why highly flat molecules, usually show considerably lowered bandgap as in the case of porphyrin cores. Another important parameter to take into account is the resonance energy of the monomeric unit. This energy, E^{res} , may be affected for instance by a contribution from the insertion of heteroatoms or of the bridging group between the two aromatic cycles. All these factors contribute to the magnitude of the HLG. However, in some cases, even the interactions between individual molecules responsible for a specific organization into a condensed phase, may have marked effects on the bandgap

energy. The energetic term can be then related to the supramolecular interactions exhibited by the molecules and it can be expressed as E^{int} .

All these effects are then responsible for the bandgap energy of oligo aromatic π -conjugated species, which can be thus defined as the sum of each contribution:

$$\Delta E = E^{sub} + E^{\delta r} + E^{\theta} + E^{Res} + E^{int} \quad (\text{eq. 3})$$

The primary goal of this equation is to demonstrate that the structural features of π -conjugates have crucial effects on the control of the energy gap. Thus, it is of a great importance to be capable of designing synthetic strategies in order to reach specific properties for future applications. In particular, synthetic strategies are mainly dedicated to those molecules showing reduced bandgap, where one or more of the energy contributions in eq. 3 become void.

1.1.1. The Bond Length Alternation (BLA) Effect, $E^{\delta r}$

The simplest way to define the BLA effect is to consider the trans-polyacetylene **1** (Figure 1). This molecule would ideally be a metallic conductor if the distance between all carbon atoms were identical. In this case, the double bonds are really delocalized along the polymeric chain, as it shown in Figure 1a. The bandgap of this particular situation is zero, as for infinite chains the energy difference between a bonding ground state and the anti-bonding excited state are degenerated. However, the equidistant linear chain structure is unstable towards a structural deformations and the result is a finite band gap ΔG (E_g in Figure 1). The BLA is due to a gain in electronic energy that overcompensates the loss of elastic energy, and is called the *Peierls* effect.^[10] Several examples are reported in the literature explaining how a reduction of this effect can lead to a smaller bandgap that sensitively affects the properties of the molecule.^[11, 12]

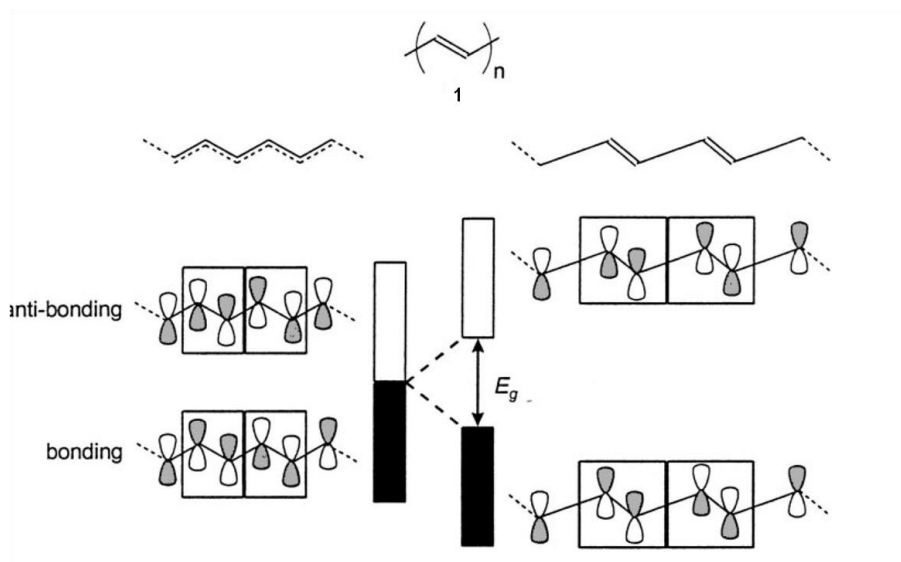


Figure 1. Bandgap formation by localization of double bonds in trans-polyacetylene **1**.^[13]

The oligothiophenes **2** and their derivatives constitute a good example to address the BLA alternation effect. These systems present a high bandgap energy (~ 2 eV), due to the energetically unfavorable quinoid structure to the ground state of molecule, resulting in a pronounced single bond character of the thiophene-thiophene linkage and

hence a large BLA contribution. Increasing the double-bond character of the thiophene-thiophene linkage can be accomplished by making the quinoidal structure energetically more favorable. This is the case in polyisothianaphthene (PITN) **3**. Since the discovery of PITN, many publications have appeared on a variety of chemical and electrochemical syntheses,^[14-16] as well as on the theoretical investigation of the origin of the PITN's bandgap.^[17, 18] As shown in Figure 2, upon going from the aromatic to the quinoid state, the loss of aromaticity is the smallest in **3** because its fused six membered ring gains aromaticity. This results in a reduction of the BLA effect and thus a bandgap for **3** of roughly 1 eV, one electronvolt smaller than that of polythiophenes **2**.

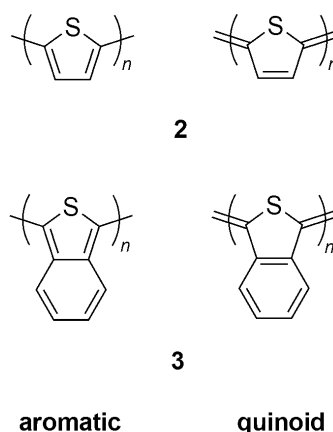


Figure 2. Polythiophene, **2**, and polyisothianaphthene (PITN), **3**, structures exhibiting the aromatic and the quinoid characters.

1.1.2. The Planarity Effect, E^θ

Despite the exceptional properties that systems with an extended π -conjugation exhibit, they may lead to serious problems, such as chemical instability, poor solubility and conjugation saturation behavior that arises through the Effective Conjugated Length (ECL).^[1, 19] The ECL defines the extent of π -conjugated systems in which the electronic delocalization is limited and at which point the optical, electrochemical, and other physical properties reach a saturation level. A straightforward strategy to maximize π -overlap may be to hold the systems coplanar within a tapelike framework by fusing the units edge-to-edge, to make a covalently linked long, flat array. Fused and planar π -conjugated structures are not only promising in circumventing the above ECL limit as seen for the $[n]$ acene series ($n = 1$, to 7),^[1] but also they show extremely low bandgap. When consecutive π -conjugated units are not planar, a mean dihedral angle θ contributes to limit the delocalization of π -electrons along the conjugated backbone and hence to increase ΔE by a quantity E^θ .

In this regard, porphyrins are intriguing building blocks to construct large π -conjugated molecules. Different examples have, in fact, been reported involving the rigidification of the porphyrin system by covalent fastening of elemental units.^[20-22] In particular, *Osuka* and coworkers have been the pioneers in this field, describing fully conjugated porphyrin tapes with different numbers of units. Increasing the numbers of consecutive porphyrins connected, these structures exhibited very low HOMO-LUMO gaps without the presence of the ECL effect, and absorption bands in the near IR.^[23] Figure 3 illustrates the general synthesis of the fused porphyrin tapes starting from the corresponding non-planar oligomers described by *Osuka*. This synthetic methodology led to very good yields for the fused tapes (**4**: 75%; **5**: 91%; **6**: 78%; **7**: 77%; **8**: 85%; **9**: 60%; **10**: 73%). In the same Figure the plot of the first one-electron oxidation potential of the fused porphyrins versus N^{-1} (N : number of porphyrins) is reported. Herein is clear that the expansion of the π -electronic system, with the increase of porphyrin units, tends to raise the HOMO, as

the oxidation potential becomes more and more negative. They calculated a bandgap of $\text{ca. } 1500 \text{ cm}^{-1}$ for the oligomers with 12 units **10**.

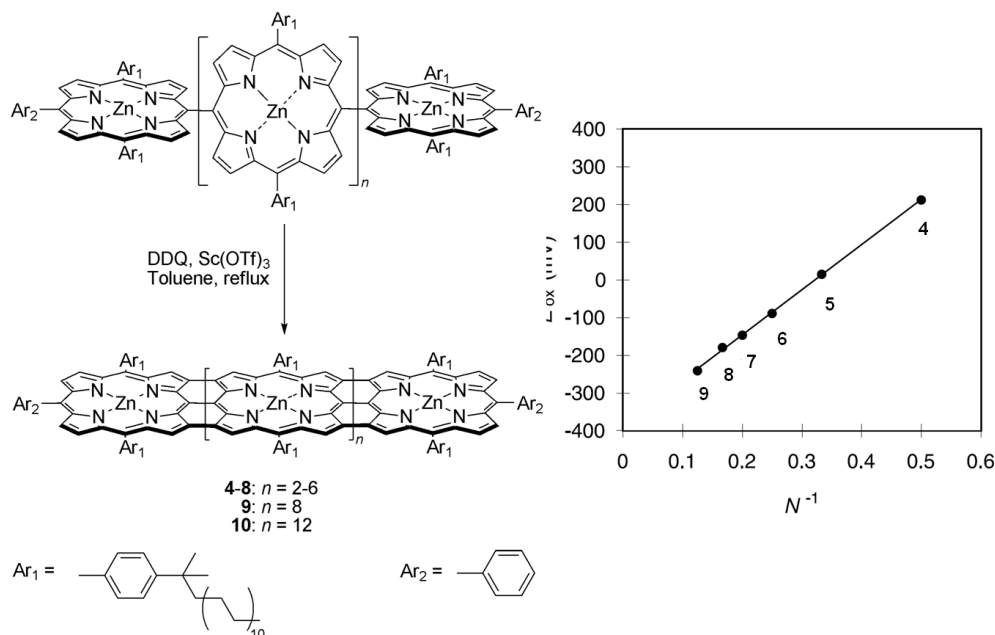


Figure 3. Synthesis of the fused porphyrin tapes **4-10** and plot of the first one-electron potentials $[E_{\text{ox}} \text{ (mV)} \text{ vs } \text{AgClO}_4/\text{Ag} \text{ taken in } \text{CHCl}_3] \text{ vs } N^{-1}$.^[23]

To summarize, covalent rigidification of π -conjugated systems represents an efficient strategy for band gap control. Furthermore, the large enhancement of electron delocalization and photoluminescence efficiency inherent to this approach opens interesting perspectives for applications in photonic systems such as nonlinear optics, light-emitting devices or solar cells. However, a major limitation is that this approach implies, in general, complex multi-step syntheses, which may be the source of problems in technological applications requiring cost-effective, large-scale production.

1.1.3. The Resonance Effect, E^{Res}

The energy of resonance of the π -conjugated structures plays an important role in the final value of ΔE . In general the widely used method to modify the HOMO and LUMO levels of a π system that primary affects the E^{Res} involves the insertions of lateral groups in the main backbone. If these groups have electron-donating and electron withdrawing abilities than this is the case of a push-pull system. These structures will be discussed later on in this dissertation. However, other parameters may have effects on the value of the E^{Res} . To be consistent with the topic of this thesis we will focus on the contribution of the heteroatom in aromatic structures.

When inserted as substitutes of carbon atoms in the aromatic rings, heteroatoms may affect the aromaticity of the cycle. The high aromaticity of thiophene ring, for instance, enhances the benzenoid character and, thus, lowers the HOMO energy level with wider HOMO-LUMO gaps. On the contrary, less aromatic hetero-doped structures may lead to opposite behaviors. The aspect of aromaticity of hetero-doped structures and its relationship with the bandgap of a π -conjugated molecule, has been recently reported by the group of Bendikov.^[24] In this work, the authors described the electronic properties of a series of modified poly(3,4-ethylenedioxythiophene) (PEDOS), a selenium analogue of PEDOT (poly(3,4-ethylenedioxythiophene)), which show very low bandgaps. Specifically, they considered three heteropolymers, polythiophenes **11**, substituted with fused selenophene rings, polyselenophene **12**,

substituted with fused thiophene rings, and polyselenophene **13**, with substituted fused selenophene rings (Figures 4 a-c). In general they report that the effect of a heavier element on the main polymeric chain, such as selenium, should endorse a lower bandgap and a more quinoid character of the structure. Consequently, polyselenophenes are attractive candidates for the synthesis of low bandgap conjugated polymers. When the heavy atom is, instead, fused to the cycles constituting the main polymeric chain, they exhibit a different behavior. Selenophenes are less aromatic than thiophene, so a fused selenophene ring augments the aromaticity in the main ring favoring a larger bandgap because of a decrease in the quinoid character of the main chain. Specifically, spectroelectrochemistry studies of films of polymers **11-13** on ITO electrode, were necessary to evaluate the optical bandgap of each electropolymerized polymer and to elucidate the effect of the heteroatom. In Figures 4 d-f the spectroelectrochemical spectra of each polymer are reported. Herein, it is possible to follow the variation of absorbance of the π - π^* electronic transition as a function of the applied voltage in the electrochemical cell and from the onset to extract the bandgap value. Therefore, the measured optical bandgap of **11**, which has a polythiophene backbone and a selenium atom in the peripheral ring, is 0.96 eV ($\sim$ 1290 nm) (Figure 4d). In agreement with the aromaticity effect discussed before, polyselenophene-based **12** with a more aromatic thiophene ring in the periphery generated a lower bandgap of 0.72 eV (Figure 4e). A similar value of bandgap was reported for polymer **13** with 0.76 eV (Figure 4f).

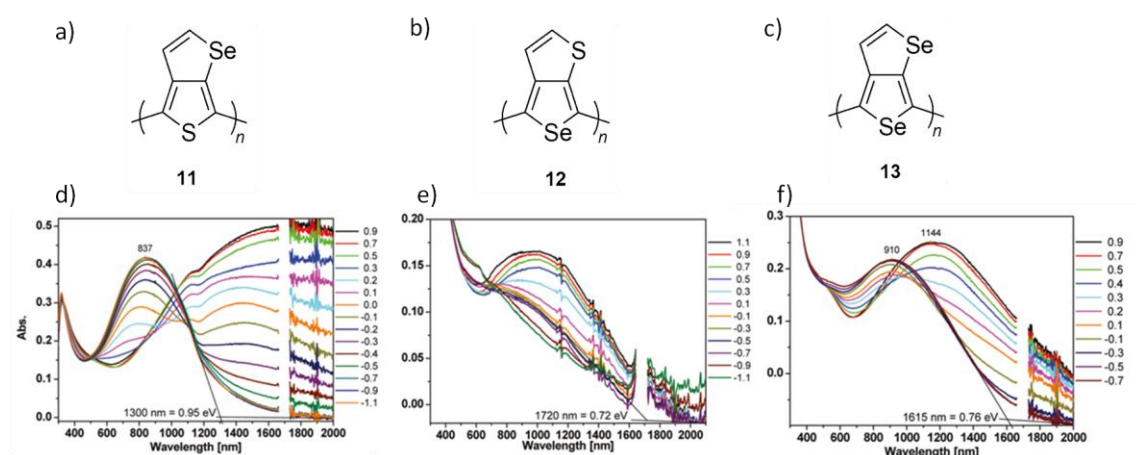


Figure 4. a-c) Structures of heteropolymers **11-13** investigated by Bendikov *et al.*. Spectroelectrochemistry of films of d) **11** in CH_3CN , e) **11** in CH_2Cl_2 and f) **13** in CH_3CN .^[24]

This study represents one of the very few in which the use of different combinations of heteroatoms, sulfur and selenium, in the main or peripheral rings, led to the achievement of bandgap control in very low bandgap conjugated polymers.

1.1.4. The Supramolecular Effect, E^{int}

Supramolecular interactions can significantly influence the magnitude of the bandgap. In this last section of the chapter, only few representative examples of possible approaches capable of contributing to a supramolecular control of the electronic properties of π -conjugated materials are briefly discussed.

Perhaps one of the most promising ways to achieving supramolecular control of the bandgap is to bring conjugated systems together at short intermolecular distances by means of covalent bonds. As a matter of fact, several examples in the literature have shown that when stacks of aromatic systems are fastened by short covalent linkages, frontier orbital overlap induces an increase of the HOMO level. For instance, uniform stacking of planar π -systems is the

basic principle for the construction of conducting organic crystals, in which overlap of frontier molecular orbitals forms conducting bands.^[25, 26]

An early example of this approach concerns the studies conducted on cyclophanes for which the shortening of the inter ring distance by a decrease in n produced a considerable redshift of the absorption edge.^[27] Figure 5a reports the absorption spectra of the paracyclophanes and it compares it with an open chain model. The cyclophanes **14-16**, featuring different sizes of distance n between the aromatic rings, present the higher wavelength band bathochromically shifted with respect to the open model. In addition, the smaller the distance between the rings more bathochromic is the shift of the band as demonstrated the spectrum of molecule **14**, suggesting a smaller bandgap for this cyclophane derivative.

More recently, this phenomenon was also demonstrated with a covalently linked molecular stack **17** (Figure 5b).^[28] The better orbital overlap resulting from the fastening of the benzene rings produces drastic changes in the cyclic voltammetry of **17** which exhibits two reversible oxidation waves at 1.28 and 1.74 V vs Ag/AgCl (Figure 5b). These changes represent a decrease of more than 1.20 V in the oxidation potential of benzene thus confirming that covalent fastening of aromatic rings can represent a powerful approach for the control of their electronic properties.

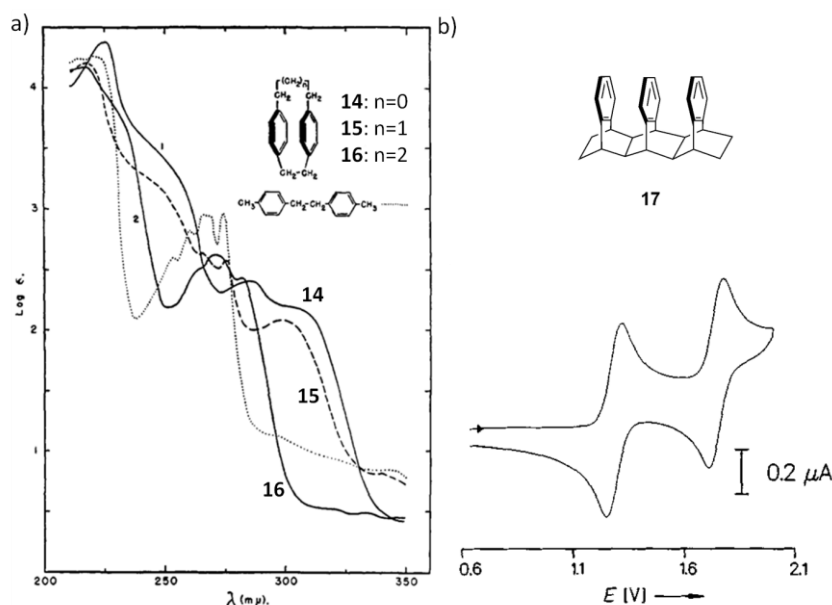


Figure 5. a) Absorption spectrum of paracyclophanes **14-16** compared with an open chain model; b) structure of stacked benzene rings in **17** and cyclovoltammogram of the oxidation of **17** in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$.^[27, 28]

1.2. Outline of the Dissertation

The aim of this dissertation is to provide an insight view on the relationships between structure and properties of different classes of π -conjugated structures. For the reasons discussed before, these compounds possess extraordinary electronic properties that make them exploitable as functional materials for a broad series of applications. The work here presented is divided into two main chapters.

Figure 6 schematically represents the outline of this doctoral dissertation. *Chapter 2* is dedicated to linear π -conjugated systems addressed as wavelength shifters for medical imaging techniques. To this end, two main approaches were considered, the “push-pull” and the “heteroatom” effects. Therefore, push-pull diphenylacetylene structures and hetero-doped benzazole-based linear modules were investigated. Specifically, the synthesis,

Chapter 1

luminescent properties and implementation as functional devices in the Positron Emission Tomograph were mainly addressed. Furthermore, benzazole-based modules, substituted with elements belonging to the sixth group of the periodic table, namely oxygen, sulfur, selenium and tellurium, were also photophysically analyzed to investigate the heteroatom-effect on the luminescent properties and on the solid state arrangement.

Chapter 3 addresses instead a different category of π -conjugates, namely the extended π -conjugated systems, the porphyrin macrocycle. Porphyrins were here exploited to study their interactions with different types of surface. Specifically, in view of organizing ordered assemblies formed through non-covalent interactions onto metallic surfaces, pyridyl porphyrins were synthesized to exploit the metal-ligand coordination interaction onto Cu(111) surface. The non-covalent assemblies, formed *via* the sublimation of the porphyrin modules onto the metallic substrates, were then characterized by the Scanning Tunnelling Microscopy (STM) technique. In the same chapter, porphyrin molecules were also synthesized to explore their interaction with a different type of surface, the external wall of carbon nanotubes (CNTs). In particular, in view of preparing new types of organic materials for solar conversion, the covalent functionalization of porphyrin derivatives onto carbon nanotubes was unraveled. Specifically, the interaction between the porphyrin moieties and the nanotubes was investigated by means of structural and photophysical analysis. These studies were conducted in solution and into solid matrixes in order also to assess the morphology of these materials in view of a future application into photovoltaic devices.

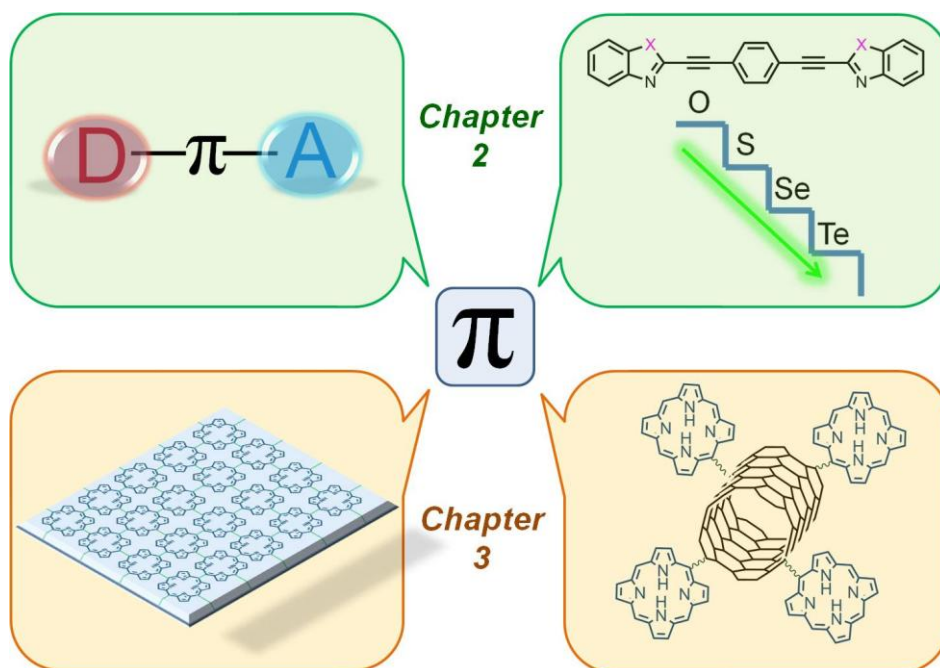


Figure 6. Schematic representation of the outline of this doctoral dissertation.

2. Acetylenic-Based Chromophores: from Push-Pull to Hetero-Doped Systems

In this chapter the synthesis and the photophysical properties of a series of linear π -conjugated organic molecules constituted by acetylenic cores are described. These compounds were investigated with the aim of designing wavelength shifters for medical imaging techniques. To this end, two different approaches, the push-pull and heteroatom effect, were taken into account.

The chapter is divided into four main parts: *i)* section 2.1 includes a general introduction on the “STRuctured scintillator for medical imaging” (STRING) project aimed at preparing wavelength shifters for the Positron Emission Tomography (PET); *ii)* section 2.2 focuses on the types of approach chosen towards the design of the wavelength shifters, namely the push-pull and the heteroatom approaches; *iii)* section 2.3 gathers the results obtained with the synthesis of push-pull and hetero-doped wavelength converters; *iv)* section 2.4 reports the photophysical characterizations of the synthesized shifters, highlighting the push-pull and the heavy-atom effects.

The work presented in this chapter was carried out jointly with Dr. Barbara Ventura and Dr. Andrea Barbieri of the *Istituto per la Sintesi Organica e la Fotoreattività (CNR - ISOF)*, Bologna, Italy. Furthermore, Bernadette Norberg from Prof. Johan Wouters’s group, and Dr. Adrian Kremer and Federica De Leo from the University F.U.N.D.P. of Namur are kindly acknowledged for their collaboration.

2.1. “STRuctured scintillator for medical imaging” (STRING) Project

The project described in these sections formed part of a collaborative EU Specific Targeted Research or Innovation Project, named “*Structured Scintillator for Medical Imaging*” (acronym: STRING). The aim of the STRING research network was to improve the performance, increase safety and decrease the cost of an important medical imaging technique, the Positron Emission Tomography (PET).

PET is a nuclear medicine imaging technique that produces 3-Dimensional (3D) images of functional processes in the body. The heart of the system consists in a cylinder shaped scintillator stack which detects pairs of γ -rays emitted indirectly by a positron-emitting radionuclide (tracer) that is introduced into the body *via* a biologically active molecule. 3D images of tracer concentration within the body are then constructed by computer analysis. The technique has transformed in the past decade from the research domain to mainstream clinical applications. Indeed, for oncology PET is emerging as the technique of choice for diagnosis, staging, therapy monitoring and assessment of recurrence in cancer and cardio-vascular diseases.

To achieve the goals of the STRING project, the research activity has focused its attentions in developing a novel concept of scintillator material involving an innovative ceramic thin film with radically new properties. Specifically, a novel designed scintillator stack has been produced consisting of a fast scintillator incorporating multifunctional ceramic thin films for spectral conversion.

Currently, the scintillator materials of the PET scanners are composed of silicate-based materials doped with lanthanide ions, such as Ce^{3+} . These ions absorb the γ -rays and re-emit the absorbed energy in the visible part of the spectrum, wherein the PET photodetectors have high sensitivity.^[29] However, this system presents several drawbacks, such as the relatively long lifetime of Ce^{3+} emission, the low conversion efficiency and the high cost of the single crystals. Therefore, the STRING activities have been focused on the implementation into silicate material of faster emitting ions. Pr^{3+} and Nd^{3+} were the first alternative ions considered. However, the energy emitted by these ions is located in the UV part of the spectrum, typically between 200 and 300 nm, lowering the sensitivity of the system.

To prevent the problem of sensitivity, the idea proposed in this project, and thus the focus of the present part of this manuscript was to prepare a wavelength converter thin layer. This consisted of an organic dye possessing exceptional abilities of UV-absorption and visible-emission. In addition, in order to preserve the stability of the organic dye under UV irradiation and to avoid photodegradation phenomena, the incorporation of the dye into a polymeric matrix has also been a project objective.

Before going through the objects of the present part of this doctoral thesis, the following sections will include a brief introduction on the current state of the PET technique and on the improvements that the research network of STRING project was intended to realize in the scintillator stack of the instrument.

2.1.1. The Positron Emission Tomography (PET): State of The Art

The history of Positron Emission Tomography is rich in technological achievements and advancements, and is characterized by a pursuit for better sensitivity and spatial resolution.^[30] The first medical application suited for positron was discovered and reported by *Sweet* at Massachusetts General Hospital (MGH) in 1951.^[31] This was a simple brain probe to localize tumors. Subsequently, *Brownell* along with *Sweet* and the physics group at MGH developed and built the first brain probe using two opposite sodium iodide detectors. In the same year, *Wrenn*, *Good* and *Handler* described and published studies of positron annihilation for localizing brain tumors.^[32] These two independent papers represent the first attempts to record positron data for use in medical applications. Between 1960's and 1970's, many research groups were involved in improving the image reconstruction techniques for primitive PET exemplars. It was only in 1973 that *Phelps* and co-workers were able to build the first PET tomograph, at Washington University. The principles of PET as we know them today were published from studies from this and from a second revised tomograph, also developed by *Phelps* and co-workers, and are coined as "Event 1" in the development of modern PET. An example of the modern version of a PET scanner is represented in Figure 7a.

In the PET process multiple steps are involved, combining the selection and production of a suitable molecular probe, a pharmaceutical labeled with a positron-emitting radionuclide, the administration of the probe to the patient and finally the imaging of the distribution of the probe into the patient.

Radionuclides used in PET scanning are typically isotopes such as ^{11}C ($\tau_{1/2} = 20$ min), ^{13}N ($\tau_{1/2} = 10$ min), ^{15}O ($\tau_{1/2} = 2$ min), and ^{18}F ($\tau_{1/2} = 110$ min). These radionuclides are incorporated either into compounds normally used by the body such as glucose (or glucose analogues), water, or ammonia, either into molecules that bind to receptors or other sites of drug action. It is important to recognize that PET technology can be used to trace the biologic pathway of any compound in living humans, and many other species can be radiolabeled with a PET isotope. At the present time, however, the most commonly used radiotracer in clinical PET is fludeoxyglucose, an analogue of glucose that is labeled with ^{18}F (Figure 7b).^[33] Cancer cells demonstrate up regulation of glucose: uptake of glucose or glucose-analogues, as deoxy-glucose is very fast in these type of cells. Thus, labeling deoxy-glucose with the positron emitting radionuclide ^{18}F to form ^{18}F -FDG allows the detection of these cells by PET technique. Furthermore, the ^{18}F tracer is very useful because of its long half-life and also because it decays by emitting positrons having the lowest positron energy which contributes to high-resolution imaging acquisition.

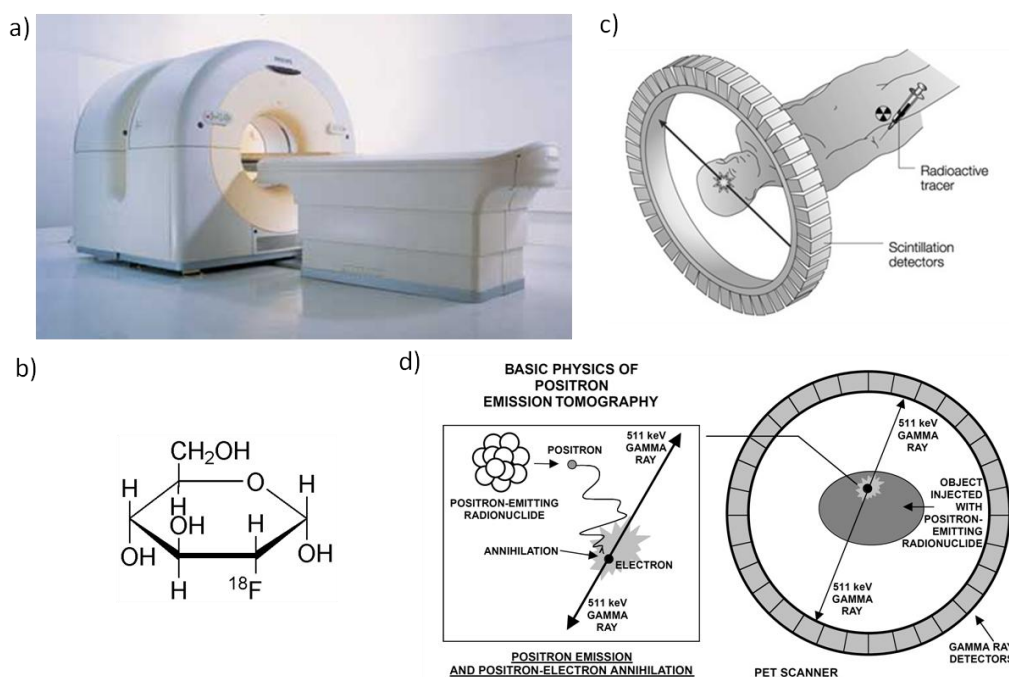


Figure 7. a) Typical Positron Emission Tomography facility; b) structure of fludeoxyglucose ^{18}F -FDG; schematic representation of c) injection of radiolabeled probe into the patient placed inside the scintillator stack and d) principles of PET imaging.^[34]

The principles of imaging tissue function *in vivo* with modern PET are summarized in Figures 7c and d. The analysis usually takes place inside the cylinder-shaped scintillator. After the injection of the probe to the patient (Figure 7c), there is a waiting period while the metabolically active molecule becomes concentrated in tissues of interest. As the radioactive isotope undergoes positron emission decay, it emits a positron. After travelling up to a few millimetres the positron loses energy through the interaction with the surrounding tissues until it annihilates with an electron producing two high energy γ -photons moving in almost opposite directions (Figure 7d). These γ -rays carry energy of 511 keV independent of the radionuclide involved. As soon as they reach the scintillator material, they are absorbed by the doping atoms present here, and then re-emitted creating a burst of light which is detected by a photomultiplier tube (Figure 7d). The pairs of coincident photons, or events, are stored in matrices where each row in the matrix represents a parallel projection of the activity distribution of the doped-metabolite in the patient at a specific angle (ϕ) and axial position (z). An image reconstruction algorithm is then applied to this matrix to recover the underlying radioactivity distribution, thus indirectly mapping the functional process that created the distribution of positron emitters.

2.1.2. The STRING Concept of the PET Scintillator

In terms of technology development the STRING project aimed at: *i*) developing new low cost scintillator materials with higher efficiencies and shorter response times for medical imaging; *ii*) creating multifunctional ceramic thin films for spectral conversion in the new concept of PET scintillator stacks.

Current scintillators in PET scanners contain more than 17000 single crystal scintillators with dimensions typically in the order of $1 \times 1 \times 4 \text{ cm}^3$. As previously mentioned, research investigations on scintillators deal with materials composed of gadolinium silicate (GSO), Gd_2SiO_5 , or lutetium silicate (LSO), Lu_2SiO_5 , single crystals doped with Ce^{3+} as the emitting ion, presenting emission decay times generally longer than 30 ns.^[29] Faster emissions, than the ones of Ce^{3+} , are necessary to achieve an improvement in the medical image quality. Therefore,

the idea of the STRING project was to rely on other ions, such as Nd^{3+} and Pr^{3+} whose emission decay time is considerably shorter, *ca.* 10 ns. Their emission, however, is located in the deep-UV. This posed an additional challenge, as the detection electronics of PET machines have very high sensitivity in the visible part of the spectrum. Therefore, STRING network needed to develop a ceramic thin film converter layer, which transforms the deep-UV radiation into visible light with a high efficiency. Organic materials are well suited for the role of wavelength converter with respect to the inorganic counterpart, due to the fact that inorganic materials have a slow emission decay time when they exhibit visible emission.^[29] To protect the organic converting material from the UV radiations, which might induce photodegradation processes, an inorganic matrix was designed to embed the dye. This new concept of the STRING scintillator is schematically summarized in Figure 8, in comparison with the old concept of PET scintillator.

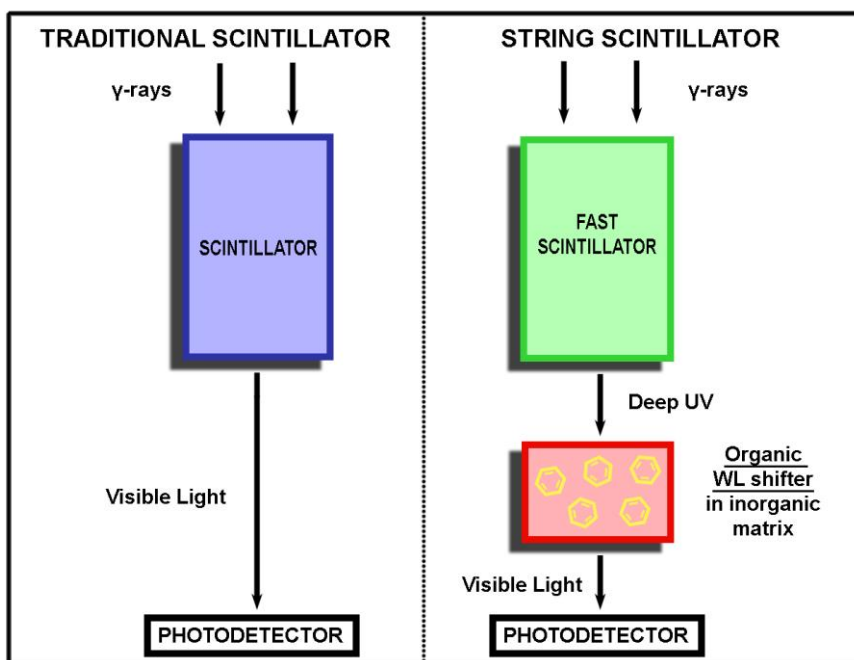


Figure 8. Comparison between the state-of-the-art concept of scintillator in PET instrumentation and the corresponding STRING improvements.

Numerous types of solid matrix were the object of the first stages of the STRING project. Although organic polymers are commonly used as a solid matrix for hosting organic molecules,^[35, 36] they generally suffer from lack of photostability and optical quality. Thus, STRING activities focused on different types of material, the inorganic glasses. These structures can be prepared by a well-established process named the sol-gel technique.^[37] The sol-gel is a wet chemical method used to create nanocrystalline or nanoscaled amorphous materials. By applying this technique pure inorganic materials, inorganic-organic polymers or nanocomposites have been processed to form nanoparticles, coatings, fibers or bulk materials. From the synthetic point of view this process is based on the exceptional properties of organosilicon compounds to form siloxane polymers. Specifically, hydrolysis and condensations of monomeric silicon alkoxide precursors upon addition of water are the main steps involved in this process. Two methodologies are known to insert organic molecules into glass substrates. They can be covalently linked to the glass functional groups or simply embedded in it by carrying out the same hydrolysis and condensation steps in the presence of the organic compound. In this case, only weak interactions exist between both phases. The advantages of an inorganic matrix for the embedding of functional chromophores are attributed to the more rigid environment as well as much higher

migration stability and strongly increased photostability compared with organic polymer matrices. Many examples of luminescent organic molecules embedded into glass hosts have been reviewed.^[38, 39]

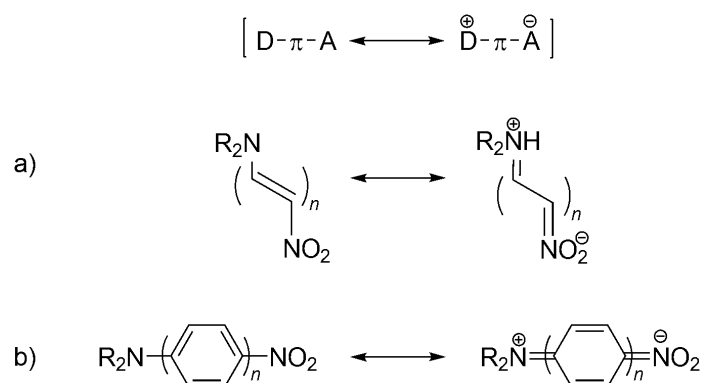
2.2. Approaches towards the Wavelength Shifters: the Push-Pull and Heteroatom Effects

To achieve the goal of designing organic wavelength shifters, for medical imaging applications, two strategies were considered. The push-pull effect in π -conjugated linear molecules was chosen as a first strategy. As an alternative method, wavelength converters were achieved exploiting the insertion of electron rich heteroatoms within a π -conjugated structure. These two approaches will be tackled in general terms in the following sections.

2.2.1. The Push-Pull Approach

The push-pull approach in organic chemistry has been investigated for decades.^[40-44] Nevertheless, organic push-pull chromophores still represent target compounds for numerous applications in materials science due to their promising optoelectronic properties such as second- and third-order Non-Linear Optical (NLO) effects.^[45, 46] In addition, they find numerous applications as functional materials in molecular devices.^[47]

A push-pull system is a molecule with an electron-rich donor, typically an amine or another nitrogen-based functional group, and an electron-deficient acceptor, typically a nitro or cyano group. These moieties are commonly separated by a π -conjugated bridge, which favors an efficient Internal Charge Transfer (ICT) between the donor and acceptor, upon $S_0 \rightarrow S_1$ excitation. Therefore, the push-pull effect has a strong influence on the long-wavelength electron transitions that, for this reason, is called charge transfer band. The π -conjugation plays an important role as it creates a state of intrinsically low band-gap due to the narrowing density of states in the π molecular orbitals. These structural features are combined producing a molecule with a HOMO consisting of electron density localized in the donor and the LUMO whose electron density is localized at the acceptor. This creates, upon excitation, a difference in the polarizability and thus a marked variation of the dipole moment of the molecule.



Scheme 1. Participation of zwitterionic resonance structures for the illustration of the push-pull effect in conjugated oligomers.

By combining different types of donor or acceptor groups, the HOMO-LUMO gap can be easily tuned. As introduced in the first chapter of this thesis, the push-pull approach is one of the most used strategy to lower the bandgap of organic molecules with the view of obtaining new highly conductive organic materials which may compete with the inorganic analogous.

There are a number of parameters that can influence the push-pull effect. The most notable of which is the strength of the donor and acceptor groups that can be easily obtained from the values of the σ of Hammett.^[48] It also depends on the conjugated π -system, to which a zwitterionic resonance structure should contribute (Scheme 1). Upon excitation, the energy of the dipolar resonance structure is determined by the charge separation as well as the change in the π -system. The latter influence is smaller for a pure oligoene chain (Scheme 1, path *a*) rather than for repeating units consisting of aromatic rings (Scheme 1, path *b*), where zwitterionic resonance structures have *p*-quinoid character. These two effects have been largely investigated in many literature reports.^[49-52] Herein, a couple of key examples, showing separately the two effects, are discussed.

The effect of the donor and acceptor groups in linear π -conjugated systems was studied by Meier *et al.* with series of donor- acceptor-substituted 1,4-oligophenyleneethynylenes and 1,4-oligophenylenevinyls.^[53, 54] As discussed before (Chapter 1), conjugated oligomers usually exhibit a convergent bathochromic shift of both the absorption and the fluorescence when the number of repeating units, *n*, is increased. It is a common belief that this shift of the lowest-energy CT band reflects a better donor acceptor π -conjugation.^[2] Contrary, several conjugated oligomers, such as 1,4-oligophenyleneethynylenes or 1,4-oligophenyleneethynylenes may behave as an exception showing a hypsochromic shift induced by the extension of the conjugated units length.^[42, 52] In the case described by Meier, a series of oligophenyleneethynylenes characterized by the increase of the conjugation units (*n*) were substituted with didodecylamino groups as the electron donors and nitrile (series **18b-21b**), formyle (series **18c-21c**), and nitro groups (series **18d-21d**) as electron acceptors (Figure 9).^[53] In parallel, a series of compounds without any acceptor moiety (series **18a-21a**) was analysed as reference compounds. The analysis of the absorption features of these derivatives showed for all the series the presence of a long-wavelength band, typical of the ICT of the push-pull system. While the **18a-21a** reference series exhibited a bathochromic shift upon increasing of *n*, the series **18c-21c** and **18d-21d** presented a hypsochromic trend. Additionally, the series featuring the cyano group as acceptor moiety, **18b-21b**, did not show any appreciable change in the position of the ICT band. To rationalize this behavior not only the number of repeating units *n*, but also the ICT has to be considered. The transition energy of the donor-acceptor oligomers is preferentially described by two contributes. The first one is relative to the value *n* and mainly considers the effect of the donor or the acceptor groups. This term perfectly describes the behavior of the reference series, provoking the cited bathochromic shift. The other term is relative to the effect of the ICT in the push-pull series **18-21 (b-d)**, and diminishes with the decreasing of the ICT (increasing *n*). Thus, it is clear that the two terms have opposite effects, and in the case investigated by Mayer, the decrease of the ICT effect with increasing *n* prevails in the series **18-21 (c-d)** resulting in an overall hypsochromic shift. Contrary, in compounds **18b-21b** both effects are present but they annul each other. It is important to point out that it is the type of donor-acceptor couple that indicates which effect will dominate. Therefore, in the **18b-21b** systems the presence of the moderate cyano acceptor ($\sigma_p = 0.66$) with respect to the nitro group ($\sigma_p = 0.78$),^[48] is the reason for the unchanged long-wavelength band absorption.

$$(C_{12}H_{25})_2N \left[\text{C}_6\text{H}_4 \text{---} \text{C} \equiv \text{C} \right]_n \text{C}_6\text{H}_4 \text{---} \text{A}$$

$\begin{smallmatrix} \diagup n \\ \diagdown A \end{smallmatrix}$	1	2	3	4	From
-H λ_{max}	18a 341	19a 374	20a 379	21a 378	Bathochromic
-CN λ_{max}	18b 387	19b 387	20b 384	21b 379	
-CHO λ_{max}	18c 400	19c 390	20c 382	21c 388	
-NO ₂ λ_{max}	18d 432	19d 403	20d 380	21d 382	Hypsochromic

Figure 9. 1,4-phenyleneethynylenes investigated by Mayer *et al.* The observed absorptions of the ICT bands (nm) are reported in the table, showing for each class the relative bathochromic or hypsochromic shift. For the **18b-21b** series the absorption values are almost constant.^[53]

In the context of push-pull organic chromophores and the relationships between their structure and properties, a great research contribute was given by the group of Diederich.^[42, 49, 50, 55-61] In particular, the effect generated by the nature of the π -conjugated system on the properties of push-pull dyes has been unraveled in several articles reported by the group. Herein, one of the most representative examples is described.^[59] The class of molecules considered in this work is a hybrids coming from the family of tetraethynylethene (TEE) and tetracyanoethene (TCNE), the cyanoethynylethenes (CEEs) derivatives (Figure 10). In this work, the conjugation in CEEs compounds is achieved by the substitution with *N,N*-dimethylamino (DMA) donor groups that, together with the cyano acceptors, constitute a new class of intramolecular charge-transfer (CT) chromophores. The analysis of the absorption features of the push-pull derivatives described, exhibited the presence of a long-wavelength band, typical of the ICT of the push-pull system. The effect of the π -conjugated system was especially shown by the results obtained comparing two regioselective isomers **22** and **23** (Figure 10). Chromophore **22** features four linearly conjugated donor acceptor pathways, whilst **23** bears two linearly and two cross-conjugated, or germinal, donor and acceptor pathways (Figure 10). As from previous reports it was demonstrated that the conjugation in linear D-A,^[49, 61] **22** results more conjugated than its regioisomer **23**. On the other hand, the longest wavelength absorption maximum of **23** is bathochromically shifted by 39 nm with respect to **22** (see the UV-Vis spectrum in Figure 10), suggesting a larger HOMO-LUMO gap for **22**. Consequently, a more efficient D-A conjugation may lead to large bandgaps, depending on the type of π -linker, if keeping constant the D-A groups.

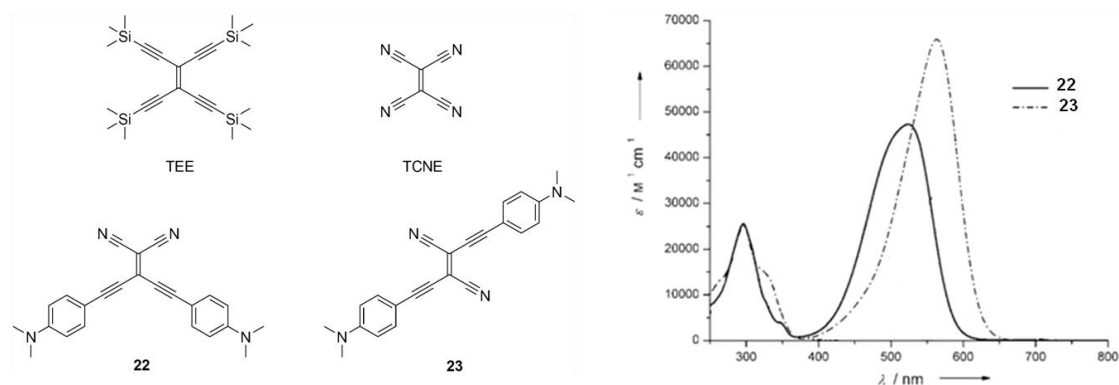


Figure 10. Left: structures of TEE and TCNE backbones and some of CEE derivatives investigated in the work of Diederich; Right: corresponding UV-Vis spectra exhibiting the characteristic ICT absorption band.^[59]

2.2.2. The Heteroatom Approach

2.2.2.1. Introduction to the Heavy-Atom Effect

Pure organic phosphorescent materials are of growing interest in the generation of novel devices for White Organic Light Emitting Diodes (WOLEDs) and solid state lighting technologies.^[62-65] The overall advantage of an organic phosphorescent material versus the inorganic analogous resides in the general difficulty of employing the latter in large area displays or on flexible substrates because of the brittle crystals growth by expensive methods. As a consequence, organic compounds have now been considered to be promising alternatives.

Despite this fact very few organic molecules have been found to be capable of efficient room temperature phosphorescence from triplet states because of their extreme sensitivity to collisional quenching by oxygen and other impurities. Phosphorescence is a forbidden relaxation of an excited state with spin symmetry different from the ground state, and, involves the decay from a triplet to a singlet state (Figure 11). Due to the mostly forbidden character, a triplet to singlet transition is usually slow. Nevertheless, triplet emission is partially allowed in the presence of spin-orbit coupling, a phenomenon strongly dependent on the atomic number of the atoms present in the structure. In particular, an increase in the rates of spin-forbidden radiative or non-radiative transitions is often observed on molecules where higher atomic numbered atoms, for instance, elements belonging to the sixth and seventh group of the periodic table, have been introduced. The so called Heavy-Atom (H-A) effect is the phenomenon related to the insertion in the molecule's skeleton (internal) or simply in the reaction medium (external), of an higher atomic numbered atom than carbon. This approach causes the enhancement of radiative and non-radiative intercombination transitions responsible for fluorescence quenching and the shortening of phosphorescence lifetimes.

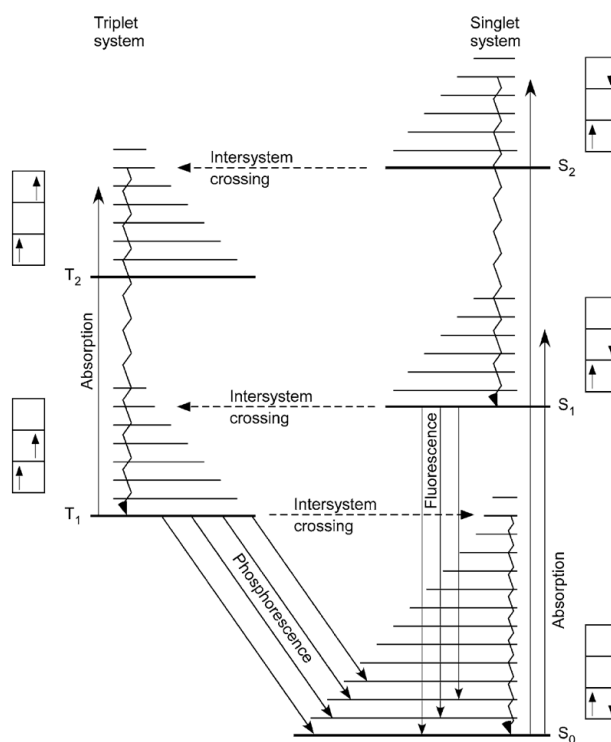


Figure 11. Energy levels of singlet and triplet states, showing the paired (or opposite) electron spins in singlet states, and unpaired (or parallel) electron spins in triplet states.^[66]

The very first example of photophysical H-A effects on organic molecules was reported by *McClure* in late 1940's. In his work, *McClure* investigated the phosphorescence lifetimes of various H-A substituted benzene and naphthalene derivatives (internal), observing a marked decrease in the phosphorescent lifetime as the atomic number of the H-A substituent increased.^[67]

More recent examples in this field are the H-A effects exhibited by organic molecules used in the PDT,^[68] where molecules capable of generating, upon excitation, triplet states react with other triplet ground state species such as oxygen causing the formation of the singlet oxygen. The singlet oxygen is a very important scavenger for target cancer cells, thus its production is extremely desirable. One of the most used sensitizers in PDT is the porphyrin macrocycle. To produce singlet oxygen in high yield, the triplet excited state of the porphyrin must have a long lifetime ($\tau > 5 \mu\text{s}$). Therefore, a common way to induce a long-lived triplet excited state in porphyrins is the H-A effect. Extensive research has been carried out on halogenated porphyrins and metalloporphyrins. *Azenha et al.* reported that *tetrakis*-phenyl porphyrins with chlorine atoms in *ortho* positions are particularly efficient in promoting singlet to triplet intersystem crossing.^[69] Specifically, the k_{isc} increases of two orders of magnitude from a non-substituted porphyrin to a corresponding chlorinated one (from $6.9 \cdot 10^7$ to $4.5 \cdot 10^9$) and the fluorescence quantum yield decreased from 0.10 to 0.005 for the corresponding chlorinated porphyrin.

As mentioned previously, it should be noted that H-A effects can also be observed as well if the heavy atom is present only in the reaction medium, *e.g.* the solvent. This is the case when external heavy atom effects are present. One of the first external H-A phenomena was reported by *Kasha*, studying the fluorescence signal decreasing of aromatic compounds in the presence of small amount of H-A functionalized alkyl halides in the mixture.^[70]

2.2.2.2. The Heteroatom Approach in π -Conjugated Architectures: Synthetic Achievements and Physical Properties of Electron Rich-doped Systems

Until few decades ago, among the so-called *chalcogen* atoms, only sulfur was intensively utilized in organic synthesis as versatile reactive element. Several years later, selenium and subsequently tellurium chemistry has rapidly developed, due to the growing interest in the physical and chemical properties of *chalcogen* derivatives.^[71] In contrast to the electron deficient atoms, the elements of group VI are strong electronic donating groups if connected or inserted in π -conjugated structures. This leads to unusual electronic properties if, for example, they are combined with acceptor moieties, for instance, enhancing the charge-transfer properties of the molecule.^[72, 73]

Belonging to the same group as that of oxygen, sulfur-, selenium- and tellurium-based structures should exhibit many similar characteristics. However significant differences exist amongst them. These are mainly due to the increase of the number in electrons in the outer shells and hence the atom size, rendering the heteroatoms more polarizable. The high polarizability and the manifested electron-rich characters are responsible for the whole pattern of different electronic and structural properties among the organo-*chalcogen* compounds.

In view of supramolecular abilities of sulfur-bearing organic architectures, one of the most explored research fields is provided by the chemistry of thiophene and the series of its derivatives. The electron-rich character of thiophene rings makes their derivatives suitable structures for a large variety of applications in electronic devices as, for example, conducting materials.^[74] Poly(thiophene)s and oligo(thiophene)s have been the most widely studied because of their conducting properties as highly ordered polymers for organic electronic devices such as light-emitting diodes,^[75] field-effect transistors,^[76] and organic solar cells,^[77] to name a few. The versatile synthesis of those classes of compounds has been intensively reviewed over the past decades and it is not the purpose of this section to redo it. In this part, the synthesis and the properties of a couple of examples of fused thiophene-based molecules have been reviewed.

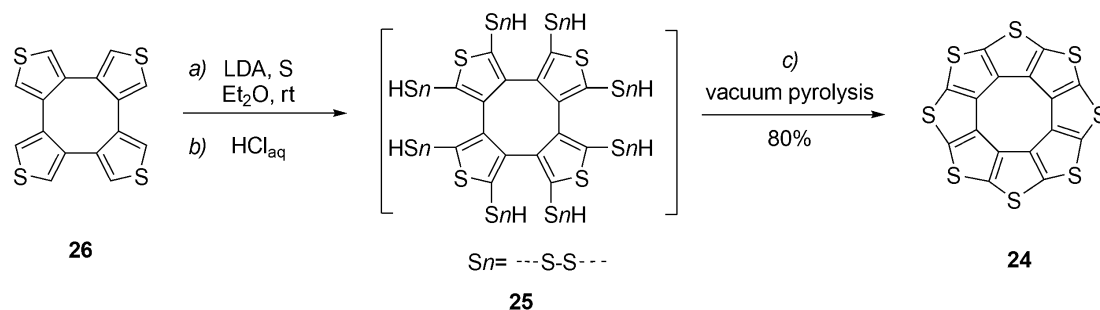
Chapter 2

Contrary to sulfur, the potentialities of selenium and tellurium as doping elements for supramolecular architectures have been unknown for many years due to the difficulties in finding high-yielding synthetic methods. For this reason, the employment of these two elements in organic supramolecular chemistry represents a challenge not only from the synthetic point of view but also for the discovery of new properties. To be consistent with the work carried out in this thesis, a brief overview is given in this section on the discoveries of S-, Se- and Te-doped supramolecular architectures through key examples from literature.

2.2.2.2.1. Sulfur-, Selenium- and Tellurium-Annulated Aromatic Structures

The main limitation of mono-linked oligothiophenes when compared with the fused oligothiophenes, lies in the structural deviation from planarity, which dramatically reduces the extension of the π -conjugation. The conversion of these structures into more rigid derivatives would make these oligothiophene derivatives more suitable as semiconductors, as the intrinsic conductivity increases with the enhancement of the π - π conjugation. Innovative structural engineering in this context would be the preparation of fused oligothiophene derivatives, in which thiophenyl units are doubly linked to neighboring rings. This would enhance the high structural planarity, producing extended flat pathways for π -conjugation, lowering the molecular HOMO-LUMO gap and thus giving rise to unique conducting properties.

In view of new fused oligothiophene derivatives, much attention has been given to polythiacirculene as a new class of compounds. They consist of annulated thiophenic rings with the formula $(C_2S)_n$ for any number of rings (n), and for this reason they are classified as a novel form of carbon disulfide. A great contribution to this field has been given from *Dopper* and *Wynberg* in the early 70's.^[78] They synthesized the first examples of S-containing heterocirculenes, reporting their first photophysical properties. Recently, the interest in these molecules has increased due to the great potential applications available for them in the entire field of electronics.^[79-81] In this respect, the group of *Nenajdenko* was the first to describe the synthesis of octathio[8]circulene **24** (Scheme 2),^[82] renamed as “sulflower” referring to its particular shape similar to a flower. They developed a short and effective strategy to obtain their compound, starting from tetrathiophene **25**, which had already been synthesized from the same group. Treatment of precursor **26** with 16 equivalents of LDA and elemental S at room temperature followed by acidification with an aqueous solution of HCl, led to the precipitation of a polythiol intermediate (Scheme 2, paths *a* and *b*). The precipitate was subjected to vacuum pyrolysis, giving the desired octathio[8]circulene **24** with an overall yield of 80% (Scheme 2, path *c*).



Scheme 2. Synthetic pathway towards “sulflower” **24**.

The excellent stability combined with the greater charge carrier mobility shown by these molecules, pushed the same group to investigate, a few years later, the properties of thin films of heterocirculene **24**, as conducting materials.^[83] At the solid state these systems are packed in π -stacked columns showing a strong charge transport

within the column but little or no electronic communication between the columns. With the introduction in the circulene core of heavier atoms, such as S, greater interaction between columns is provided by close S··S contacts (3.25 Å) improving the 3D charges transport. Considering these interactions, they fabricated one of the first models of thin-film transistor of **24** deposited on Si/SiO₂ substrate pre-patterned with Au circular electrodes, studying the charge mobility as a function of the morphology of these systems on the surface. The performance of the resulting Organic Field Effect Transistor (OFET) involving the “sulflower” as an organic semiconductor was measured in a N₂ saturated atmosphere. The **24**-based thin film showed a high hole field effect mobility and an on/off current ratio of about $9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 10^6 , respectively. Moreover, a higher threshold voltage, from -40 to -46 V, was observed for this device. These phenomena could be explained by considering the very low HOMO of **45** (-5.7 eV) and the resulting hole injection barrier at the Au electrode. In parallel, the analysis by Atomic Force Microscopy (AFM) measurements under vacuum conditions, at different times has been performed to study the morphology of the system (Figure 12). In the films they observed one-dimensional deposition of “sulflower” on the substrate, which suggested good abilities in charge mobility (Figure 12a). Increasing the surface coverage, the thin-films display needle-like arrangements, continually growing in one dimension (Figure 12b) until they reach the point in which the surface is fully covered and the linear disposition is no longer accessible. Therefore a vertical growth, perpendicular to the substrate, is observed. This, unfortunately, prevents the formation of long conducting films, causing serious limitations in the charge mobility of **24** (Figure 12c).

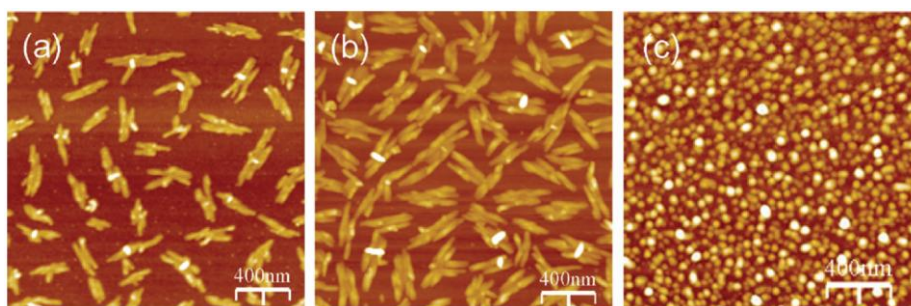


Figure 12. AFM images showing the growth of thin films of **24** on Si/SiO₂ substrate at different times a) 1 min, b) 2 min and c) 10 min.^[83]

The same group reported the synthesis of a hybrid version of the flower-type structure called “selenasulflower” (molecule **27** in Figure 13a) where selenium replaced four atoms of sulfur.^[84] The same synthetic methodology as that reported for molecule **24** was used for the synthesis of tetrathiatetraselenacirculene **27**, using Se powder at the place of elemental S (yield 50%). Co-deposition of 1,3,5-tricarboxylic acid (TMA) and circulene **27** on Highly Oriented Pyrolytic Graphite (HOPG) surface, featured the formation of hexagonal-like pores (formed by the intermolecular H-bonding interactions between the octanoic acid and TMA) filled by molecules of selenacirculene (Figure 13b) at the solid-liquid interface (solvent: octanoic acid), as imaged by Scanning Tunneling Microscope (STM). In Figure 13c a high resolution STM image of TMA-**27** interaction on HOPG is reported.

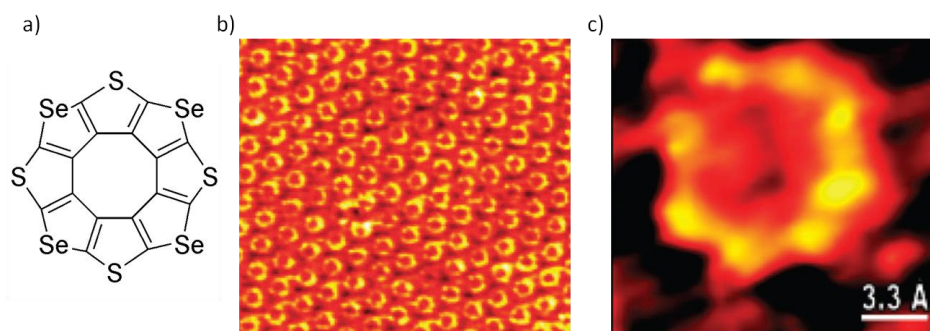
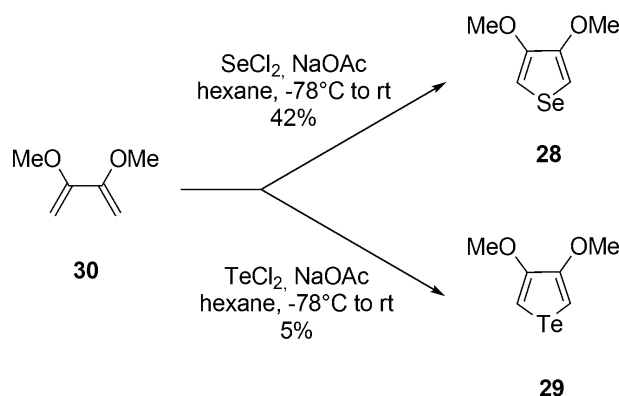


Figure 13. a) Structure of tetrathiatetraselenacirculene **27**; b) STM image of a **27**-TMA host-guest interaction on HOPG ($I = 0.3$ nA, $U = 0.3$ V); c) high resolution STM image of **27**-TMA host-guest interaction on HOPG ($I = 0.3$ nA, $U = 0.6$ V).^[84]

As briefly introduced in the example of the sulflower molecule, besides the electronic properties, *chalcogen*-doped π -conjugated heteroarene structures are of special interest in supramolecular chemistry as they can display a variety of different intermolecular recognition interactions such as heteroatom-heteroatom interactions, which can template and direct the formation of self-assembled structures displaying important optoelectronic properties applicable to various electronic devices, like OLEDs, solar cells, and NLO materials. Although these types of interactions have been largely described in *chalcogen*-doped macrocyclic structures, such as heterocalixarene and heterocyclophane compounds,^[85-87] very little is known about the corresponding fused aromatic structures.

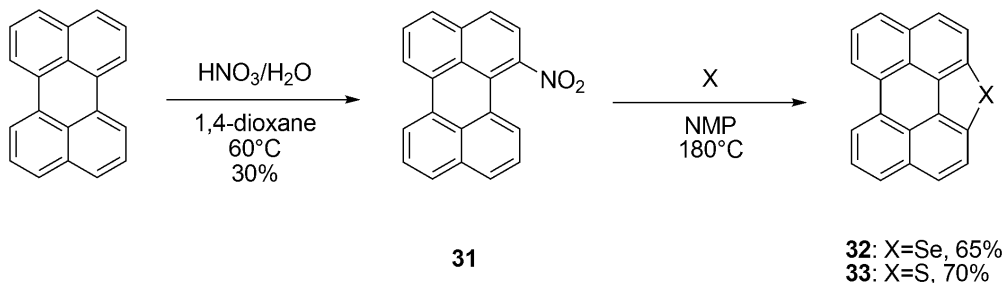
One of the few examples was reported by the group of *Bendikov*, in two distinct works. They employed a new one-pot synthetic methodology to prepare 3,4-dimethoxyselenaphene **28**^[88] and 3,4-dimethoxytelluraphene **29**.^[89] The synthesis of these molecules is outlined in Scheme 3. The authors envisaged the use of 2,3-dimethoxy-1,3-butadiene **30** as precursor material. Thus, butadiene derivative **30** has reacted separately, in the presence of NaOAc in hexane, with SeCl_2 at -78°C and with freshly prepared TeCl_2 at room temperature affording the desired products **28** and **29**, in 42% and 5% yield, respectively. X-ray crystal analysis showed that each five-membered ring intermolecularly interacts with each other via $\text{Se}\cdots\text{Se}$ or $\text{Te}\cdots\text{Te}$ contacts (heteroatom distances are 3.80-4.04 Å and 3.78 Å for **28** and **29**, respectively), showing the shorter distances for the $\text{Te}\cdots\text{Te}$. Despite the large amount of publications based on thiophene compounds, involving oligo and polythiophenes, the electronic and supramolecular arrangements of seleno- and telluro-parent monomers along with their polymeric derivatives have not yet been deeply explored, and it is still a topic under investigation.



Scheme 3. Synthetic pathway towards 3,4-dimethoxyselenaphene **28** and 3,4-dimethoxytelluraphene **29**.

Wang et al. recently investigated the effect of elemental Se in perylene-type structures.^[90] They set up a one-pot synthetic methodology based on the incorporation of Se into the nitro substituted perylene scaffolds (Scheme 4).

Hence, starting from 1-nitroperylene **31**, obtained by a nitration reaction of an unsubstituted perylene molecule, perylo[1,12-*b,c,d*]selenaphene **32** was obtained in good yield (65%) in NMP at 180°C. The same procedure was applied to synthesize the parent sulfur derivative, perylo[1,12-*b,c,d*]thiaphene **33**.



Scheme 4. Synthetic pathway towards the perylo[1,12-*b,c,d*]selenaphene **32** and perylo[1,12-*b,c,d*]thiaphene **33**.

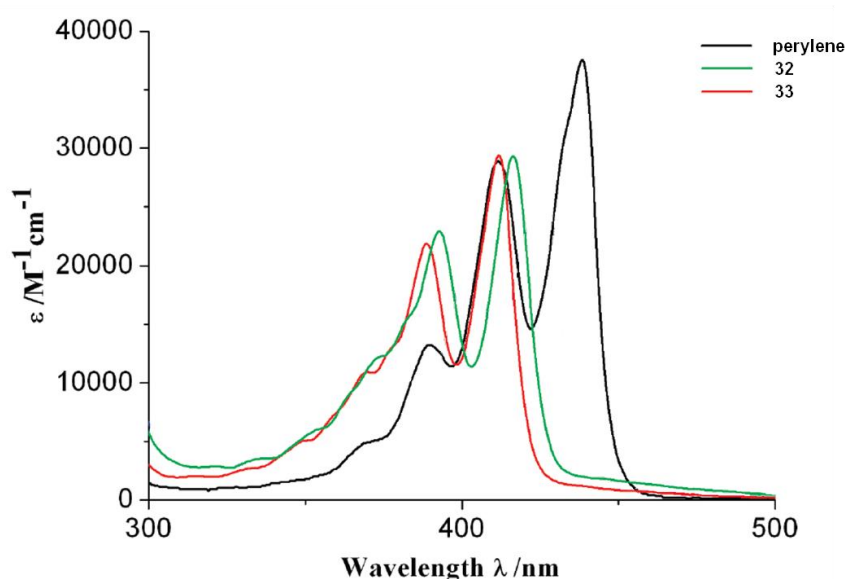


Figure 14. UV-Vis spectra of perylene (black line), **32** (green line) and **33** (red line) in CHCl_3 at room temperature (1.0×10^{-5} M).^[90]

In addition to the synthesis reported in this work, UV-Vis measurements of **32** and **33**, and perylene used as reference compound, were carried out (Figure 14). Specifically, a weak bathochromic shift was measured going from perylo[1,12-*b,c,d*]thiaphene to its Se-doped derivative **32** (**33**: $\lambda_{\text{abs}} = 412.0$ nm; **32**: $\lambda_{\text{abs}} = 416.5$ nm, in CHCl_3), in agreement with the higher electron-donor character exhibited by the selenium atom. On the contrary, these absorption values were found to be slightly blue-shifted compared to the value measured for the unsubstituted perylene ($\lambda_{\text{abs}} = 438.5$ nm, in CHCl_3). This behavior can be explained considering the aromatic character of the latter compared to its parent compound. Beside the photophysical properties, in the same work the authors reported the solid state organization of the three perylene based chromophores. Thus, crystals of **32** and **33** suitable for single-crystal X-ray analysis, obtained by evaporation of a dilute solution, were grown. In particular, the crystal structure of perylo[1,12-*b,c,d*]selenophene **32** showed almost planar molecular conformations, regularly stacked along the *b* axis, with similar interplanar distances of 3.47 Å. In addition, marked Se··Se short contacts (3.49 Å) shorter than S··S short contacts (3.51 Å) were observed between molecules of neighboring stacks, indicating that **32** has a more compressed packing

structure (Figure 15). This extraordinary double-channel superstructure makes **32** an attractive candidate for device applications.

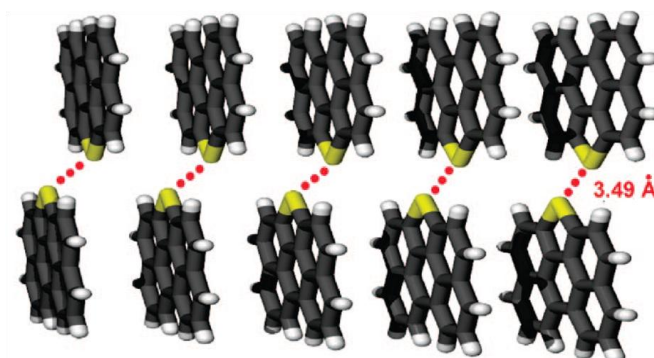


Figure 15. X-Ray crystal packing mode of perylo[1,12-*b,c,d*]selenaphene **32** exhibiting the Se...Se contacts between two molecules aligned in an antiparallel way.^[90]

2.2.2.3. Research Objectives towards Wavelength Shifters for Medical Imaging Applications

The aim of this project within the STRING network concerned the investigation of luminescent dyes for spectral conversion. The best dye candidates as wavelength converters must have well defined photophysical properties. These required properties can be summarized as follows: *i*) absorption in deep UV and emission in the visible part of the spectrum; in particular, the shifter's absorption, located in the UV between 200-300 nm, has to result superimposable to the scintillator ion's emission wavelength to maximize the energy transfer efficiency (*e.g.* for Pr^{3+} $\lambda_{\text{em}} = 309 \text{ nm}$); *ii*) good ability to absorb light ($\epsilon > 10^4 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$) and high fluorescent quantum yield ($\Phi > 0.8$); *iii*) fast response time (luminescent decay time $\tau < 2 \text{ ns}$); *iv*) large Stokes shift to avoid self-absorption; *v*) good photochemical stability to deep UV radiation.

With respect to the inorganic counterpart, organic materials are well suited for the role of wavelength converters. Although highly fluorescent inorganic substances may be used as wavelength shifters, they usually demonstrate slow decay times when the emission is located in the visible ($\sim 1 \mu\text{s}$).^[29] Amongst all, a short lifetime results as the most stringent requirement to design wavelength shifter for the PET technique. Short lifetimes account for higher images acquirement frequencies, speeding up the PET measurement. For this reason any type of inorganic wavelength shifter was so far used in PET scanners. Therefore, organic materials were considered in this project to design wavelength shifters in PET scanners.

The first three requirements (*i-iii*) are easily met, because most of the organic luminescent dyes with aromatic systems show very intense ($\epsilon > 10^4 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$) π - π^* transitions between 200-300 nm, broad emission bands extending into the visible part of the spectrum, and Stokes shift in the range $1.500\text{-}3.500 \text{ cm}^{-1}$ (but typically larger than 2.000 cm^{-1}). Conversely, the requirement of a 2 ns decay time and a quantum efficiency of more than 80% (*iv* and *v*) results in a strong decrease in the number of applicable compounds. Many organic materials used in OLEDs (*e.g.* naphthalene, anthracene, perylene, fluorene, carbazole, pyrene, etc.) present high fluorescent quantum yields at the solid state; however, they often have lifetimes higher than 2 ns, in some cases larger than 5 ns that render very difficult their employment in the PET technology. It is worth noting that no commercial material exists that possesses all the desired properties at once.

Semiempirical calculations were then employed to identify suitable classes of organic materials for wavelength converting in PET scanners. Molecules with π -conjugated electron systems showed promising properties as wavelength shifters. In particular, the calculations pointed out few design rules: *i*) the larger the conjugated aromatic

molecules, the larger the transition dipole moment; *ii*) changing the molecule size can modify the transition energy and larger molecules show transitions at lower energies; *iii*) linear conjugated aromatic molecules have larger transition moments than non-linear ones; *iv*) the molecules should have a high symmetry. These results suggested that linear π -conjugated systems such as diphenyl acetylenes and similar structures are very suitable for the purposes of the project. Specifically, linear organic molecules designed following the push-pull and the heteroatom approaches, were selected as novel wavelength shifters for PET scanners.

With respect to the first approach diphenyl acetylene derivatives substituted at opposite sides by an electron donor *N,N*-dihexylamino and various electron acceptor groups, **34-40** (Figure 16a), were investigated in this work. These systems have shown to be good candidates for the role of wavelength shifters.^[1, 42, 49, 51, 55-61] Due to the push-pull effect of the donor and acceptor groups, upon photoexcitation a large change in the charge distribution is induced in the excited-state, resulting in an ICT from the donor to the acceptor side.^[44, 91, 92] The large change in the molecular dipole moment in going from the ground state to the low-lying charge-transfer excited state makes this class of chromophores widely studied in terms of their nonlinear optical (NLO) properties with potential application in energy conversion devices, organic electronics, optical communication, and information storage.^[93-95] Moreover, with respect to other classes of linear push-pull dyes, the diphenyl acetylenes allowed a certain degree of rigidity, a crucial parameter for achieving some of the photophysical requirements of the project.

In parallel, within the research activities of the STRING project a new type of system characterized by benzoxazole cycles, was investigated. Benzoxazole-based molecules represent intriguing structures as, due to their manifold chemical and physical properties, they are exploitable in a broad series of applications, extending from the biomedical to the material science fields. Their structure is considered one of the most commonly used in medicinal chemistry, as they exhibit a variety of biological activities such as antimicrobial and antitumor capabilities.^[96-98] Additionally, in the last decade benzoxazoles have drawn great attention due to their luminescence properties and are largely considered as chromophores finding various applications such as brightening agents as well as NLO materials for two-photons absorption devices.^[99-102] When inserted in π -conjugated systems they provide a large charge displacement both in absorption and emission. This increases the radiative transition probability and hence decreases the radiative lifetime of the excited state (τ_r), resulting in high fluorescence quantum yields. This behavior has been observed, for instance, by comparing various benzoxazol-2-yl substituted aromatic rings with their unsubstituted precursors.^[103] As shown in Table 1, in some systems the increase in the rate of the radiative transition on introducing benzoxazolyl groups is quite dramatic: in benzene and in phenanthrene the radiative rate increases by a factor of 200, in biphenyl by a factor of 100, and in naphthalene by a factor of 400.

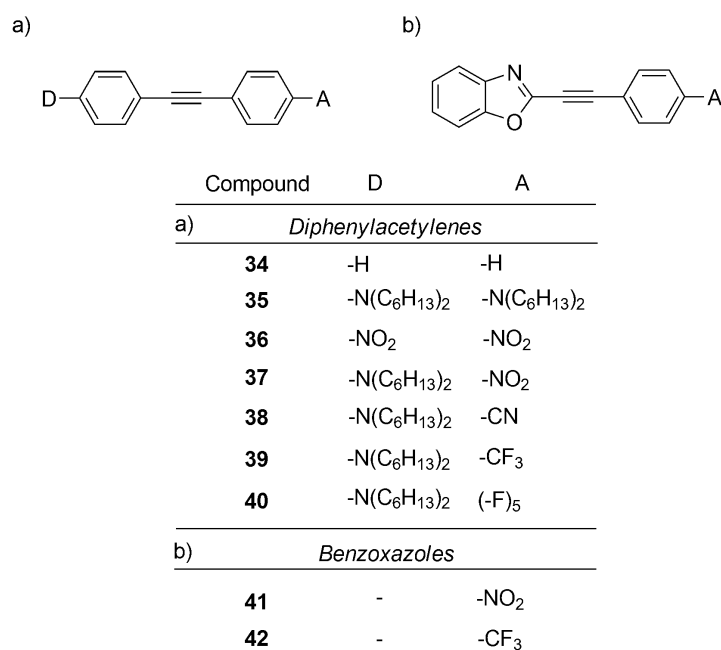
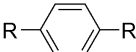
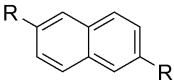
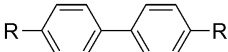
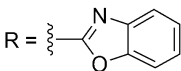


Figure 16. a) Structures of push-pull systems investigated in this work; b) structures of acceptor substituted benzoxazole-based dyes.

It is for this reason that these chromophores were selected to be part of the push-pull modules considered in this thesis. Therefore, two donor acceptor substituted compounds were synthesized and analyzed wherein the benzoxazole played the role of the electron releasing moiety.¹ In the present case, acceptor nitro and trifluoromethyl groups were chosen with the view of building push-pull π -conjugated benzoxazole dyes **41** and **42** (Figure 16b).

Table 1. Effect of benzoxazolyl group on the lifetimes of the excited singlet state of some aromatic rings (solvent: CHCl₃).

	τ_r (ns)		
			
R = H	407	89	417
R = 	1.4	1	1

In the context of the second approach towards the design of wavelength shifters for medical imaging techniques, the doping of heavy heteroatoms on π -conjugated aromatic structures was investigated. Attention was also focused on the change of emission type, from fluorescence to phosphorescence, as soon as heavy atoms are inserted in the organic backbone. The heavy atoms involved are the elements belonging to the sixth group of the periodic table. The introduction of these electron rich and highly polarizable atoms dramatically affects the chemical environment of the molecules, implying significant variation on their macroscopic properties. The organic species taken into account had a 1,4-diethynylphenyl central core where the triple bonds are linked to two benzoxazole moieties **43**. Subsequently,

¹ The benzoxazole ring may also act as an acceptor of electrons.^[104, 105] Depending on the characteristics of the opposite chromophore in a push-pull system, the benzoxazole ring can play the role of the electron releasing or withdrawing unit.^[106]

the two benzoxazoles groups were replaced with two benzothiazoles, **44**, and benzoselenazoles, **45** (Figure 17). In the following sections of the dissertation the synthetic attempts carried out to insert two benzotellurazole moieties at the extremities of the 1,4-diethynylphenyl central core, in view of preparing tellurium-doped bisbenzazole derivative **46** (section 2.2.3.3), are also reported. With the aim of exploring the solubility in polar solvents bisbenzoxazole derivative **47**, bearing two long alkoxy chains on the central aromatic core, was also developed.

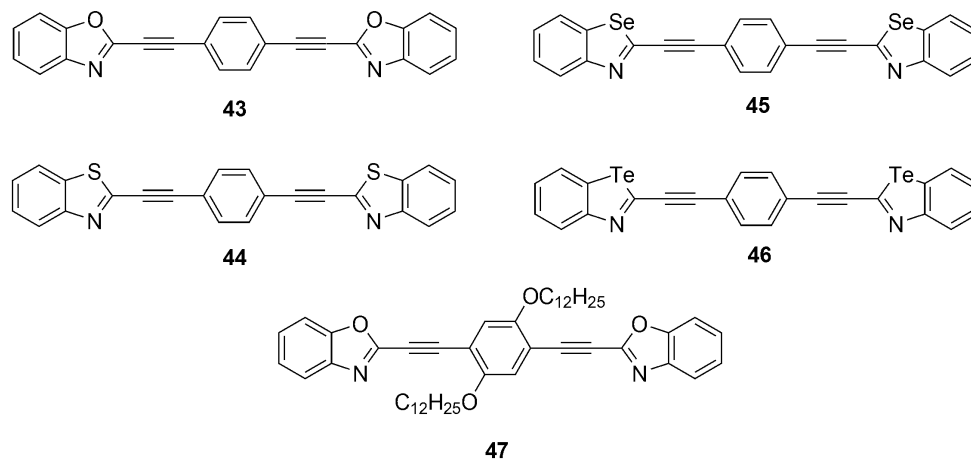


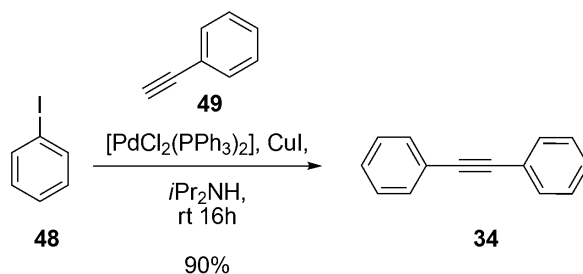
Figure 17. Structures of the doped benzazole-based modules synthesized and photophysically characterized in this thesis.

2.3. Synthesis of Wavelength Shifters

2.3.1. Diphenyl Acetylene Modules 34-40

The most efficient method to prepare a 1,2-diphenylethynylene derivative involves the classical Pd-catalyzed *Sonogashira* cross-coupling reaction between an aryl iodide and free terminal alkyne moieties.^[107]

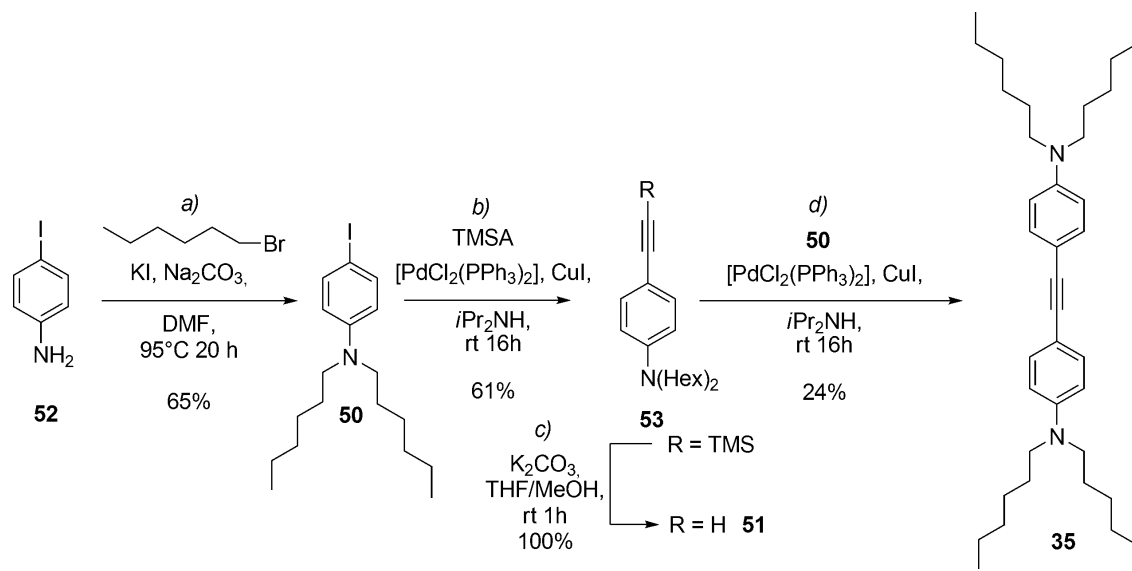
The synthesis of the targeted push-pull dyes began with the preparation of symmetrical diphenylethynylene derivatives used as reference compounds. To this end, 1,2-diphenylethyne **34** was produced in 90% yield, when 4-iodobenzene **48** and phenylacetylene **49** were allowed to react in presence of catalytic amounts of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI with $i\text{Pr}_2\text{NH}$ used as a solvent (Scheme 5).



Scheme 5. Synthesis of diphenyl acetylene **34**.

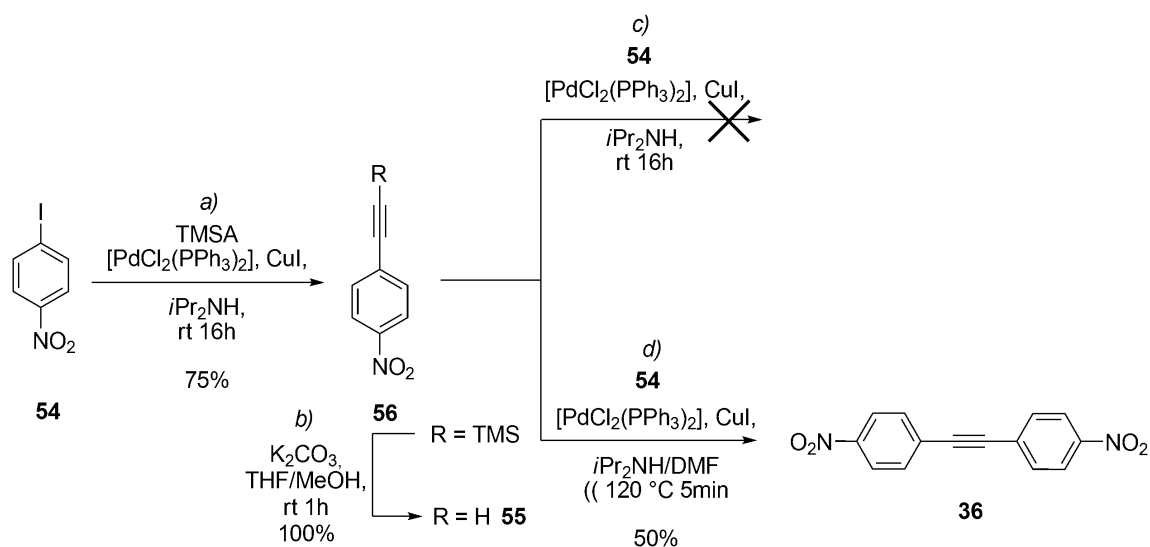
Similar reaction conditions were employed to synthesize symmetrical *N,N*-dihexylamino functionalized diphenyl acetylene **35** prepared with a poor yield (24%) starting from *N,N*-dihexylamino functionalized iodobenzene **50** and the corresponding terminal alkyne derivative **51** (Scheme 6). Molecules **50** and **51** have been in turn synthesized

following a similar pathway. A first substitution reaction of 1-bromo-*n*-hexane, with 4-iodoaniline **52** produced the intermediate **50** in 65% yield (Scheme 6, path *a*). This was then converted into its acetylenic TMS-protected derivative **53** through a Pd-catalyzed cross-coupling reaction in the presence of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI in *i*Pr₂NH, and subsequently deprotected under basic conditions to give **51** in quantitative yield (Scheme 6, paths *b* and *c*).



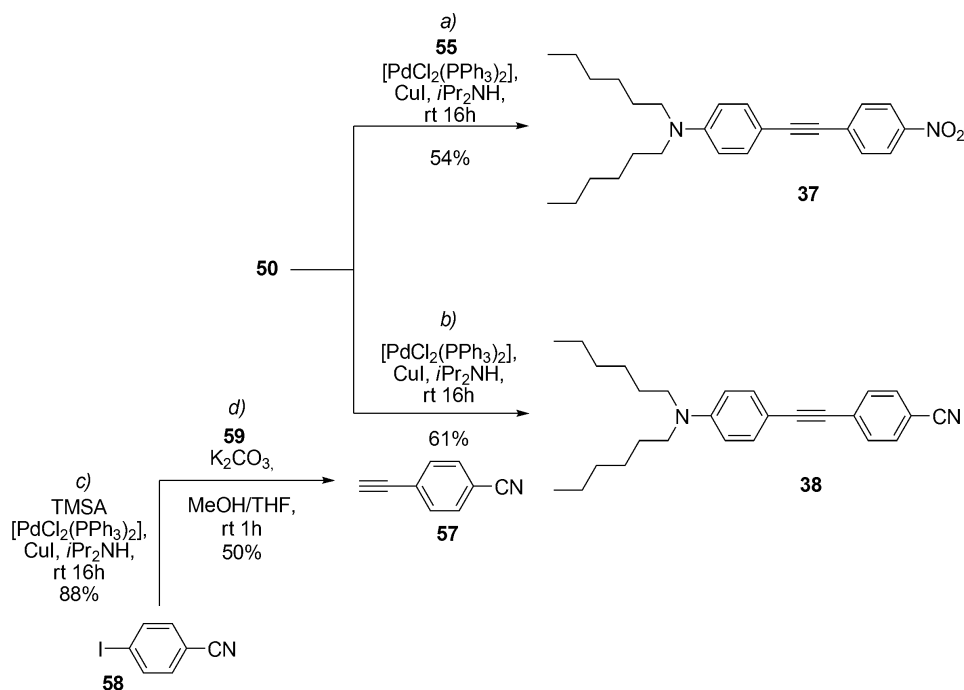
Scheme 6. Synthesis of *N,N*-dihexylamino-functionalized diphenyl acetylene **35**.

Similarly to molecules **34** and **35**, the standard *Sonogashira* procedure has also been applied to produce the symmetrical diphenyl acetylene core bearing at the opposite *para* positions two nitro groups as electron withdrawing functions, **36** (Scheme 7). In this case, however, the reaction between commercial 4-iodo-nitrobenzene **54** and 4-ethynyl-nitrobenzene **55**, as obtained from the Pd-catalyzed cross-coupling reaction underwent by **54** (**56**, Scheme 7, path *a*) followed by the quantitative cleavage of the TMS-protecting group (Scheme 7, path *b*), afforded a complex mixture of compounds impossible to separate (Scheme 7, path *c*). An alternative approach was, therefore, identified to perform the synthesis of **36**. This new methodology is used in many subsequent syntheses in this work and exploits microwave irradiation as a way of carrying out Pd-catalyzed *Sonogashira* reactions. Use of the microwave technique brought several advantages, e.g. it allowed cleaner and faster reactions. Microwave-based chemistry is based on the efficient heating of materials by “microwave dielectric heating” effects.^[108] This phenomenon is dependent on the ability of a specific material (solvent or reagent) to absorb microwave energy and convert it into heat. Another great advantage of the microwave technique is the rapid increase in the internal temperature that is attained when irradiating in a microwave field. As a consequence, there have been many reports showing a strong rate enhancement of the irradiated reactions. In addition, depending on the type of substrate, microwave technique offers the possibility to perform oxygen-free reactions, such as the large majority of transition metals-catalyzed couplings, without pre-degassing the solution. Thus, irradiating for 5 min at 120°C a mixture of **54** and **55** dissolved in *i*Pr₂NH and DMF and in the presence of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI, it was possible to obtain the desired bis-nitro substituted diphenyl acetylene **36** in 50% of yield (Scheme 7, path *d*).



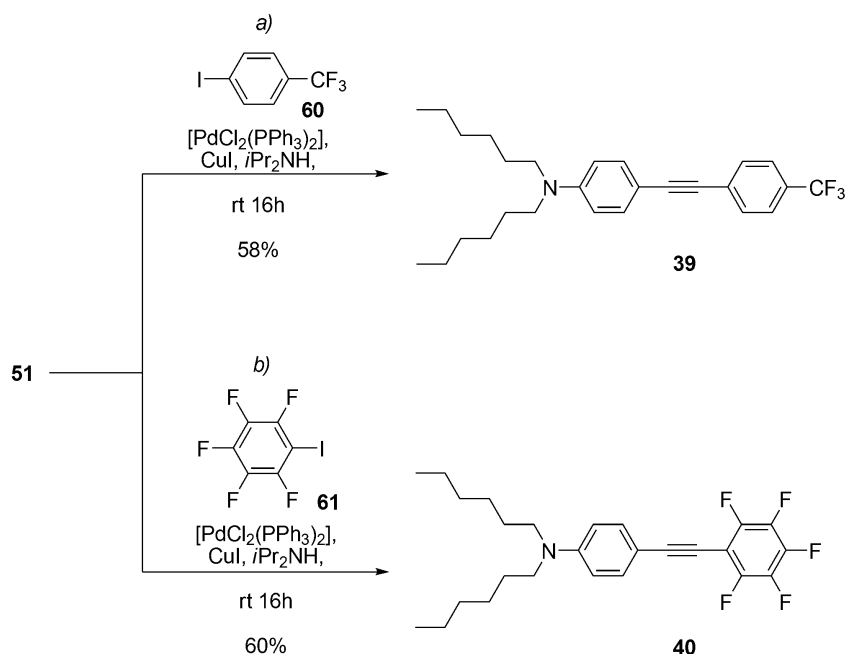
Scheme 7. Synthetic attempts towards the preparation of symmetrical diphenyl acetylene **36**.

On the way to push-pull diphenyl acetylenes **37** and **38**, 4-*N,N*-dihexylamino iodobenzene **50** was reacted under *Sonogashira*-type coupling conditions with the corresponding electron withdrawing substituted ethynylbenzene moieties (Scheme 8). Thus, 4-nitroethynyl benzene **55** was successfully coupled with **50** under Pd-catalyzed conditions, giving rise to module **37** in 54% yield (Scheme 8, path *a*). In parallel, the target molecule **38** was prepared *via* the reaction between **50** and 4-ethynylbenzonitrile **57** (Scheme 8, path *b*), obtained from 4-iodobenzonitrile **58** which underwent a Pd-catalyzed insertion of a TMS-protected acetylene (**59**, Scheme 8, path *c*) followed by the cleavage of the silylated group in basic conditions (Scheme 8 path *d*).



Scheme 8. Synthetic pathways towards the preparation of unsymmetrical push-pull diphenyl acetylenes **37-38**.

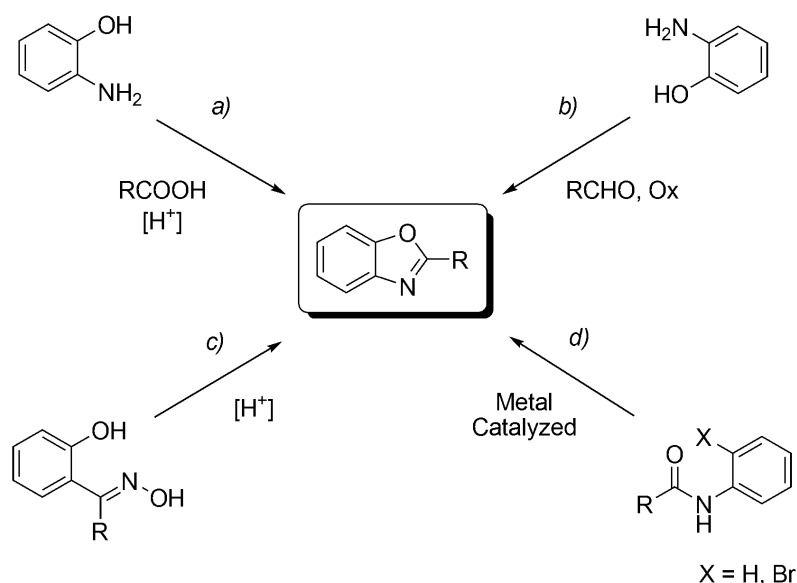
A different route was developed to prepare trifluoro- and pentafluoro-phenyl substituted push-pull modules **39**-**40**. Therefore, starting with **51** the two electron-withdrawing moieties were successively inserted by applying two Pd-catalyzed coupling reactions with 4-trifluoromethyl iodobenzene **60** and pentafluoro iodobenzene **61**, leading to push-pull derivatives **39** and **40** in 58% and 60% yield, respectively (Scheme 9, paths *a* and *b*).



Scheme 9. Synthetic pathways towards the preparation of unsymmetrical push-pull diphenyl acetylenes **39**-**40**.

2.3.2. Benzoxazole-based Push-Pull Modules 41-42

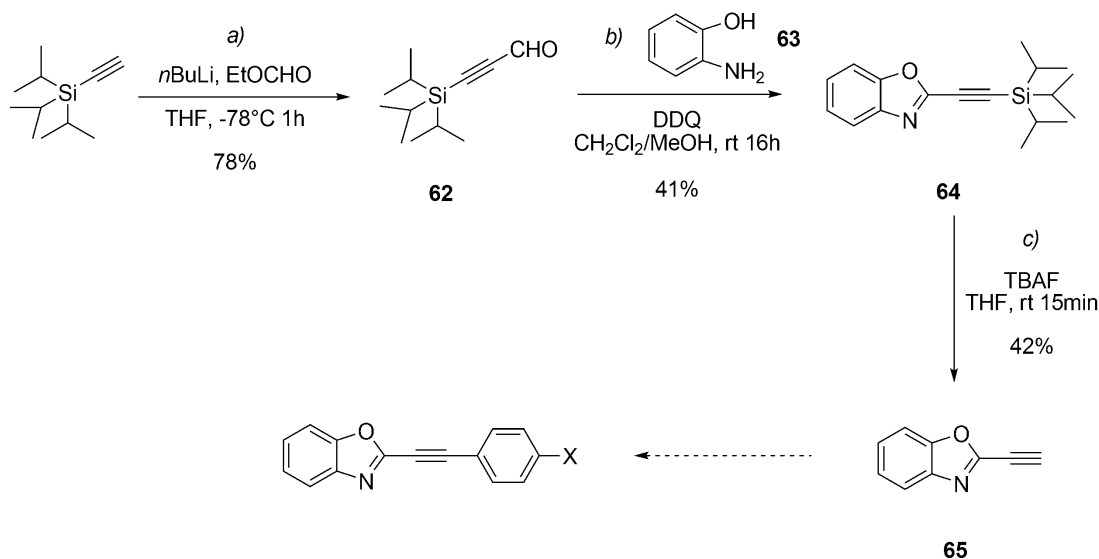
Benzoxazoles represent an important class of heterocycles that are encountered in a large number of natural products and are used in both drug and agrochemical products. For this reason since early 1950, their synthesis has received wide attention and different methods of preparation have been envisaged. Scheme 10 presents an overview of the principal synthetic methodologies to prepare benzoxazole rings reported so far in the literature. Classical methods involve the condensation of 2-aminophenol with either a carboxylic acid derivative under strong acid/high temperature conditions, or an aldehyde followed by oxidation (Scheme 10, paths *a* and *b*). The condensation with carboxylic acid was the first reported procedure for the synthesis of benzoxazole compounds and was formerly applied for the preparation of the parent benzimidazole-based compounds.^[109] The harsh conditions required in this case, included the use of H_3PO_4 or H_3BO_4 and the reflux of the solution in high boiling point solvents.^[110, 111] As a way to avoid strong acid catalysis and to employ general milder reaction conditions, some examples report the condensation of 2-aminophenol with aldehydes. The heating of the 2-aminophenol in the presence of the aldehyde gives rise to the formation of the phenolic Schiff base which is then oxidized by various oxidants, such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),^[112] $\text{PhI}(\text{OAc})_2$,^[113] MnO_2 ,^[114] $\text{Ba}(\text{MnO}_4)_2$,^[115] and $\text{Pb}(\text{OAc})_4$.^[116] The benzoxazole ring can be obtained following a different strategy that involves the *Beckmann* rearrangement of *o*-acylphenol oximes followed by an intramolecular ring closure (Scheme 10, path *c*). This reaction was carried out in the presence of ZnCl_2 in a microwave reactor; it was also described using zeolite catalysts or else a combination of phosphoryl chloride and *N,N*-dimethylacetamide.^[117]



Scheme 10. Main synthetic strategies towards the preparation of 2-substituted benzoxazoles.

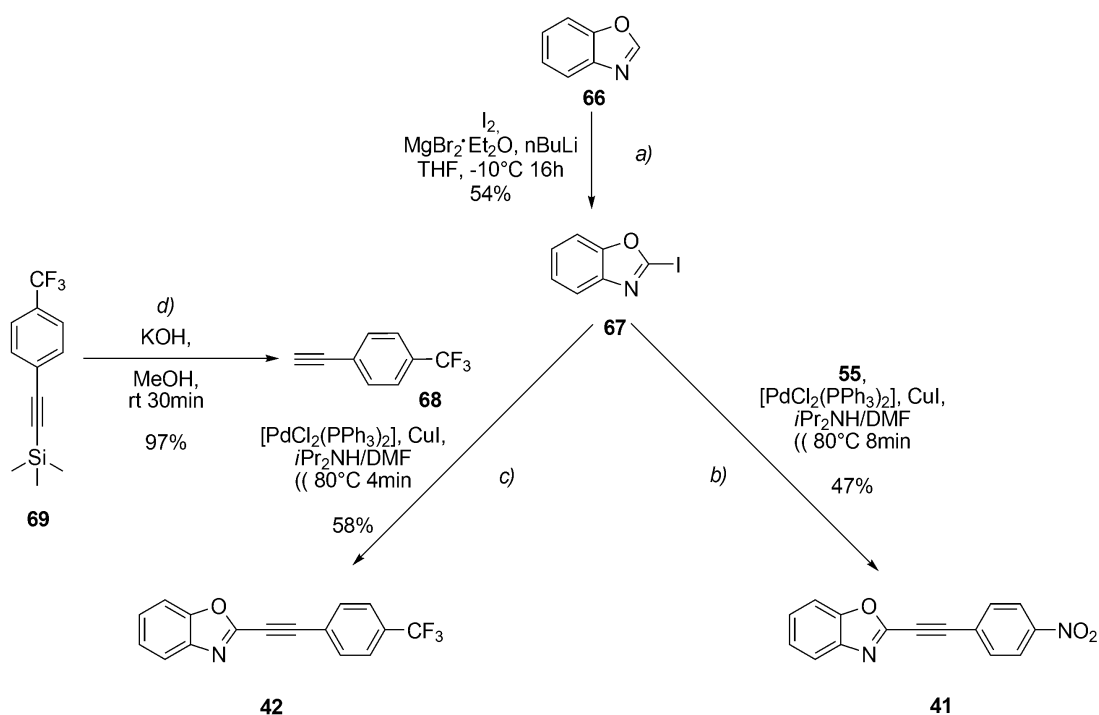
The last synthetic strategy that has been reported for the synthesis of 2-substituted benzoxazoles takes into account the reaction of 2-haloanilides or simple anilides which undergo a metal catalyzed intramolecular coupling between the oxygen of the anilide and the sp^2 aromatic carbon (Scheme 10, path *d*). In the example reported by the group of *Batey*, the intramolecular cross-coupling of 2-bromoanilide was promoted by Cu(I) catalyst, and 1,10-phenanthroline used as a ligand in basic and anhydrous conditions.^[118, 119] This procedure was found to be applicable for the preparation of both 2-aryl and 2-alkyl benzoxazoles. A similar pathway was also designed years later by the group of *Nagasawa* for the synthesis of 2-aryl benzoxazoles.^[120] Herein, they developed a straightforward and versatile method to obtain functionalized benzoxazoles by copper-catalyzed intramolecular oxidative aromatic C-O bond formation in readily available benzanilides. Specifically, benzoxazoles have been produced through C-H bond activation and subsequent intramolecular coupling with the amide oxygen of the anilide. The control of the regioselectivity is influenced by the substituent present on the aromatic ring of the anilide. The authors observed that the intramolecular cyclization occurs at the less sterically hindered position affording 2,5-disubstituted benzoxazoles. However, when the anilide bears coordinative substituents, such as carbonyl groups, the ring closure yield exclusively 2,7-disubstituted benzoxazoles.

The condensation of 2-aminophenol with an aldehyde derivative, was the first strategy envisaged in this work for the preparation of 2-substituted benzoxazoles **41** and **42**. Therefore, 3-(triisopropylsilyl)-2-propynal **62**, obtained from the deprotonation of TIPSA with *n*BuLi followed by a nucleophilic attack on the EtOCHO (Scheme 11, path *a*), was refluxed with 2-aminophenol **63** in MeOH. The formed Schiff base was then oxidized *in situ* by DDQ affording the corresponding TIPS-protected 2-ethynyl benzoxazole **64** in 41% yield (Scheme 11, path *b*). The TIPS group was then deprotected in a mixture of THF and MeOH, yielding the free ethynyl benzoxazole **65** in 42% (Scheme 11, path *c*). The latter was found to be highly unstable in solution at ambient conditions. Although all the precautions were taken to avoid the air contact, only ^1H -NMR characterization was carried out (Chapter 4). After the NMR analysis, the pale yellow CHCl_3 solution of **65** turned light green first and dark green after ten minutes, resulting in a mixture of uncharacterized byproducts.



Scheme 11. First synthetic attempts for the synthesis of push pull benzoxazole derivatives **41** and **42**.

The instability of derivative **65** meant that an alternative route for the synthesis of targeted dyes **41** and **42** needed to be found. Following a procedure reported in literature,^[121] commercially available 2-*H*-benzoxazole, **66**, was iodinated with I_2 and in the presence of $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ leading to 2-iodobenzoxazole **67** in 54% yield (Scheme 12, path a). Then, **67** underwent two microwave-assisted *Sonogashira* cross-coupling reactions with 4-ethynynitrobenzene **55** (Scheme 12, path b) and 4-ethynyltrifluoromethylbenzene **68** (Scheme 12, path c), as obtained from the deprotection of the corresponding TMS-protected precursor **69** (Scheme 12, path d), yielding two targeted compounds **41** and **42** in 47% and 58%, respectively. Melting point, ^1H -, ^{13}C -, ^{19}F -NMR, UV-Vis, IR and APCI-HRMS were performed to prove the structures of the two benzoxazoles (Chapter 4). The benzoxazole group was identified by 1D- and 2D-NMR analysis of CDCl_3 solutions of the dyes. To give an example, the ^1H - and HMQC-NMR spectra of **42** are reported in Figures 18 and 19. The ^1H -NMR spectrum reports four areas of peaks; the first two multiplets integrating for 5H, are related to H-atoms belonging to the phenyl bearing the CF_3 group ($\text{H}_{e,f}$), the additional proton was assigned to H_d for comparison with literature data of similar structures. Between δ 7.57-7.39 ppm is the area referred to $\text{H}_{a,b,c}$. In particular, the doublet at δ 7.57 ppm is assigned to H_a , while the complex system at δ 7.47-7.39 ppm named as doublet of triplets is the signal of $\text{H}_{b,c}$. To provide additional proofs to this interpretation, 2D Heteronuclear Multiple Quantum Correlation (HMQC) experiment was also carried out (Figure 19). This analysis allows ^1H -NMR (y axis) correlation with ^{13}C -NMR (x axis) in order to establish the link between proton and carbon atoms. Therefore, the HMQC spectrum of **42** presents that the first multiplet at δ 7.79-7.77 ppm correlates with two different carbon atoms, one belonging to the phenyl group (as it is the more intense) and the other belonging to the benzoxazole ring (Figure 19, light blue dashed lines). The doublet of triplets at δ 7.47-7.39 ppm also correlates with two different carbon atoms belonging to the benzoxazole moiety (Figure 19, green and red dashed lines).



Scheme 12. Synthesis of targeted benzoxazole-based push pull dyes **41** and **42**.

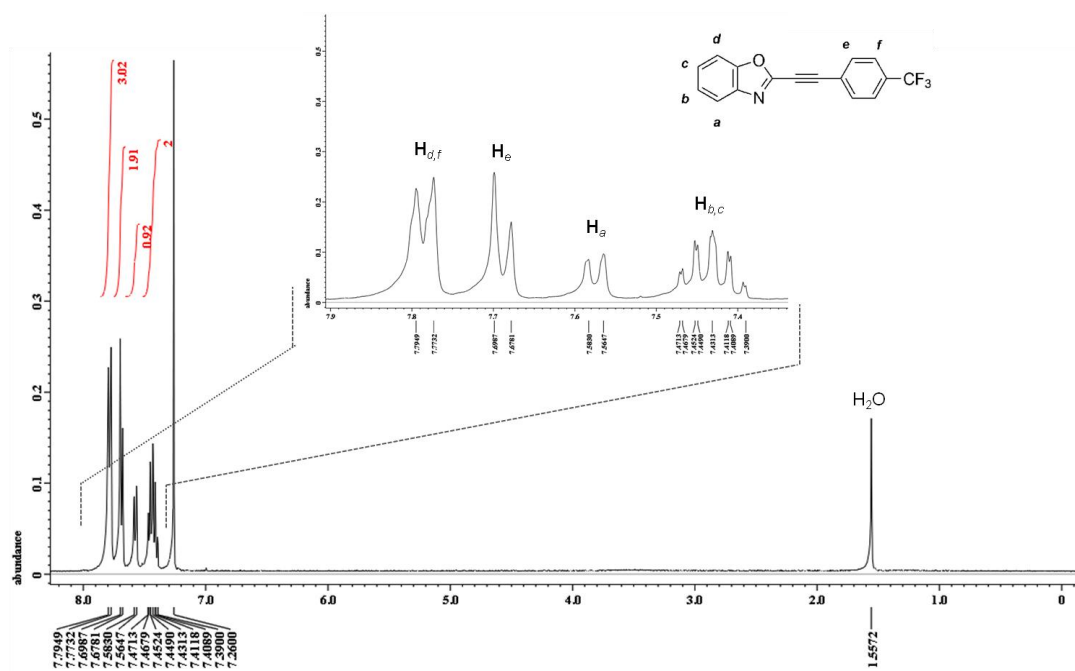


Figure 18. ^1H -NMR spectrum (400 MHz, CDCl_3) of benzoxazole **42**. Inset: zoom of the 8.0-7.3 ppm area.

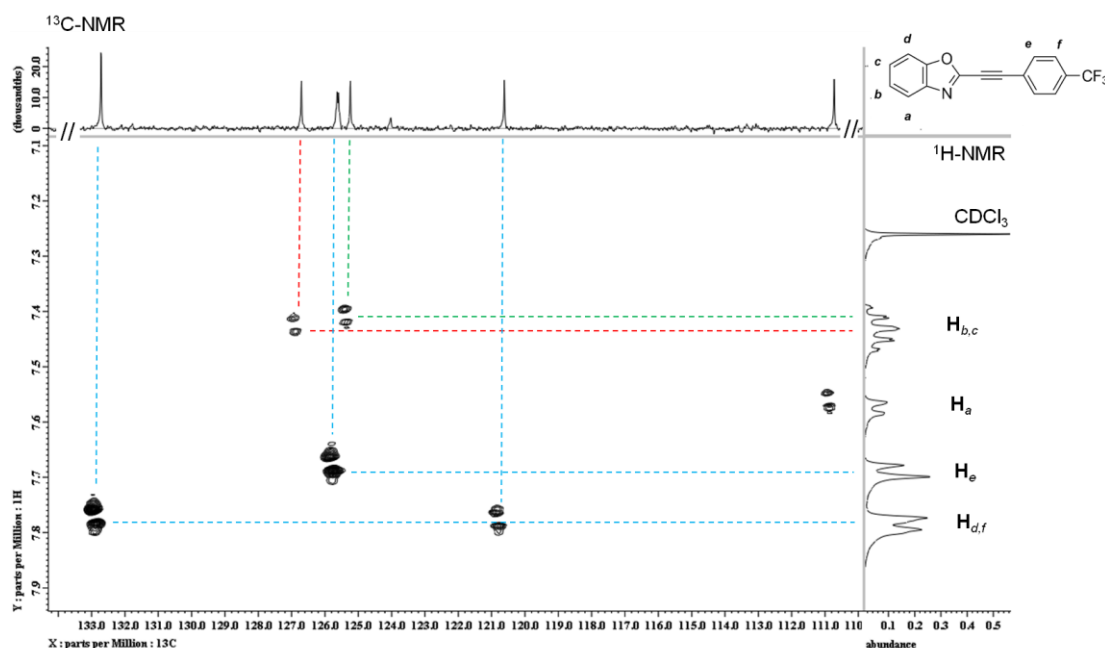


Figure 19. 2D-HMQC NMR correlation spectrum (400 MHz, CDCl₃) of benzoxazole **42**. ¹H- and ¹³C-NMR are zoomed in the area of interest (see the text).

To gain information on the spatial arrangement of push-pull chromophores **41** and **42**, single crystals of **42** suitable for X-Ray crystallographic analysis were obtained. Unfortunately, crystals of **41** were unable to be obtained due to the low solubility shown by the compound in most of the common organic solvents. Therefore, transparent crystals were grown by evaporation of a CHCl₃ solution of **42**. Figures 20a-c displays the ORTEP representation of crystallized **42** together with two orientations of the packing mode of the crystal (for more details on the X-Ray analysis see *Appendix*). Module **42** arranges at the solid state according to a P-1 space group. Specifically, the crystal packing of **42** shows a slipped parallel stacking of the chromophores of about 1.5 Å and exhibits a favorable antiparallel dipolar alignment in the stacks, with a ring centre-to-centre distance of 3.5 Å which witnesses the π - π stacking character of the packing.

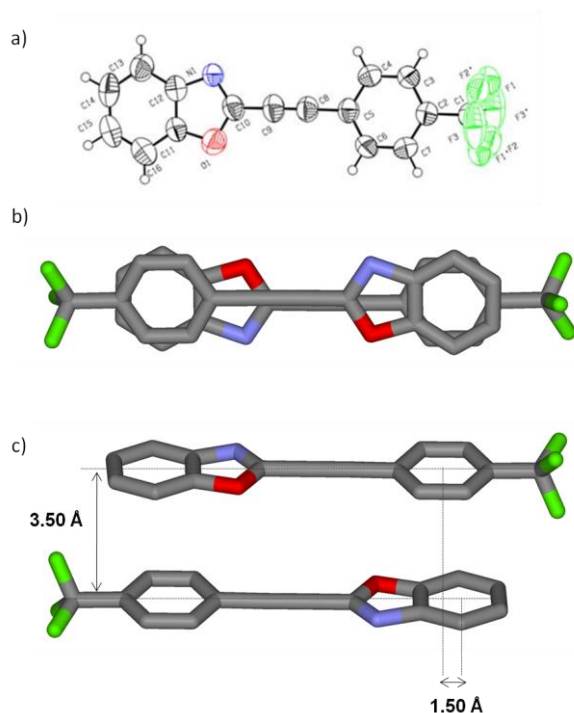


Figure 20. Crystal structure of push-pull derivative **42** determined by X-Ray analysis. a) ORTEP representation of **42** with vibrational ellipsoids at 243 K. Selected bond length (Å) and angles (°): C1-C2 1.493(6), C2-C3 1.390(6), C3-C4 1.360(5), C4-C5 1.380(6), C5-C6 1.376(5), C6-C7 1.366(6), C7-C2 1.371(6), C5-C8 1.448(5), C8-C9 1.192(6), C9-C10 1.421(6), C10-N1 1.312(6), C10-O1 1.328(5), N1-C12 1.328(5), O1-C11 1.391(5), C11-C12 1.374(6), C12-C13 1.379(6), C13-C14 1.384(7), C14-C15 1.381(8), C15-C16 1.350(8), C16-C11 1.371(6), C1-F1 1.345(5), C5-C8-C9 179.1(4), C8-C9-C10 179.3(5), C1-F1-F2 105.3(3), C10-N1-C12 103.9(3), C10-O1-C11 103.8(3), N1-C12-C13 130.5(4), O1-C11-C16 129.6(4); b-c) crystal packing of **42**, showing the antiparallel overlap of two molecules and witnessing the presence of π - π stacking.

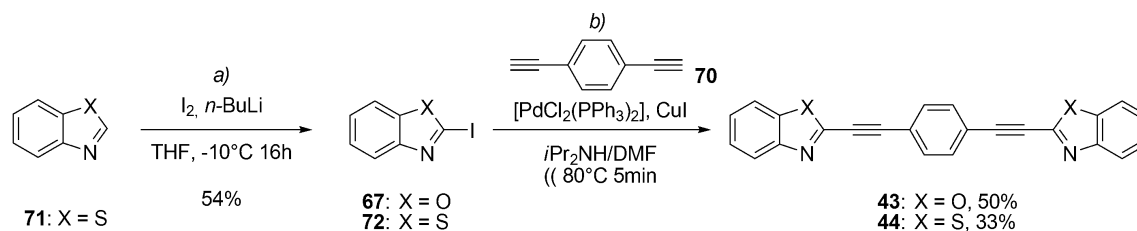
2.3.3. Synthesis and Solid State Arrangements of Hetero-doped Benzazole-based Organic Emitters 43-47

The greatest challenge encountered in this work concerned the ethynyl substitution at the 2-position of the benzazole fused ring. While few examples of 2-acetylene substituted benzoxazole and benzothiazole scaffolds have already been exploited,^[99, 100, 102, 122] this is the first contribution, among the ones presented in the literature, on the synthesis of a 2-ethynyl functionalized benzoselenazole derivative.

2.3.3.1. Synthesis of Bisbenzoxazole, Bisbenzothiazole, **43-44**, and Alkylated Bisbenzoxazole **47**

The synthetic pathway towards bisbenzazole derivatives **43-44** is outlined in Scheme 13. Bisbenzoxazole compound **43** was synthesized starting from 2-iodobenzoxazole **67** as prepared after the iodination of commercially available 2-*H*-benzoxazole **66** (section 2.3.2: Scheme 12, path *a*). Iodinated benzoxazole **67** was then reacted with 1,4-diethynylbenzene **70** in the presence of catalytic amounts of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI in a mixture of *i*Pr₂NH and DMF, following a *Sonogashira*-type procedure accomplished by microwave irradiation. The first targeted module was, thus, prepared in 50% yield (Scheme 13, path *b*). Following a similar procedure as the one described for the synthesis of iodinated benzoxazole **67**, 2-*H*-benzothiazole **71** was firstly deprotonated by *n*BuLi and subsequently substituted with iodine by reacting with I₂ (Scheme 13, path *a*). The so-formed 2-iodobenzothiazole **72** was coupled

with **70** following a Pd-catalyzed *Sonogashira*-type reaction accomplished by microwave irradiation, producing desired bisbenzothiazole module **44** in 33% yield (Scheme 13, path *b*).



Scheme 13. Synthetic pathway towards the bisbenzoxazole, **43**, and bisbenzothiazole, **44** targeted molecules.

The structures of the two bisbenzazoles was confirmed by melting point, ^1H -, ^{13}C -NMR, UV-Vis, IR and HRMS (ESI and APCI) techniques (Chapter 4). The purity of the two compounds was proved *via* reverse phase HPLC using CH_3CN as eluent (Figure A1 in Appendix). The ^1H -NMR spectra of the two dyes present similar patterns (Figures 21 and 22). Both show four signals, two doublets coupled with a J_{para} not discernable from the spectra ($\text{H}_{d,a}$) at δ 7.79 and 7.58 ppm for **43** and δ 8.10 and 7.90 ppm for **44**. These peaks are also coupled with a complex system given by $\text{H}_{b,c}$ (**43**: δ 7.46-7.39 ppm; **44**: δ 7.56-7.46 ppm) with a J_{ortho} of 6.6 Hz for bisbenzoxazole **43** and of 8.0 Hz for derivative **44**. This signal is of the same type of that observed for push-pull benzoxazole **42** (section 2.3.2) and is characteristic for the hetero-doped benzazole compounds. In addition, both dyes present an intense singlet peak assigned to the 4H of the central aromatic rings ($\text{H}_{e,f}$). Further structural confirmations have been possible with 2D-HMQC. In Figure 23, as an example, the NMR HMQC spectrum of bisbenzothiazole **44** is illustrated. The HMQC spectrum was important to characterize the benzazole moiety. In this respect, the spectrum presents the coupling between the 4H belonging to the phenyl ring and the corresponding carbon signal in the ^{13}C spectrum (light blue dashed line) and that of the complex system $\text{H}_{b,c}$ with the corresponding carbon peaks (red and green dashed lines). These couplings were found to be common for benzazoles **43-44** and for parent modules **45** and **47**.

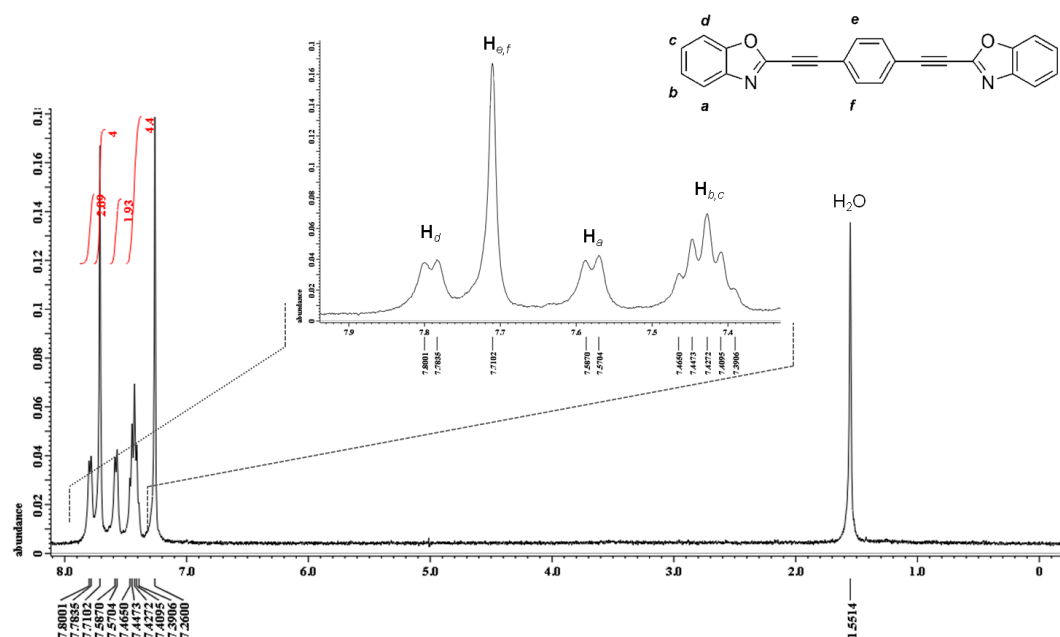


Figure 21. ^1H -NMR spectrum (400 MHz, CDCl_3) of bisbenzoxazole **43**. Inset: zoom of the 8.0-7.3 ppm area.

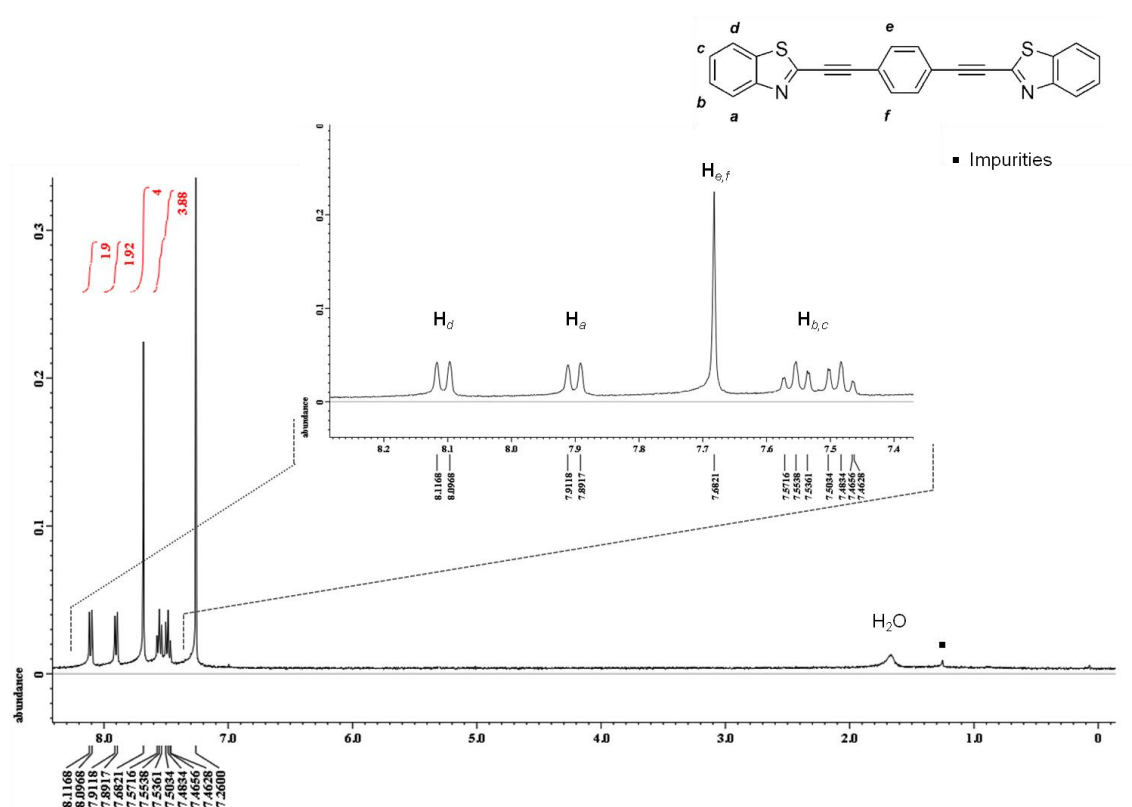


Figure 22. ^1H -NMR spectrum (400 MHz, CDCl_3) of bisbenzothiazole **44**. Inset: zoom of the 8.3-7.3 ppm area.

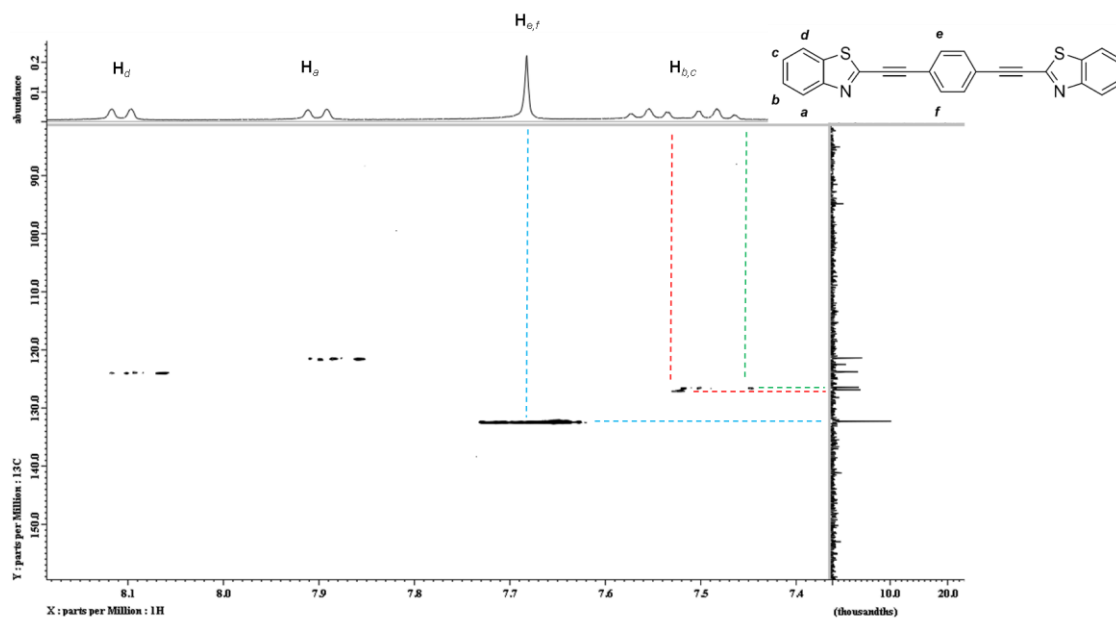
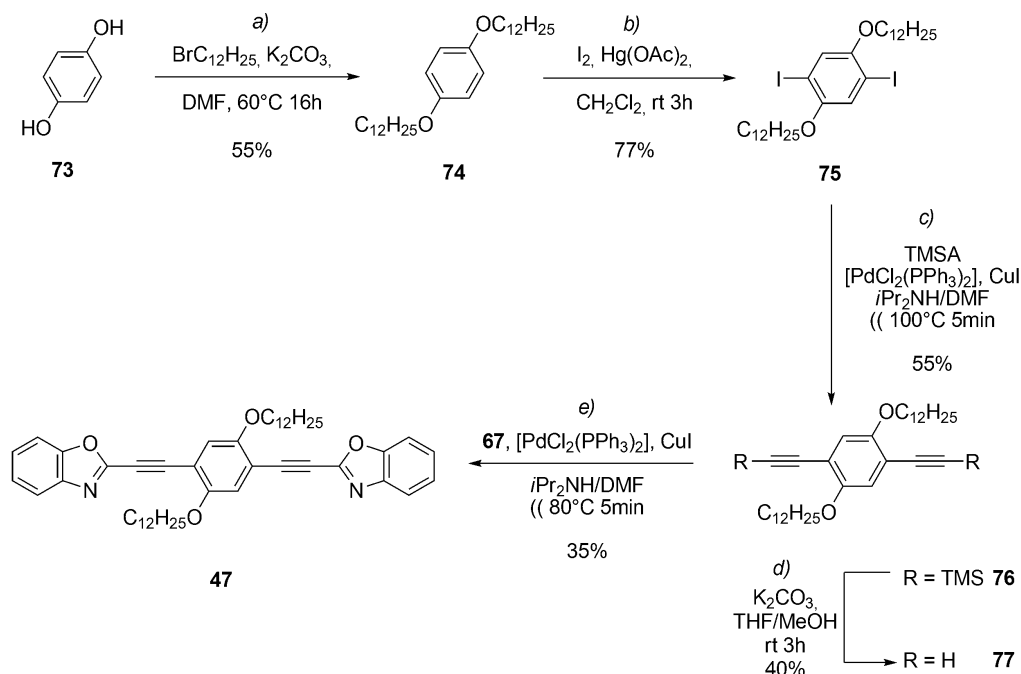


Figure 23. 2D-HMOC NMR correlation spectrum (400 MHz, CDCl_3) of bisbenzothiazole **44**. ^1H - and ^{13}C -NMR are zoomed in the area of interest (see the text).

To favor the implementation into the new PET machine as wavelength converters, as required by the STRING project, these compounds have to show good dispersability in polar matrices. Thus, a novel module featuring two long alkoxy chains on the central phenyl core was designed. The synthesis of alkoxy-modified bisbenzoxazole

compound **47** is reported in Scheme 14. Commercial hydroquinone **73** was alkylated by means of K_2CO_3 and 1-bromododecane leading to intermediate **74** in 55% yield (Scheme 14, path *a*). Subsequently, alkylated hydroquinone **74** was iodinated at the 2- and 5-positions of the ring with $Hg(OAc)_2$ in CH_2Cl_2 producing bis-iodo hydroquinone **75** in very good yield (Scheme 14, path *b*). The microwave-assisted Pd(II)-catalyzed coupling of **75** with TMSA in a mixture of iPr_2NH and DMF, led to TMS-protected acetylene derivative **76** with 55% yield (Scheme 14, path *c*). **76** was then TMS-deprotected under basic conditions producing free ethynyl hydroquinone **77** in 40% yield (Scheme 14, path *d*). The latter was then coupled twice with **67** following a microwave-assisted *Sonogashira* reaction affording targeted molecule **47** in 35% yield (Scheme 14, path *e*). Similarly to parent compounds **43-44**, the structure of alkylated benzazole **47** was confirmed by ^1H -, ^{13}C -NMR, IR, UV-Vis and ESI-HRMS (Chapter 4). In particular, the ^1H -NMR analysis presented an analogous pattern as described above for bisbenzazole **43-44**, involving two doublets (δ : 7.77 and 7.55 ppm) and a doublet of triplets (δ : 7.45-7.37 ppm) for the benzoxazole ring and a singlet corresponding to the 2H of the central phenyl ring.



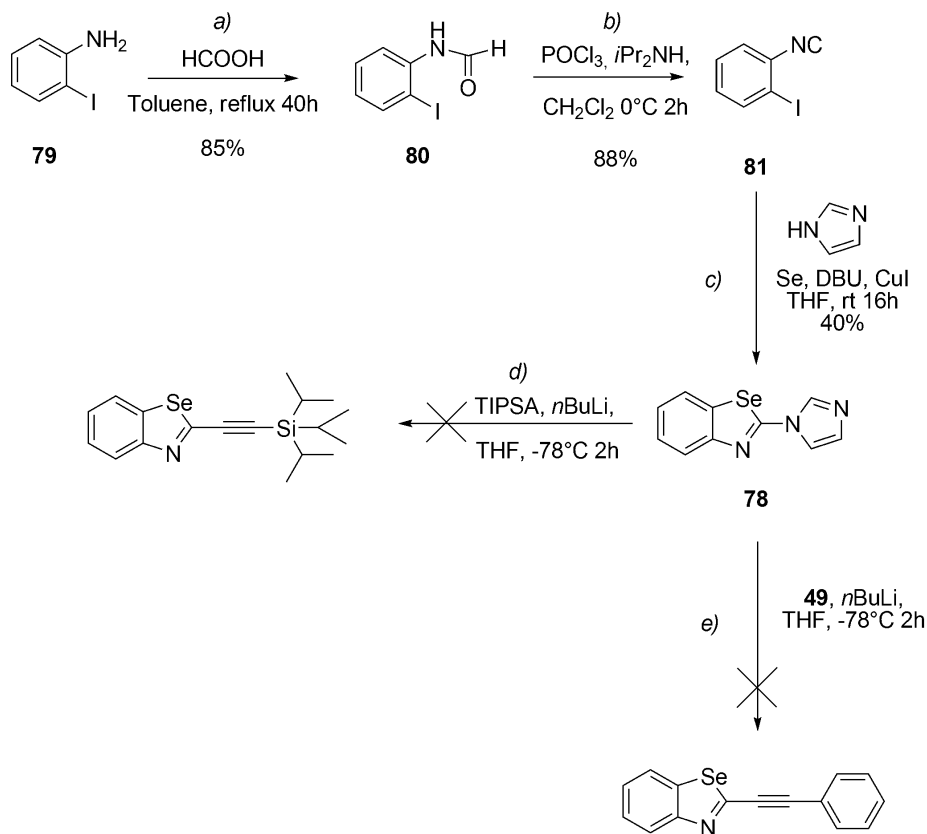
Scheme 14. Synthetic pathway towards bisbenzoxazole **47**.

2.3.3.2. Synthesis of Bisbenzoselenazole **45**

A diverse strategy has been employed to prepare Se-doped derivative **45**. The 2-*H*-benzoselenazole is not commercially available and its synthesis is characterized by low yields and instable intermediates.^[123, 124] Therefore, a new synthetic strategy involving the *in situ* formation of the benzoselenazole ring was taken into account. This is a highly efficient method to prepare, by a Cu(I)-catalyzed reaction, 1,3-benzoselenazole having a heteroatom substituent at the 2-position of the benzoselenazole ring, such as NRR' , OR or SR groups.^[125] The initial idea was to synthesize a 1,3-benzoselenazole bearing at the 2-position good leaving groups so that ethynyl moieties can be inserted through an S_N2 -type reaction at that position. To this end, the synthesis of 2-(1-imidazolyl)-1,3-benzoselenazole **78** (Scheme 15), where the imidazole function acts as a leaving group, was carried out. Thus, 2-iodoaniline **79** was refluxed with formic acid in toluene affording corresponding isoamide **80** as a mixture of two

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tautomers (Scheme 15, path *a*). These were used for the following step and reacted with POCl₃ in basic conditions affording desired 2-iodoisocyanide **81** (Scheme 15, path *b*). The latter revealed to be highly unstable under ambient conditions and for this reason was not further purified. **81** was, then, reacted with Se in the presence of catalytic amounts of CuI, imidazole and DBU leading to desired 1,3-benzoselenazole derivative **78** in 40% yield (Scheme 15, path *c*).



Scheme 15. Synthetic pathway towards the imidazole-bearing benzoselenazole **78** (paths *a-c*), and failed attempts for the S_N2-type insertion of the triple bond in 2-position of the benzoselenazole ring of **78** (paths *d-e*).

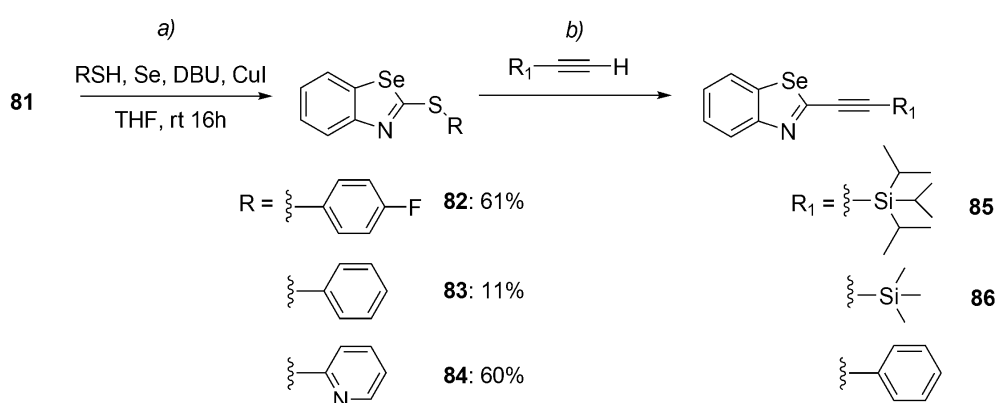
In view of synthesizing targeted bisbenzoselenazole molecule **45**, two attempts to substitute the 2-position of benzoselenazole **78** were then carried out (Scheme 15). In the first reaction, TIPSA was deprotonated by *n*BuLi and subsequently added to a cold THF solution of **78** (Scheme 15, path *d*). In the second attempt, *n*BuLi was used to deprotonate phenylacetylene **49**, which was successively reacted with **78** as in the previous case (Scheme 15, path *e*). Unfortunately, none of the two reactions proceeded and after 2 hours both attempts resulted in the recovery of the intact starting material **78** and traces of unrecognizable byproducts. It should be noted that all the attempts carried out with 1,4-diethynylbenzene **70** failed as well due to an unexpected precipitation of the corresponding bisanion after the treatment with *n*BuLi.

An alternative route to the insertion of the triple bond at the 2-position of a 1,3-benzoselenazole ring, could be retrieved in the replacement of the imidazole moiety with another leaving group. Inspired by the possibility to develop a desulfative-type *Sonogashira* cross-coupling reaction at the 2-position of the benzoselenazole ring, the synthesis of 2-thiolated 1,3-benzoselenazole derivatives was carried out. Desulfative cross-couplings catalyzed by transition metals have already been described in literature. In particular, modified Pd- and Ni-catalyzed cross-coupling reactions have recently been applied where organosulfur compounds play the classical role of the organic halides.^[126-131] According to these reported studies, the involved mechanism of these desulfative reactions most likely

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occurs through the oxidative addition of the metal catalyst to the C-S bond of the thiolated starting material, followed by transmetallation and reductive elimination steps affording the desired product.^[129, 131]

In the present case, 2-thiolated 1,3-benzoselenazole derivatives were prepared in view of carrying out desulfative *Sonogashira*-type reactions, to afford 2-ethynyl 1,3-benzoselenazole main building block. In this respect, following the same procedure as the one described before for the imidazole-bearing 1,3-benzoselenazole, three different 2-thiophenol substituted 1,3-benzoselenazole compounds were prepared (Scheme 16). Specifically, 2-phenylthio, **82**, 2-*p*-fluorophenylthio, **83**, and 2-pyridinethio, **84**, 1,3-benzoselenazole derivatives were prepared by means of isocyanide **81**, elemental Se and DBU in 11%, 60% and 61% yields, respectively (Scheme 16, path *a*). All these intermediates were used as starting materials for the insertion in the 2-position of ethynyl functions (Scheme 16, path *b*). Different conditions and reagents were exploited for this reaction and the results are summarized in Table 2.



Scheme 16. Synthetic steps towards 2-thiolated-1,3-benzoselenazole derivatives **82-84**, and their conversion into 2-ethynyl-1,3-benzoselenazole. The reaction conditions of step *b* are reported in Table 2.

A first screening of the three substrates was carried out with TIPSA as the ethynyl source. Specifically, solutions of benzoselenazoles **82-84** in diisopropylethylamine (DIEA) were reacted at room temperature overnight with TIPSA in the presence of catalytic amounts of $[PdCl_2(PPh_3)_2]$ (5% mol) and CuI (10% mol) (entries 1-3, Table 2). In these conditions only benzoselenazole **82** was found to react affording a 10% yield of the desired TIPS-protected 2-ethynyl-1,3-benzoselenazole **85** (entry 1, Table 2). Even the two attempts carried out with molecule **84**, [5% mol $[PdCl_2(PPh_3)_2]$, 10% mol CuI, 100% mol $BF_3 \cdot EtO_2$ (entry 3, Table 2) and 100% mol CuI (entry 4, Table 2)], done to exploit the abilities of the nitrogen atoms of the benzoselenazole and pyridine to coordinate the Lewis acid or the CuI did not afford the desired molecule but only the starting materials were recovered.

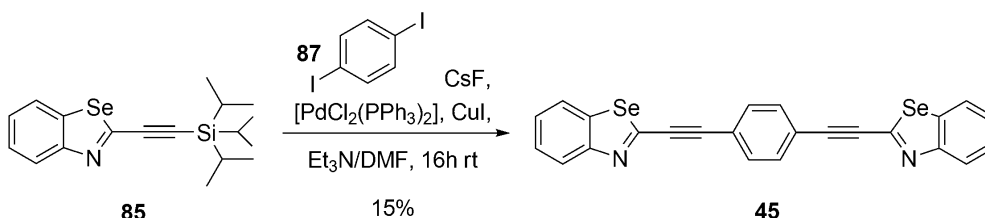
In light of the described results the presence of the fluorine substituent in derivative **82**, played a decisive role in the development of the reaction due to its inductive effect on the aromatic ring. For this reason, the yield of the desulfative *Sonogashira*-type reaction was further optimized with 2-*p*-fluorophenylthio benzoselenazole **82** as the reactive substrate. When the reaction described in entry 1 of Table 2 was performed under microwave irradiation for 20 min using a range of temperatures from 45°C to 90°C, the yield increased up to 29% (entry 5, Table 2). The low yield obtained at this stage was rationalized with a deactivation pathway underwent by the palladium catalyst. The thiolated-leaving group of **82** may in fact attack the phosphine ligands on the palladium center or further coordinate it causing the poisoning of the catalyst.^[132, 133] To prove this poisoning the same reaction was performed with higher concentrations of catalyst, spanning from 8% to 50% mol (entries 6-8, Table 2), obtaining a considerable increase in the yield reaching the 100% of isolated **85** in entry 8. To study the role of the CuI and of the phosphine ligand in the deactivation of the Pd-catalyst, the coupling between **82** and TIPSA with catalytic $[PdCl_2(PPh_3)_2]$ (5% mol) and one equivalent of CuI (entry 9, Table 2) was then performed. The reaction proceeded with the formation of **85** in 26%

yield. This yield is comparable with the yield of entry 5 suggesting a limited effect of the halide on the deactivation of the Pd-catalyst. However, when the coupling was performed in the presence of 5% mol of $[\text{PdCl}_2(\text{PPh}_3)_2]$, 10% mol of CuI and 10% mol of PPh_3 , decomposition of the starting 1,3-benzoselenazole **82** occurred (entry 10, Table 2). This result can be rationalized with the poisoning of the catalyst. In parallel to the last attempt, the coupling between **82** and TIPSA was performed under the same conditions exploited in entry 10 increasing the concentration of PPh_3 up to 100% mol (entry 11, Table 2). In this reaction only starting materials (**82** and PPh_3) were recovered.

To investigate the role of the ethynyl source, the desulfative coupling was also performed with TMSA and phenylacetylene **49**. Specifically, the reaction between **82** and TMSA (entry 12, Table 2), performed in a sealed *Schlenck* tube with catalytic $[\text{PdCl}_2(\text{PPh}_3)_2]$ (5% mol) and CuI (10% mol) heated up to 130°C , led after 16 hours to 12% of TMS-protected benzoselenazole **86**. This was found to be unstable in the air, probably due to the higher reactivity of the TMS- with respect to the bulkier TIPS-group. When phenylacetylene was selected as ethynyl source, the coupling of **82** with **49** was conducted under the same reaction conditions described in entries 1-3 of Table 2 (e.g. $[\text{PdCl}_2(\text{PPh}_3)_2]$ (5% mol), CuI (10% mol), DIEA, 16 hours, rt). In this case, any 2-ethynyl 1,3-benzoselenazole was isolated but only unreacted starting materials were recovered (entry 13, Table 2).

TIPS-protected 2-ethynyl benzoselenazole, **85**, was then used for the last step of the synthesis, shown in Scheme 17. As introduced in section 2.3.2, intermediates such as 2-ethynyl 1,3-benzoxazole **65** tend to easily decompose at ambient conditions. Therefore, the analogous **85**, was immediately coupled with 1,4-diiodobenzene, **87**, applying a modified Pd-catalyzed Sila-*Sonogashira*-type reaction,^[134-136] which involved CsF as deprotecting *in situ* agent in a mixture of Et_3N and DMF. In this way it is possible to avoid the isolation of the unstable 2-ethynyl benzoselenazole intermediate and bisbenzoselenazole targeted module **45** was produced in 15% yield (Scheme 17).

The structure of bisbenzoselenazole **45** was confirmed by ^1H -, ^{13}C -NMR, UV-Vis, IR, and ESI-HRMS (Chapter 4). As in the case of previous bisbenzazoles **43-44** and **47** the ^1H -NMR spectrum (Figure 24) exhibited four areas of peaks. The benzoselenazole ring was retrieved in the first two doublets integrating for 2H ($\text{H}_{a,d}$) and the system at δ 7.55-7.38 ppm ($\text{H}_{b,c}$) integrating for 4H. The latter is in the form of two coupled triplets (δ 7.53 and 7.40 ppm) with a J_{ortho} of 8.2 Hz.



Scheme 17. Final step of the synthesis of bisbenzoselenazole derivative **45**.

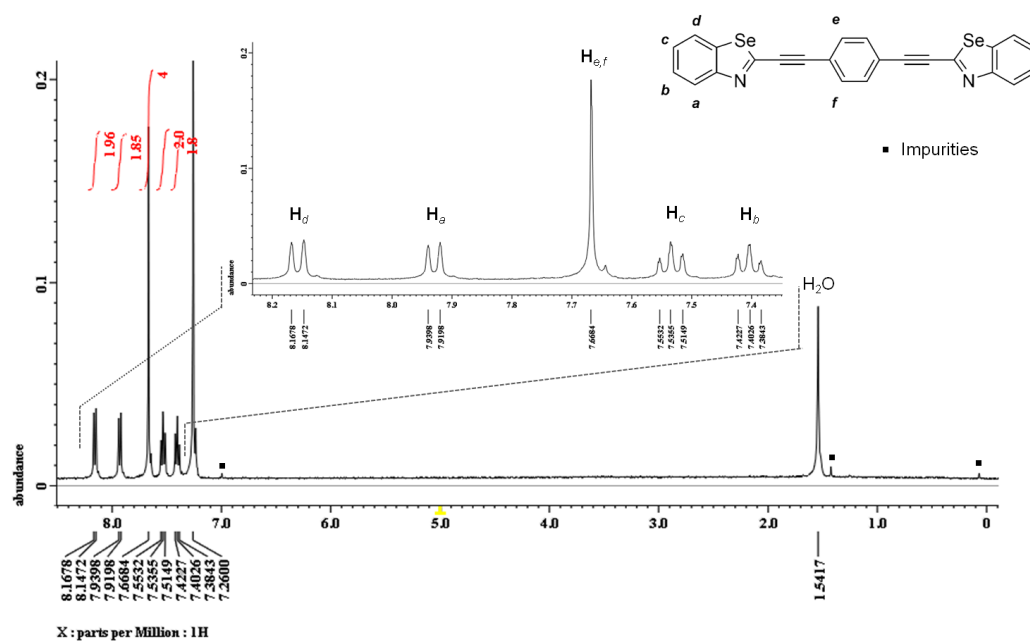


Figure 24. ¹H-NMR spectrum (400 MHz, CDCl₃) of bisbenzoselenazole **45**. Inset: zoom of the 8.3-7.3 ppm area.

Table 2. Optimized conditions for the introduction of ethynyl function on thia-substituted benzoselenazole derivatives **82-84**.

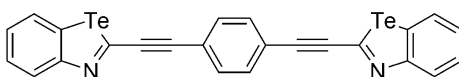
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Entry	Substrate	Step <i>b</i>				Product	Yield % ^b
		R ₁ -C≡C-H	Catalytic System	Base/Solvent	Time/°C		
1	82	TIPS-	[PdCl ₂ (PPh ₃) ₂] 5% CuI 10%	DIEA	16h, rt	85	10
2	83	TIPS-	[PdCl ₂ (PPh ₃) ₂] 5% CuI 10%	DIEA	16h, rt		0 ^c
3	84	TIPS-	[PdCl ₂ (PPh ₃) ₂] 5% CuI 10% BF ₃ ·Et ₂ O 100%	DIEA	16h, rt		0 ^c
4		TIPS-	CuI 100%	DIEA/DMF	16h, rt		0 ^c
5 ^a	82	TIPS-	[PdCl ₂ (PPh ₃) ₂] 5% CuI 10%	DIEA/DMF	20min, 45°-90°C	85	29
6 ^a		TIPS-	[PdCl ₂ (PPh ₃) ₂] 8% CuI 80%	DIEA/DMF	20min, 90°C	85	40
7 ^a		TIPS-	[PdCl ₂ (PPh ₃) ₂] 25% CuI 50%	DIEA/DMF	20min, 90°C	85	60
8 ^a		TIPS-	[PdCl ₂ (PPh ₃) ₂] 50% CuI 100%	DIEA/DMF	20min, 90°C	85	Quant.
9 ^a		TIPS-	[PdCl ₂ (PPh ₃) ₂] 5% CuI 100%	DIEA/DMF	20min, 90°C	85	26
10 ^a		TIPS-	[PdCl ₂ (PPh ₃) ₂] 5% CuI 10% PPh ₃ 10%	DIEA/DMF	20min, 90°C		0 ^d
11 ^a		TIPS-	[PdCl ₂ (PPh ₃) ₂] 5% CuI 10% PPh ₃ 100%	DIEA/DMF	20min, 90°C		0 ^c
12		TMS-	[PdCl ₂ (PPh ₃) ₂] 5% CuI 10%	DIEA	16h, rt		0 ^c
13		-Ph	[PdCl ₂ (PPh ₃) ₂] 5% CuI 10%	DIEA	16h, 130°C	86	12

^a Reaction performed under microwave irradiations; ^b isolated yields; ^c recovered starting materials; ^d decomposition of starting materials.

2.3.3.3. Synthetic Attempts towards Bisbenzotellurazole Derivative **46**

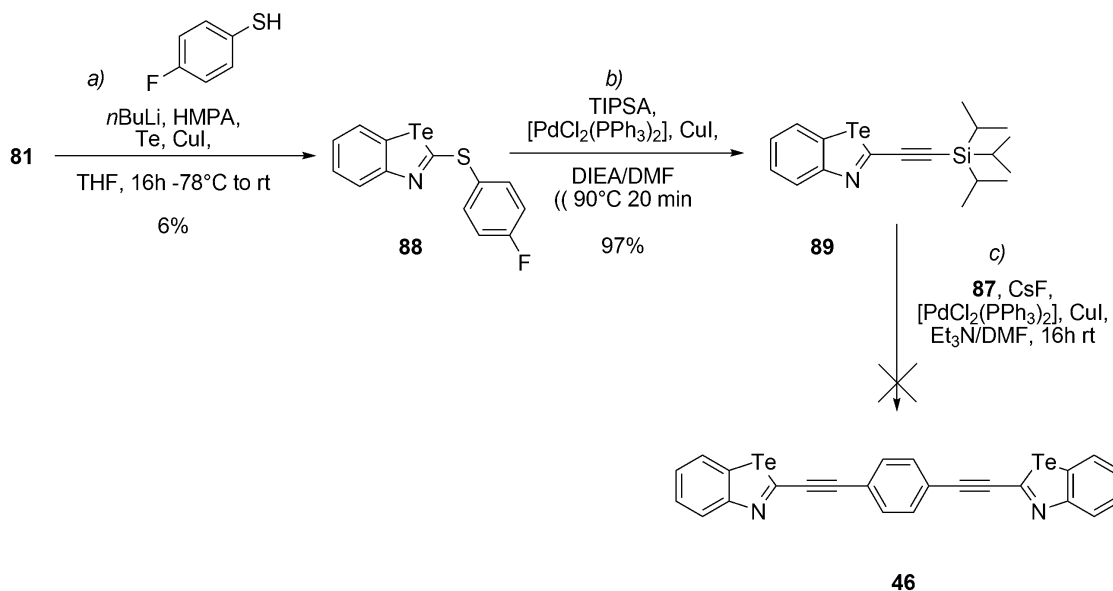
In order to continue the studies of the heavy-atom effect on the bisbenzazole derivatives, going down into the sixth group of the periodic table, the synthesis of tellurium-doped bisbenzazole module **46** was also addressed in this work (Figure 25).



46

Figure 25. Structure of the bisbenzotellurazole **46**.

The synthetic strategy utilized followed the same pathway described for its Se-doped equivalent **45**. Therefore, Te fine powder and 2-iodoisocynide **81**, as synthesized in section 2.3.3.2, were added to a solution of 4-fluorothiophenol previously treated with *n*BuLi and hexamethylphosphoramide (HMPA) at -78°C , affording *via* a Cu(I)-catalyzed cyclization desired 2-thiolated 1,3-benzotellurazole **88** in 6% yield (Scheme 18, path *a*). The latter was then reacted in a mixture of DIEA and DMF with TIPSA applying the conditions optimized for the desulfative Pd(0)-catalyzed *Sonogashira* described for the Se-analogous **82** (Table 2), yielding TIPS-protected 2-ethynyl 1,3-benzotellurazole **89** in 97% (Scheme 18, path *b*).

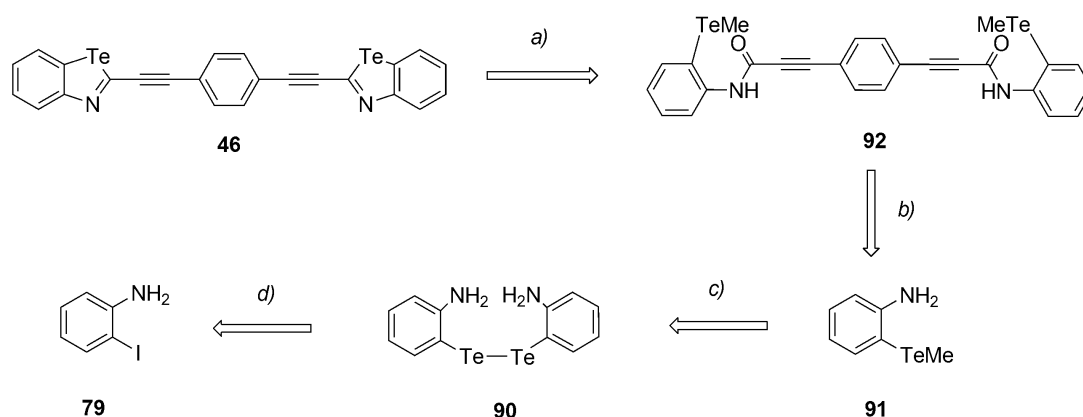
**Scheme 18.** Synthetic pathway towards bisbenzotellurazole compound **46**.

By applying the same reaction conditions used for the synthesis of the bisbenzoselenazole **45** (Scheme 17), benzotellurazole **89** was deprotected *in situ* by CsF and subsequently treated with 1,4-diiodobenzene **87** in a modified version of the sila-*Sonogashira* reaction (Scheme 18, path *c*). However, in this case the reaction did not afford the expected compound but only the decomposition of the starting materials was observed.

Reaction conditions were then revised and modified and most representative results are collected in Table 3. The same reaction was performed under microwave irradiation for 1 hour at 100°C , keeping constant both the deprotecting agent, CsF, and the equivalents of catalyst and halide ($[\text{PdCl}_2(\text{PPh}_3)_2]$ 5% mol and CuI 10% mol, entry 1, Table 3). However, as in the previous case, even with these conditions the reaction afforded byproducts due to the decomposition of the starting materials. In order to avoid these byproducts, a shorter time of reaction was believed to help the formation of the desired molecule **46**. Therefore, 30 minutes irradiation at 100°C was exploited for the coupling between **89** and 1,4-diiodobenzene **87** described in entry 2 of Table 3. Unfortunately, the changing of the reaction time was not effective and the reaction afforded similar byproducts isolated in the previous attempts. At this stage, the reaction was strictly followed each 30 minutes irradiation, applying the same conditions but different

temperatures, starting at 40°C and slightly increasing the temperature until a maximum of 80°C (entry 3, Table 3). After the first 30 minutes at 40°C, the presence of starting materials was still observed. The temperature was then increased by 10°C and the reaction microwave-irradiated for additional 30 minutes. At this stage, together with the starting materials, byproducts coming from the decomposition of the benzotellurazole were also observed. The temperature and the time of the reaction were boosted until the total conversion of the starting materials (2h, 80°C) was achieved. However, molecule **46** was not observed in the reaction mixture after the spectroscopic analysis. Similar unsuccessful results were obtained using a different Pd-catalyst, as demonstrated by the attempts carried out with [Pd(PPh₃)₄] performed under microwave irradiation and under normal conditions (entries 4-5, Table 3). The last attempts collected in Table 3, involved TBAF as deprotecting agent instead of CsF used in the previous examples. In one case, TBAF was added to a solution of benzotellurazole derivative **89** at 0°C and 1,4-diiodobenzene **87**, 5% mol of [PdCl₂(PPh₃)₂] and 10% mol of CuI were subsequently combined to the reaction mixture which was stirred overnight at room temperature (entry 6, Table 3). The reaction proceeded with the formation of a dark precipitate and numerous byproducts. Due to the poor solubility in most common organic solvents, the attempts to analyze the precipitate have been unsuccessful. The same reaction was performed a second time using very diluted THF solutions of **89** and **87** (10⁻³ M with respect to 10⁻¹ M used in the previous attempts). Furthermore, in order to follow the TIPS-deprotection of **89**, the TBAF solution was sequentially added in three times over a period of 30 minutes (entry 7, Table 3). After the third addition, the analysis by TLC displayed the consumption of **89** and the presence of a new compound which was associated with the deprotected 2-ethynyl benzotellurazole. However, when the rest of the reagents were mixed with the solution the same precipitate observed in entry 6 was obtained together with undesired byproducts.

At the present time a new synthetic strategy has been designed for the preparation of targeted bisbenzotellurazole module **46**. Scheme 19 presents the retrosynthetic approach envisaged for the preparation of **46** following the new strategy. This one would involve the reaction of o-iodoaniline **79** to form in one-pot ditelluride **90**, which, successively, may lead to aniline **91**. The latter, after acylation by the appropriate acyl chloride should form the corresponding anilide, **92**. The ring closure in **92** promoted for instance by POCl₃, should afford desired bisbenzotellurazole **46**.^[137]



Scheme 19. Retrosynthetic analysis of the new strategy for the preparation of bisbenzotellurazole compound **46**.

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Table 3. Synthetic attempts for the synthesis of bisbenzotellurazole derivative **46**.

Entry	Step c				Yield %
	Deprotecting Agent	Catalytic System	Base/Solvent	Time/°C	
1 ^a	CsF	[PdCl ₂ (PPh ₃) ₂] 5% CuI 10%	Et ₃ N/DMF	1h, 100°C	0 ^b
2 ^a		[PdCl ₂ (PPh ₃) ₂] 5% CuI 10%	Et ₃ N/THF	30min, 100°C	0 ^b
3 ^a		[PdCl ₂ (PPh ₃) ₂] 5% CuI 10%	Et ₃ N/THF	2h, 80°C	0 ^b
4 ^a		[Pd(PPh ₃) ₄] 5% CuI 10%	Et ₃ N/THF	1h, 100°C	0 ^b
5 ^a		[Pd(PPh ₃) ₄] 5% CuI 10%	Et ₃ N/THF	16h, rt	0 ^b
6	TBAF	[PdCl ₂ (PPh ₃) ₂] 5% CuI 10%	THF	16h, rt	0 ^c
7 ^d		[PdCl ₂ (PPh ₃) ₂] 5% CuI 5%	THF	16h, rt	0 ^c

^a Reaction performed under microwave irradiations; ^b undesired byproducts obtained; ^c undesired byproducts and black precipitate obtained; ^d reaction performed with sequential additions of TBAF in diluted conditions (see the text).

2.3.3.4. Solid State Arrangements of Bisbenzoxazole, Bisbenzothiazole and Bisbenzoselenazole Derivatives **43-45**

To gain information on the spatial arrangement of molecules **43-45**, single crystals suitable for X-Ray crystallographic analysis were obtained. Transparent (**43**) and intense yellow crystals (**44-45**) of the investigated compounds were grown by evaporation of solutions of **43** in CHCl₃ and **44-45** in CH₂Cl₂, respectively. Figure 26 sequentially displays the ORTEP images of the crystal structures and the van der Waals (vdW) radii representations of the single molecule and the crystal packing of all modules **43-45**. All the crystal structures are arranged according to the spatial group P21/c (further details and crystallographic data are reported in the *Appendix*). Differently from the others, the crystal structure of sulfur-doped derivative **44** presents, within the heteroaromatic ring, an alternate motion of the sulfur and nitrogen elements as clearly displayed in the ORTEP representation (Figure 26d). This behavior can be rationalized considering that for this module the rotation along the C(1)-C(8) bond is not prevented even at the solid state resulting in the rotation of the benzothiazole moieties.

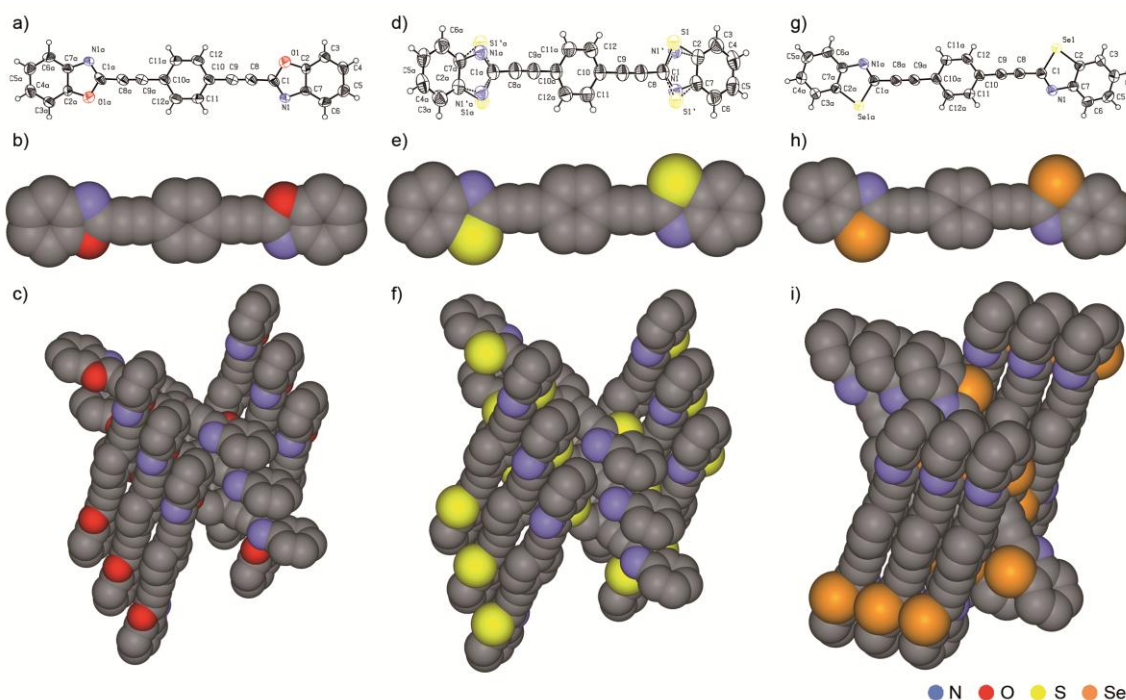


Figure 26. a) ORTEP representation of a single molecule of **43**; b) vdW radii representation of a single molecule of **43**; c) vdW radii representation of the crystal packing of **43**. Arbitrary numbering. Atomic displacement parameters are obtained at 293 K. Most relevant intramolecular contacts [Å]: C(1)-O(1) 1.357(6), C(1)-N(1) 1.303(6), C(1)-C(8) 1.405(7), C(8)-C(9) 1.197(7), C(9)-C(10) 1.434(7). Most relevant dihedral angles [°]: O(1)-C(1)-N(1) 115.2(4), C(1)-C(8)-C(9) 176.7(5), C(8)-C(9)-C(10) 179.3(5), C(9)-C(10)-C(11) 120.5(4); d) ORTEP representation of **44**; e) vdW radii representation of a single molecule of **44**; f) vdW radii representation of the crystal packing of **44** (the alternate motion of N and S atoms has not been considered in the vdW representations due to clarity reasons). Arbitrary numbering. Atomic displacement parameters are obtained at 293 K. Most relevant intramolecular contacts [Å]: C(1)-S(1) 1.728(2), C(1)-N(1) 1.306(3), C(1)-C(8) 1.423(3), C(8)-C(9) 1.195(3), C(9)-C(10) 1.434(3). Most relevant dihedral angles [°]: S(1)-C(1)-N(1) 117.21(17), C(1)-C(8)-C(9) 176.6(2), C(8)-C(9)-C(10) 179.4(2), C(9)-C(10)-C(11) 120.4(2); g) ORTEP representation of **45**; h) vdW radii representation of a single molecule of **45**; i) vdW radii representation of the crystal packing of **45**. Arbitrary numbering. Atomic displacement parameters are obtained at 293 K. Most relevant intramolecular contacts [Å]: C(1)-Se(1) 1.897(5), C(1)-N(1) 1.289(6), C(1)-C(8) 1.425(7), C(8)-C(9) 1.199(8), C(9)-C(10) 1.421(7). Most relevant dihedral angles [°]: Se(1)-C(1)-N(1) 117.0(3), C(1)-C(8)-C(9) 177.7(5), C(8)-C(9)-C(10) 178.1(5), C(9)-C(10)-C(11) 119.8(4).

As displayed in Figures 26 c-i, all derivatives appear to arrange in identical manner. However, a closer look to the packing mode of two stacked modules of bisbenzazole **43-45** revealed important differences, especially in the offset and in the π - π stacking distances. Figure 27 displays for each module two molecules closely packed and held together by weak interactions, with an average interplanar distance of 3.5 Å. Specifically, this distance increases going from the oxygen-doped benzazole **43** to the selenium derivative **45** (O: 3.46 Å, S: 3.57 Å, Se: 3.67 Å) following the increment of the heteroatom vdW radius going down through the sixth group (O: 1.52 Å, S: 1.80 Å, Se: 1.90 Å). Surprisingly, module **45** did not present the Se $\cdots$ Se type of interactions that are usually reported for Se-doped aromatic structures with a range of interaction distances of 3.5-4.0 Å (see introductory part in section 2.2.2.2.1).^[88, 138, 139]

The responsible factor for stabilizing the dimers is found to be primarily a dispersion interaction. It should be pointed out that, although always present, van der Waals attractions are not the only powerful interactions to stabilize this type of arrangements, but aromatic rings stacked above one another do find a stable arrangement when one π -system is offset relative to the other. With the π -system of one molecule lying over the edge of the one below, there is an electrostatic attraction from the positively charged σ framework with the negatively charged π cloud, especially since the positive charge is largely on the periphery and therefore on the exposed hydrogen atoms. This electrostatic attraction can only come into play in a stack if the rings are offset.

In the systems here investigated large offset distances of 3.26 Å and 3.54 Å have been measured for oxygen- and sulfur-doped modules **43** and **44**, respectively (Figures 27a and b). A very small offset (2.15 Å) was, instead, observed in bisbenzoselenazole compound **45** (Figure 27c).

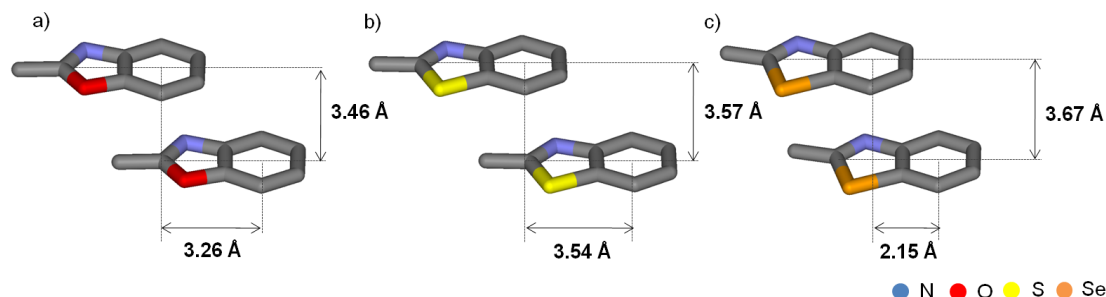


Figure 27. Interplanar and offset distances in an extrapolation of the X-Ray crystal structures of derivatives **43-45**. a) Stick representation of crystal **43**; b) stick representation of crystal **44**; c) stick representation of crystal **45**.

In general, offset distances mainly depend on quadrupolar-quadrupolar interactions and on the charge distribution. To rationalize the differences in the offset distances obtained in the crystallized modules and to get an insight into the interactions that come into play at the solid state, theoretical calculations have been performed to optimize the geometries of the crystallized molecules and to derive important structural parameters. The optimization has been carried out on the single monomers **40-42** as well as on the model dimers of each compound in order to reproduce the situations displayed in Figure 27. As similar results have been obtained for monomeric and dimeric compounds, the discussion will only focus on the dimeric species.

The geometry of dimeric models of **43** and **44** were optimized by GAUSSIAN 09 program,² at the M06L/6-311G* level of theory, the model of **45** was, instead, optimized at the M06L/TZV level of theory. The M06L functional was necessary because it takes into account the π -stacking interaction among two molecules, while for the model of Se-derivative **45** it was necessary to use a proper basis set for the third row elements. The optimization of the dimers **43** and **44** did not converge. Thus, a reduced basis set, 6-31G, was used. A single point energy calculation at the M06L/3-21G level of theory was successively used on the fully optimized geometries of the crystallized bisbenzazole dimers **43-45**, to evaluate atomic partial charges (*Mulliken* and *Hirshfeld*), a map of the surface electrostatic potential (ESP) for each module (Figure 28), and the dipole moment μ and quadrupole moment tensor Q_{xx} perpendicular to the rings plane (Table 4). The atomic partial charges reported in Table 4 refer to the three heteroatoms while the electronic moments refer to the entire molecule that contains the heteroatom.

² Gaussian 09, Revision **A.1**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

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Table 4. Molecular parameters computed at M06L/3-21G level of theory reported for the three derivatives **43-45** in dimeric models.

Molecule	Atom	Mulliken charges (ESU)	Hirshfeld charges	μ (D)	Q_{xx} (D* Å)
43	O	-0.57	-0.11	0	-42.97
	N	-0.61	-0.17		
44	S	0.81	0.11	0.0012	-48.89
	N	0.59	-0.17		
45	Se	0.71	0.07	0.0001	-48.68
	N	-0.57	-0.15		

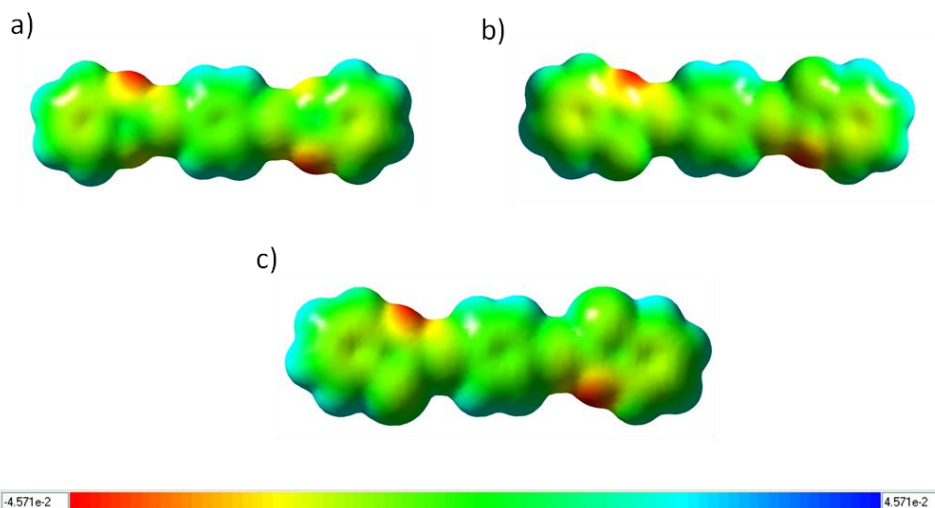


Figure 28. Molecular electrostatic potential plotted on the van der Waals surface of the three derivatives **43**(a), **44** (b) and **45** (c). In each surface the most negatively charged red coloration is assigned to the nitrogen atom position because of the relative charge distribution.

The atomic partial charges *Mulliken*- and *Hirshfeld*-types display very different values. In general the *Hirshfeld* method is considered more accurate due to the fact that the *Mulliken* analysis is sensitive to the choice of the basis set. For this reason, herein *Hirshfeld* charges will be the only ones taken into account. The values of partial charges reported in Table 4 display similar values for the N charges in the dimers and identify S as the most positively charged atom. To visualize the partial atomic charges, ESP maps were also obtained for bisbenzazoles **43-45** (Figure 28). While the quadrupole moment and the partial charges on the Se-dimer perfectly explain the smallest offset value obtained, the described theoretical data highlight the possibility that the offset distances observed in dimers **43** and **44** have different origins. The dimer of the O-doped module **43** resulted as the most negatively charged when considering the partial *Hirshfeld* charges and its offset can be related to this factor. On the contrary, the optimized dimer of **44** presented the highest value of quadrupole moment in the series, and it is believed that this is the reason for the observed offset distance of 3.54 Å.

To have additional information on the interactions observed at the solid state, a comparison of π -stacking and offset values between the X-Ray crystals and optimized dimeric models of modules **43-44** is summarized in Table 5.

Table 5. π -stacking and offset values obtained for two superimposed molecules of derivatives **43-45** in the crystal structure and after the optimized calculations.

	Dimer 43		Dimer 44		Dimer 45	
	π -stacking (Å)	Offset (Å)	π -stacking (Å)	Offset (Å)	π -stacking (Å)	Offset (Å)
Crystallized dimer	3.46	3.26	3.57	3.54	3.67	2.15
Optimized dimer	3.29	3.41	3.60	3.50	3.7	2.2

There is a precise fitting between the crystallographic and the theoretical data. A periodic trend is observed in the optimized values for the three substances. In the crystal however, the periodic trend is kept by dimer **44** and **45** but is interrupted by O-doped derivative **43**. Only in this case a higher π -stacking distance and a smaller offset are observed for the crystallized dimer with respect to the calculated results. At the present time, this behavior has been rationalized to be an effect of the crystal arrangement, but further confirmations still have to be acquired on this aspect.

2.4. Photophysical Properties of Push-Pull and Heteroatom-Doped Wavelength Shifters

2.4.1. Photophysical Properties of Push-Pull Dyes

The photophysical results obtained with diphenyl acetylenes **34-40** in solution and in a polymeric matrix, reported in this section, were the object of a recent publication.^[140]

2.4.1.1. Diphenyl Acetylenes **34-40** in Solution

Absorption. The unsubstituted diphenylethynylene **34** displays an envelope of intense absorption bands in the UV region of the spectrum, between 220 and 300 nm, which are assigned to π, π^* electronic transitions (Figure 29). The *N,N*-4-dihexylamino derivatives **37**, **38**, **39** and **40** present in addition to the same high energy π, π^* transitions, now structureless and of lower intensity (λ_{max} = 294, 266, 245 and 241 nm for **37**, **38**, **39** and **40**, respectively, in MeOH), an additional intense absorption band at lower energy (λ_{max} = 417, 378, 356 and 357 nm respectively, in MeOH), which position is solvent sensitive (Figure 29, Table 6). The polarizability of the solvent, which follows the order: $\text{CH}_2\text{Cl}_2 \gg \text{CH}_3\text{CN} > \text{MeOH}$, can account for the observed shifts.

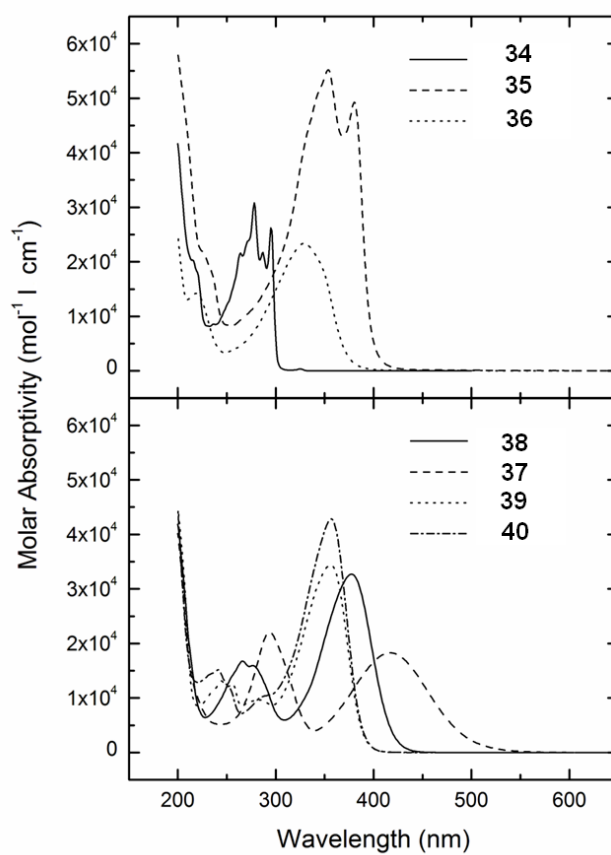


Figure 29. Absorption spectra of the symmetric **34-36** (top) and unsymmetric **37-40** (bottom) diphenyl acetylene derivatives in MeOH solutions.

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Table 6. Photophysical parameters of investigated diphenyl acetylenes **34-40** in solution.

Compound	Solvent	Absorption (rt)		Emission (rt) ^b			Emission (77 K) ^c	
		λ_{max} (nm)	ϵ_{max} (mol ⁻¹ ·l·cm ⁻¹)	λ_{max} (nm)	Φ	τ (ns)	λ_{max} (nm)	τ (ns)
34	MeOH	278 295	30.800 26.200	307	0.0015	n.d.	297	0.7
	CH ₂ Cl ₂	281 299	-	302	0.0030	n.d.		
35	MeOH	354 380	55.200 49.300	446	< 0.0001	< 0.5	410	2.4
	CH ₂ Cl ₂	360	56.700 51.100	n.d.	n.d.	n.d.	511	3.1×10 ⁶
36	MeOH	329	23.400	n.d.	n.d.	n.d.	380	2.4
	CH ₂ Cl ₂	335	25.400	n.d.	n.d.	n.d.	506	1.8×10 ⁶
37	MeOH	294 417	22.000 18.300	630	0.0016	n.d.	559	3.2
	CH ₂ Cl ₂	299 431	- ^d	618	0.0015	n.d.		
38	MeOH	267 378	16.800 32.700	514	0.0150	1.0	425	1.6
	CH ₂ Cl ₂	268 385	- ^d	484	0.3700	2.8		
	CH ₃ CN	266 379	- ^d	530	0.0500	1.0		
39	MeOH	245 282 356	13.100 9.700 34.400	456	0.0074	n.d.	401	1.6
	CH ₂ Cl ₂	246 285 362	13.800 9.300 36.200	440	0.2400	2.1		
40	MeOH	241 357	15.200 42.800	464	0.0014	< 0.5	423	1.6
	CH ₂ Cl ₂	243 363	- ^d	502 ^e	0.0260	0.5		

^a In MeOH, CH₂Cl₂ and CH₃CN solutions; ^b in CH₂Cl₂ solution; ^c In MeOH/EtOH (1:4) mixture; ^d the poor solubility of the compound made impossible the measurement; ^e apparent maximum, see discussion in the text.

A clear trend is observed in the position of the lowest energy absorption band along the series of the four studied asymmetric derivatives: a bathochromic shift occurs in passing from **39** and **40**, to **38** and to **37**, the latter presenting the most red-shifted absorption (Figure 29 bottom). The trend follows the withdrawing ability of the acceptor group present in the dye: the “pull” effect of a fully fluorinated phenyl ring is moderate and similar to that of a CF₃ *p*-substituted ring; the C≡N and, in particular, the nitro *p*-substitution have a much higher effect, as expected on the basis of the relative values of the *Hammett* constants of the substituents in the para position (σ_p = 0.54, 0.66 and 0.78 for –CF₃, –C≡N and –NO₂, respectively).^[48] These observations confirm

the operativity of the desired push-pull effect and the formation of an ICT state in the D- π -A dyes under examination; the stabilization of such ICT transition should follow the withdrawing strenght of the acceptor group. Another confirmation of the right assignment of the absorption transitions comes from the observation that the acidification of MeOH and CH₃CN solutions of **38** determines a relevant change in the absorption spectra: the low energy band disappears completely and the transitions below 300 nm closely resemble those of the unsubstituted **34** (Figure 30, Table 7). This can be explained by considering that the protonation of the *N,N*-4-dihexylamino substituent causes the loss of the electron donating ability of the “push” group and only the π,π^* transitions of the diphenylethynylene core are allowed.

The two symmetric derivatives **35** and **36** display an envelope of intense absorption bands between 300 and 400 nm (λ_{max} = 354 and 329 nm for **35** and **36**, respectively, in MeOH, Figure 29 top and Table 6). These bands can derive from $\pi(n),\pi^*$ transitions but their attribution is not straightforward. The values of the extinction coefficients, that are very high in **35** and almost double with respect to **36**, are ascribable to the presence of two strong electron donating groups in the former and two strong electron withdrawing groups in the latter attached to the aromatic core. The position of these bands slightly blue-shifts in passing from CH₂Cl₂ to MeOH (Table 6), as observed for the asymmetric derivatives.

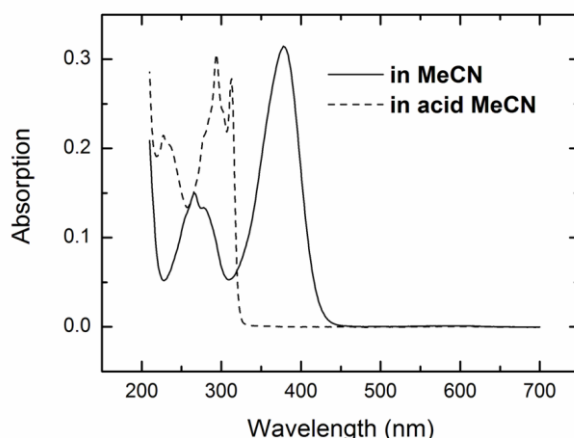


Figure 30. Absorption spectra of **38** in CH₃CN before (solid line) and after (dash line) the addition of an excess of hydrochloric acid.

Table 7. Photophysical parameters of **38** in acidified solution.

Solvent	Absorption (rt)	Emission (rt)			Emission (77 K) ^d	
	λ_{max} (nm)	λ_{max} (nm) ^a	Φ ^b	τ (ns) ^c	λ_{max} (nm) ^a	τ (ns) ^c
MeOH + H ⁺	293	330	0.29	< 0.5	314	0.6
	312				326	
MeCN + H ⁺	294	316	0.10	< 0.5	339	
	313				352	

^a Emission maxima derived from non-corrected emission spectra. Excitation at 250 nm; ^b luminescence quantum yields determined by comparing corrected emission spectra, using quinine sulfate in H₂SO₄ 1 N as a standard. Excitation at 250 nm; ^c Excitation at 278 nm; ^d In MeOH/EtOH 1:4.

Emission. For reference molecule **34**, a weak emission at room temperature was registered in both CH_2Cl_2 and MeOH (emission quantum yield, $\Phi \sim 10^{-3}$, Table 6 and Figure 31a). An intense and well resolved emission is recorded, instead, in frozen glass at 77 K (Figure 31b, top). The rt emission is not solvatochromic (Table 6).

Low emission quantum yields (1×10^{-3} to 1×10^{-2} , Table 6) have been observed at rt for the four unsymmetric derivatives in MeOH. In CH_2Cl_2 all these compounds, except for molecule **37**, show a higher quantum yield, that reaches the significant values of 0.24 and 0.37 for **39** and **38**, respectively. Differently from the behavior of precursor **34**, the emission of the D- π -A dyes presents a large Stokes shift. Its value in MeOH solutions, ca. 6.400 cm^{-1} for dyes **39** and **40**, increases to 7.000 cm^{-1} and 8.100 cm^{-1} for **38** and **37**, respectively (Table 6). These observations indicate that the energy level of the emitting state is lowered accordingly to the withdrawing ability of the “pull” substituent. The position of the emission maximum of each unsymmetric derivative also depends on the polarity of the solvent: a bathochromic shift of the maximum is observed as the polarity of the solvent increases for all compounds (Table 6), except for molecule **40** which apparent emission maximum is blue-shifted in CH_2Cl_2 with respect to MeOH. Peak fitting of the emission profile of **40** in CH_2Cl_2 , however, reveals the E_{00} transition peaks at 452 nm (a shoulder in the spectrum of Figure 31a), which is slightly red-shifted with respect to MeOH, similarly to the other compounds.

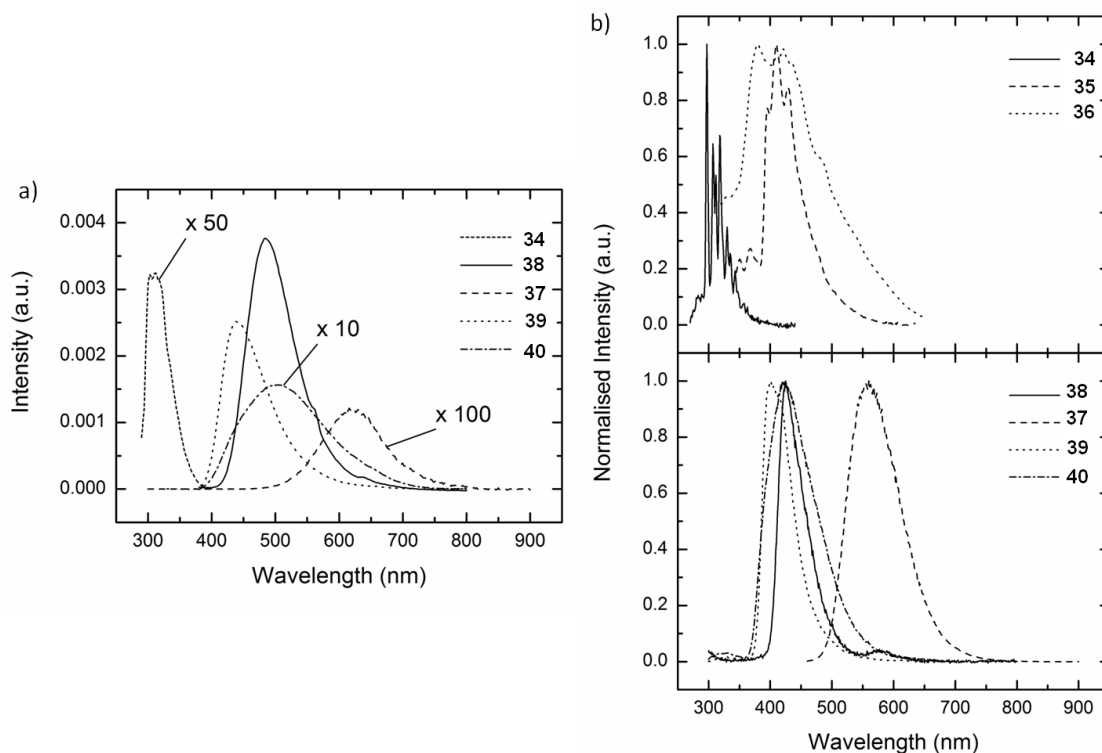


Figure 31. a) Emission spectra of four unsymmetric diphenyl acetylene derivatives and the model **34** in air-equilibrated CH_2Cl_2 solution, scaled according to the photoluminescence quantum yield; b) emission spectra of the symmetric (top) and unsymmetric (bottom) diphenyl acetylene derivatives in MeOH/EtOH 1:4 frozen glass at 77 K.

For molecule **38** the emission properties were studied in three different solvents and a linear correlation is established between the transition energy and the solvent polarity expressed by its dielectric constant (Figure 32a). This solvatochromic behaviour has been observed already for *para*-substituted push-pull diphenyl acetylenes and has been explained considering an emitting ICT state with an increased dipole moment compared to that of the ground state.^[141-144] In MeOH acid solutions the rt emission of **38** has a very low Stokes shift (Table 7) and the yield is quite high (0.29) with a lifetime below the experimental resolution ($< 0.5 \text{ ns}$), indicating a very high radiative constant. On

the other hand, the emission at 77 K is well resolved (Figure 32b) with a lifetime of 0.6 ns. The similarity of the spectroscopic features of **38** in acidified solvent with those of the precursor **34** indicates that the ICT state is destabilized in the acidified solvent, as expected considering that the protonation of the aminic nitrogen precludes the charge migration.

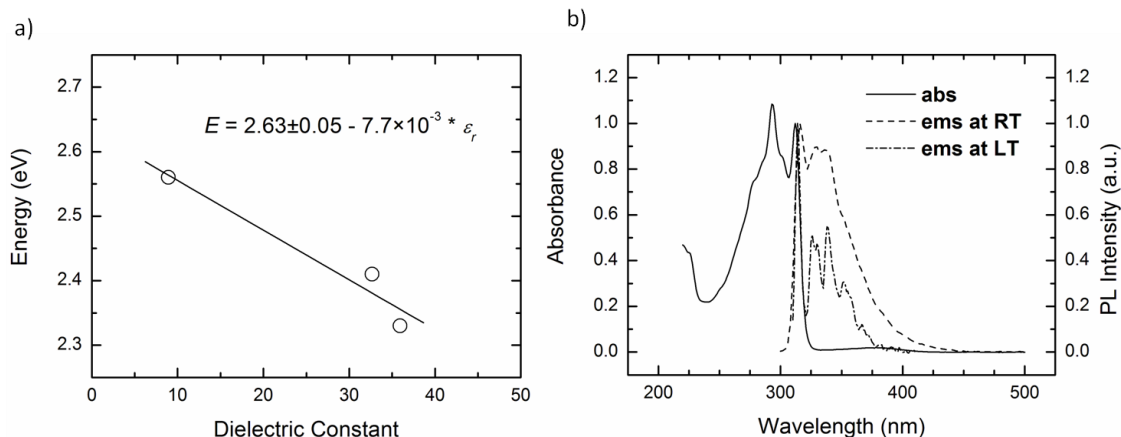


Figure 32. a) Plot of the emission maxima of **38** as function of the solvent polarity, expressed by the dielectric constant.; b) room temperature normalized absorption spectrum in acid CH_3CN (solid line) and emission spectra at room temperature in acid CH_3CN (dash line) and at 77 K in acid MeOH/EtOH 1:4 frozen glass mixture (dash-dot line) of **38**, excitation at 250 nm. Emission spectra are normalized to the intensity of the lowest energy absorption band.

For all the unsymmetric derivatives the CT nature of the emission is confirmed by the observation of an important hypsochromic shift in the maximum of the low temperature spectrum compared to the room temperature one (Table 6 and Figure 31b). It is worthwhile to note that in rigid matrix at 77 K, all examined push-pull dyes showed brighter emission with respect to the rt case, due to the decreased operativity of non-radiative deactivating pathways. This effect is also important in view of the preparation of highly performing films: all studied unsymmetric compounds present a high emission quantum yield when embedded in plastic thin films (section 2.4.1.2).

The two symmetric derivatives display a very weak, **35**, or almost absent, **36**, rt emission both in MeOH and in CH_2Cl_2 (Table 6) whereas at 77 K a weak structured fluorescence was observed (Figure 31b top and Table 6). In contrast to the unsymmetric derivatives, a phosphorescence emission, peaking around 510 nm, was observed in frozen glass at low temperature (77 K) for the symmetrically substituted compounds **35** and **36**. The normalized phosphorescence spectra are shown in Figure 33, and the corresponding photophysical parameters are collected in Table 6. In the case of the dinitro derivative **36** a vibronic structure in the emission spectrum is observed, while in the case of the amino compound **35** the bands are broadened and the vibrational peaks appear only as shoulders. The observed phosphorescence can be ascribed to Coulomb exchange and spin-orbit coupling between orbitally distinct states, enhanced by the internal heavy atoms (O or N), that would lead to a “concerted” charge recombination and intersystem crossing process, as previously stated (section 2.2.2.2).

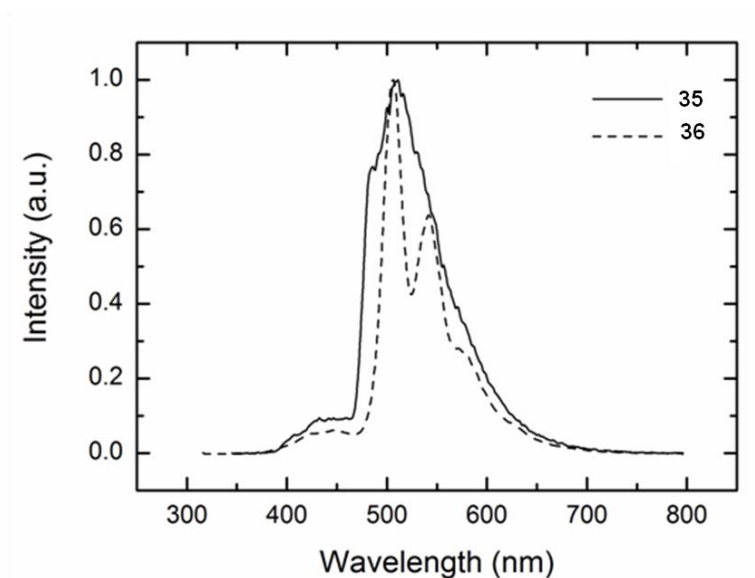


Figure 33. Phosphorescence spectra of the symmetric diphenyl acetylene derivatives **35** and **36** in MeOH/EtOH 1:4 frozen glass at 77 K.

2.4.1.2. Diphenyl Acetylenes **34-40** in Polymeric Matrix

In view of the implementation of push-pull diphenyl acetylene derivatives in the PET instrument as wavelength converters, as required by the STRING project, all the synthesized unsymmetric fluorophores were embedded into a matrix of poly(methyl methacrylate), PMMA, and the emission abilities of such materials have been studied (Figure 34). Thin films of PMMA doped with the organic dyes were prepared from PMMA solutions in CHCl_3 containing 1% w/w of organic dye; this solution was then spin coated on 1"×1" borosilicate glass substrates (see Chapter 4 for more details).

When embedded in the solid PMMA, the unsymmetric diphenyl acetylene derivatives (**n@PMMA**, $n = 34-40$) showed absorption spectra similar to those recorded in solution, with only a slight blue shift of the band maxima (Table 8). The optical density of the prepared films (thickness ca. 2.5 μm) ranges between 0.1 and 0.4 absorbance units, corresponding to 80% and 40% of transmitted light, respectively.

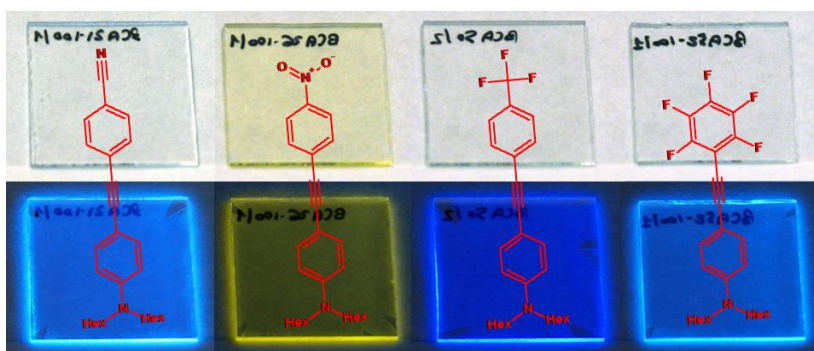


Figure 34. Unsymmetric diphenyl acetylenes **34-40** embedded in PMMA matrix displaying the corresponding emission abilities.

The emission from the **37-40@PMMA** system is blue shifted compared to the emission of the corresponding asymmetric **37-40** derivatives in solution (Figure 35, Tables 6 and 8), according to the ICT characteristics. All organic dyes showed now a mono-exponential luminescence decay with excited state lifetimes very similar to those

recorded from the emission in solution or in frozen glass matrix at 77 K (Tables 6 and 8). In general term, most of the luminescent material studied showed a neat quantum yield increase with respect to solution (see Tables 6 and 8) when the luminophore is blocked in a rigid environment. In some cases, like for dye **38@PMMA**, the increase amounts to more than an order of magnitude, reaching an almost unit yield.

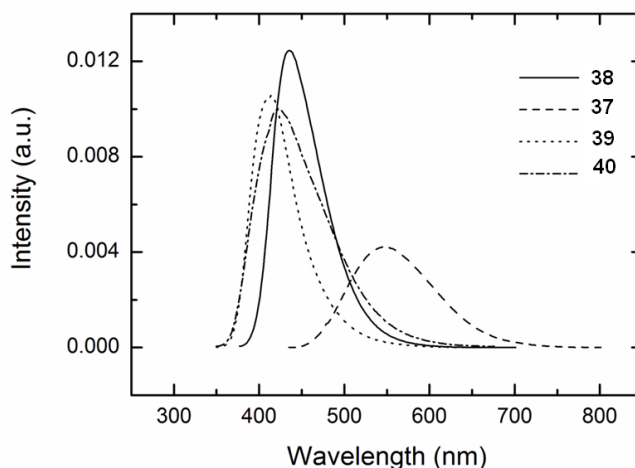


Figure 35. Emission spectra of the asymmetric diphenyl acetylene derivatives 1% (w/w) in PMMA thin film (thickness *ca.* 2.5 μm), scaled according to the photoluminescence quantum yield.

Only a faint emission has been detected from **35@PMMA**, while the other symmetric derivative **36@PMMA** and the tolan precursor **34@PMMA** have shown no luminescence at all. Although in a rigid environment, no phosphorescence was observed at room temperature from the symmetric **35@PMMA** and **36@PMMA** systems.

Table 8. Photophysical parameters of the investigated compounds **34-40** in PMMA thin films.

Compound	Absorption		Emission	
	λ_{max} (nm)	λ_{max} (nm)	Φ	τ (ns)
34@PMMA	299	n.d.	n.d.	n.d.
35@PMMA	359	422	< 0.02	< 0.5
36@PMMA	333	n.d.	n.d.	n.d.
37@PMMA	429	545	0.52 ± 0.05	2.8
38@PMMA	384	434	0.92 ± 0.01	1.9
39@PMMA	361	416	0.75 ± 0.02	1.7
40@PMMA	361	422	1.00 ± 0.05	2.4

2.4.1.3. Donor Acceptor Benzoxazoles **41-42** in Solution

Absorption, emission, and lifetime data for the pure organic luminescent materials have been recorded at room temperature in solvents of different polarity, *e.g.* MeOH, CH₂Cl₂ and toluene. Low temperature emission spectra and excited state lifetimes have been obtained in MeOH:EtOH (1:4) mixtures at 77 K.

Absorption. The lowest energy absorption bands of the synthesized benzoxazole derivatives **41** and **42** are structureless very similar in shape and are unaffected by the solvent polarity (Figure 36 and Table 9). This would suggest a low push-pull behavior if compared with the precedent investigated diphenyl acetylene derivatives, which showed a considerably strong solvatochromic effect (*section 2.4.1.1*). However, the same band results sensitive to the nature of the substituents attached to the phenyl ring. In particular, the presence of an electron withdrawing group shifts the excited state energy to higher values with respect to the values showed by the corresponding bisbenzoxazole derivatives (*section 2.4.2*).

Emission. In both cases of **41** and **42** a structured fluorescence emission from the π,π^* and/or n,π^* excited states is observed, which energy is not influenced by the temperature and medium. The emission of the two dyes is also characterized by very short lifetime ($\tau < 1$ ns) and small Stokes shifts. A phosphorescent emission is also observed in both cases in MeOH (Figure 36, Table 9). Although very promising, these data were not completely in agreement with the STRING project requirements for the desired wavelength shifters as explained in *section 2.2.2.3*. The values of the quantum yields in all the solvents employed for the analysis resulted very far in values from the desired value of 1.0. Therefore, structural modifications have been carried out to improve the photophysical parameters of these benzoxazole-based dyes and the results are presented in the following *section 2.4.2*.

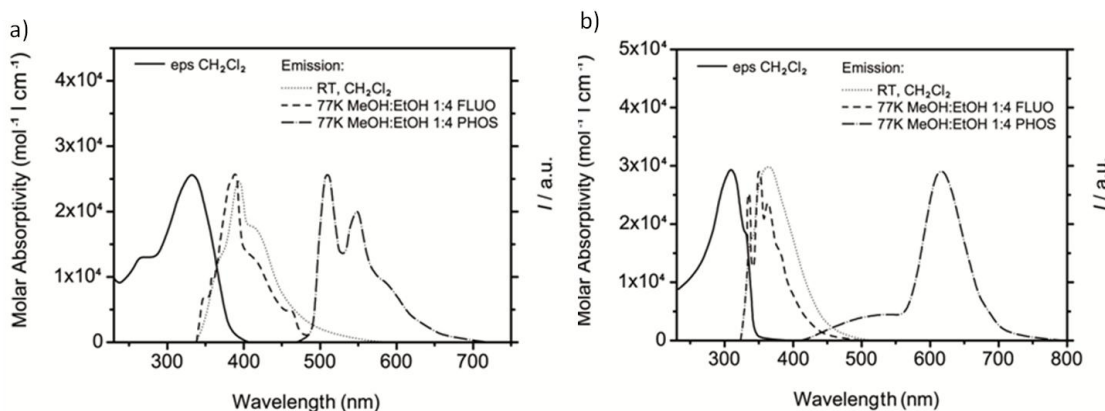


Figure 36. a) Absorption (black line) and rt emission in CH₂Cl₂ (dotted line), fluorescence and phosphorescence (dashed lines) spectra at 77 K in MeOH/EtOH frozen glass mixture of the push pull benzoxazole-based derivative **41** ($\lambda_{\text{exc}} = 330$ nm); b) absorption (black line) and room temperature emission in CH₂Cl₂ (dotted line), and low temperature emission (dashed lines) spectra of the push pull benzoxazole-based derivative **42** ($\lambda_{\text{exc}} = 300$ nm). Emission spectra are normalized to the intensity of the lowest energy absorption band.

Chapter 2

Table 9. Photophysical parameters of the investigated benzoxazole dyes **41** and **42**.

Compound	Solvent	Absorption (rt)		Emission (rt)			Emission (77 K) ^d	
		λ_{max} (nm)	ϵ_{max} (mol ⁻¹ ·l·cm ⁻¹)	λ_{max}^a (nm)	ϕ^b	τ^c (ns)	λ_{max}^a (nm)	τ^c (ns)
41	Toluene	335	24.900	365 394 416	8.8×10 ⁻⁴	0.34 1.5	389	1.0
	CH ₂ Cl ₂	334	25.800	366 393 412	9.2×10 ⁻⁴	0.33 1.0	511 ^f 549 585	0.33×10 ^{9f}
	MeOH	- ^e	- ^e	363 390 412	7.1×10 ⁻⁴	0.22 1.0	- ^e	- ^e
42	Toluene	312 333	28.700 19.200	363	0.26	0.47	335 351 364	0.91
	CH ₂ Cl ₂	310 331	29.800 18.900	363	0.21	0.39	335	0.91
	MeOH	308 328	31.900 19.600	364	0.15	0.36	617 ^f	0.25×10 ^{6f}

^a Emission maxima derived from non-corrected emission spectra. Excitation at 300 nm; ^b luminescence quantum yields determined by comparing corrected emission spectra, using quinine sulfate in H₂SO₄ 1 N as a standard. Excitation at 300 nm; ^c Excitation at 278 nm; ^d In MeOH/EtOH 1:4; ^e the poor solubility of the compound made the measurement impossible; ^f Phosphorescence.

2.4.2. Photophysical Properties of Hetero-doped Benzazole-based Organic Emitters **43-45** and **47**

In this section, the luminescence properties of synthesized bisbenzazole derivatives **43-45** and **47** are reported in view of their exploitation as wavelength shifters. In addition, attention is given to the effect shown by the heavy atoms, O, S and Se, on the emission signals of the dyes. A comprehensive study was performed by means of steady-state and time resolved techniques in different solvents at room temperature (rt) and in glassy matrix at 77 K.

2.4.2.1. Absorption Experiments

The absorption spectra of investigated compounds **43-45** have been recorded at rt in three solvents of differing polarity, such as toluene, CH₂Cl₂ and MeOH. The electronic absorption spectra in CH₂Cl₂ solution are reported in Figure 37 and the main photophysical parameters in the different solvents are gathered in Table 10. The absorption spectra of compounds **43-45** in the different solvents are very similar and exhibit a first broad, diffuse and structureless absorption band between *ca.* 300 and 400 nm, originating from an envelope of electronic transitions of ¹π,π* nature. The substitution of the O atom by S and Se atoms leads to a bathochromic shift of the band position (Table 10 and Figure 37). Additionally, a small solvatochromic shift of the lowest energy absorption band is observed, more pronounced for the Se derivative, moving from 386 to 382 nm as the solvent polarizability, decreased (stabilization order: Toluene *n* = 1.50 > CH₂Cl₂ *n* = 1.42 > MeOH *n* = 1.33).

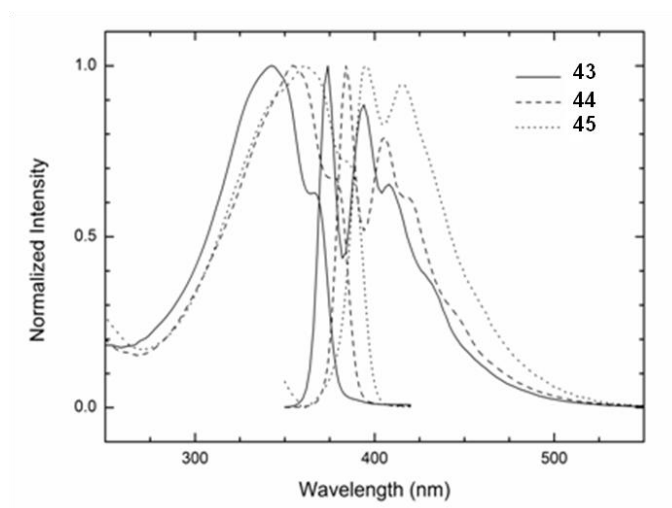


Figure 37. Normalized absorption (left) and emission (right) spectra of derivatives **43-45** in CH_2Cl_2 solution at rt.

Table 10. Photophysical parameters of the investigated bisbenzoxazole dyes **43-45**.

Compound	Solvent	Absorption (rt)		Emission (rt)		
		λ_{max} (nm)	ϵ_{max} ($\text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$)	λ_{max}^a (nm)	ϕ^b	τ^c (ns)
43	Toluene	344 369	14.100 9.200	374 394 406	0.71	0.75
	CH_2Cl_2	343 367	11.800 7.400	374 394 408	0.75	0.78
44	Toluene	355 380	37.000 25.000	384 406 420	0.50	0.40
	CH_2Cl_2	355 378	51.000 34.000	384 406 410	0.42	0.39
	MeOH	-	-	382 402 416	0.53	0.39
45	Toluene	362 386	^d	394 415	2.1×10^{-3}	<0.2
	CH_2Cl_2	361 385	^d	395 415	1.5×10^{-3}	<0.2
	MeOH	358 382	^d	394 413	2.3×10^{-3}	<0.2

^a Emission maxima derived from non-corrected emission spectra. Excitation at 300 nm; ^b luminescence quantum yields determined by comparing corrected emission spectra, using quinine sulfate in H_2SO_4 1 N as a standard. Excitation at 330 nm; ^c Excitation at 331 nm; ^d the low quantity of compound made impossible the measurement of the extinction coefficients.

2.4.2.2. Emission Experiments: from Fluorescence to Phosphorescence

The emission spectra observed in solution at rt are displayed in Figure 38 and the relevant emission maxima, together with the measured photoluminescence quantum yields and excited state lifetimes, are reported in Table 10.

An emission spectrum exhibiting discrete vibronic features is observed in all cases with a very small Stokes shift. No solvent effect on the energy and shape of emission spectra has been observed. Notably, the O and S derivatives show a remarkably high photoluminescence quantum yield in solution and a short excited state lifetime (Table 10), yielding very similar value for the radiative constant, $k_r \sim 10^9 \text{ s}^{-1}$ in both cases ($k_r = \phi/\tau$). These features make them very promising for the role of wavelength converters. On the contrary, in the Se derivative the rt fluorescence is almost completely quenched ($\phi_{em} \sim 2 \times 10^{-3}$) and the lifetime becomes shorter than our instrumental detection limit ($\tau < 200 \text{ ps}$). This pronounced quenching might be due in principle to two main factors, acting either independently or simultaneously, (i) an increased efficiency of the intersystem crossing (isc) process promoted by the presence of the selenium and highlighted by its one order of magnitude higher spin coupling constant with respect to O and S ($\zeta_1 = 154, 365 \text{ and } 1,659 \text{ cm}^{-1}$ for O, S and Se, respectively), or (ii) a coupling with the ground state through vibrational modes of different energies, induced by the increase of atomic mass passing from O and S to the Se derivative. In order to assess the most effective pathway in the fluorescence quenching in the **43-45** series, phosphorescence measurements were carried out.

The normalized luminescence (fluorescence and phosphorescence) spectra of **43-45** obtained in MeOH/EtOH glassy matrix at 77 K are reported in Figure 38 and relevant photophysical parameters (emission maxima and lifetimes) are collected in Table 11. The phosphorescence spectra have been obtained from time resolved luminescence at fixed delay.

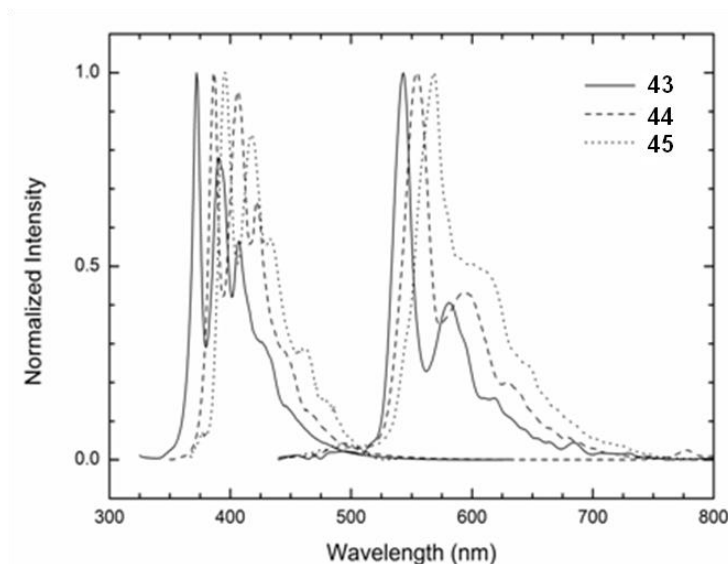


Figure 38. Normalized fluorescence (left) and phosphorescence (right) emission spectra of derivatives **43-45** in MeOH/EtOH 1:4 glassy matrix at 77 K.

At low temperature modules **43** and **44** showed a bright structured fluorescence emission from $^1\pi,\pi^*$ excited states (Figure 38). Differently, the Se derivative **45** only shows a faint fluorescence emission. Despite the approximation caused by the glassy matrix, it is possible to observe that the fluorescence emission intensity ratio between **45** and **43** well corresponds to that observed at room temperature. Conversely, the same Se derivative **45** exhibits a clear bright phosphorescence emission peaking at ca. 568 nm in frozen glass at low temperature (Figure 38

and Table 11). A less intense phosphorescence emission was also observed for the sulfur-doped module **44**, while the bisbenzoxazole **43** displayed no detectable triplet emission. However, in order to obtain phosphorescence spectra from **43**, experiments upon addition of CH_3I , to enhance ISC and triplet yield have been performed. Thus, the phosphorescence spectra of **43-45**, reported in Figure 38, display a still evident vibronic structure, although with bands more broadened with respect to fluorescence, consistent with a $^3\pi,\pi^*$ nature of the excited state. Beside a decrease of fluorescence intensity in the serie **43-45** on going from the O, S and up to the Se a simultaneous increase in phosphorescence intensity is observed. The considerably shorter phosphorescence lifetime displayed by the selenium derivative **45** is an indication of the stronger coupling of the first triplet excited state T_1 with the singlet ground state S_0 . As a general remark, a clear trend in the bathochromic shift of both fluorescence and phosphorescence is observed passing from **43** to **45** (Table 11).

Table 11. Fluorescence and phosphorescence of the investigated bisbenzoxazole dyes **43-45**.

Compound	Fluorescence		Phosphorescence	
	λ_{max}^a (nm)	τ^b (ns)	λ_{max}^a (nm)	τ^c (ms)
43	372	0.63	543	34
44	387	0.53	554	12
45	396	< 0.2	568	0.23

^a Emission maxima derived from non-corrected emission spectra; ^b excitation at 331 nm; ^c Excitation at 370 nm.

The fluorescence quenching observed upon substitution of the O atom with the two heavier elements, S and Se might be accounted by the decrease of the emission energy, and, consequently, an increase in non radiative rate constant. However, this alone does not explain the decrease by two order of magnitude of the fluorescence quantum yield shifting from **43** to **45**. Thus, another deactivation mechanism of the excited state should be taken into account. Most probably it is the ISC to the triplet state promoted by the heteroatom in the five member ring of the benzazole moiety that occurs in these conditions. The H-A effect is also witnessed by the appearance of a faint phosphorescence when the O atom ($\zeta_l = 154 \text{ cm}^{-1}$) is substituted by S ($\zeta_l = 365 \text{ cm}^{-1}$), and by the increased phosphorescence intensity, together with an almost complete fluorescence quenching, when Se is introduced ($\zeta_l = 1,659 \text{ cm}^{-1}$).

2.4.2.3. Bisbenzazole **47**: towards the Application as Wavelength Shifter for PET Imaging

As anticipated in section 2.2.2.3, the best organic dye candidates to be used as wavelength converters within the context of the STRING project must have well defined photophysical properties. Beside the requirements of the absorption in deep UV and emission in the visible part of the spectrum, the desired shifter has to have a good ability to absorb light ($\epsilon > 10^4 \text{ mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$) and high fluorescent quantum yield ($\phi > 0.8$), fast response time (luminescent decay time $\tau < 2 \text{ ns}$), large Stokes shift to avoid self-absorption and good photochemical stability to deep UV radiation. According to the reported results, these requirements were completely fulfilled by bisbenzazole **43** investigated in our work. Also alkylated bisbenzoxazole **47** resulted to be excellent wavelength shifters. In Table 12 the photophysical properties of both, **43** and **47**, matching the requirements of STRING are compared.

Table 12. Photophysical parameters of investigated bisbenzoxazole dyes **43** and **47**.

Compound	Absorption (rt)		Emission (rt)			Emission (77 K) ^d	
	λ_{max} (nm)	ϵ_{max} (mol ⁻¹ ·l·cm ⁻¹)	λ_{max}^a (nm)	ϕ^b	τ^c (ns)	λ_{max}^a (nm)	τ^c (ns)
43	343	11.800	374	0.75	0.78	372	0.63
	367	7.400	394 408				
47	330	82.000	408	0.79	2.0	428	1.70
	392	78.000	434				

^a Emission maxima derived from non-corrected emission spectra. Excitation at 330 nm; ^b absolute quantum yields determined by comparing corrected emission spectra, using quinine sulfate in H₂SO₄ 1 N as a standard. Excitation at 330 nm; ^c Excitation at 331 nm; ^d In MeOH:EtOH 1:4.

Dye **47** displays absorption bands in the UV region and emission bands in the visible part of the spectrum (Figure 39). It also exhibits high values of extinction coefficients demonstrating the good ability as light absorbers. Moreover, a very high yield was measured for **47** (0.79), higher than that measured for precursor **43** (0.75). These results are also coupled with very short lifetime values of the excited states, equal or below 2 ns.

These results obtained in solution are very promising for a future investigation of compounds **43** and **47** within a solid matrix as already described for diphenyl acetylene derivatives **34-40**.

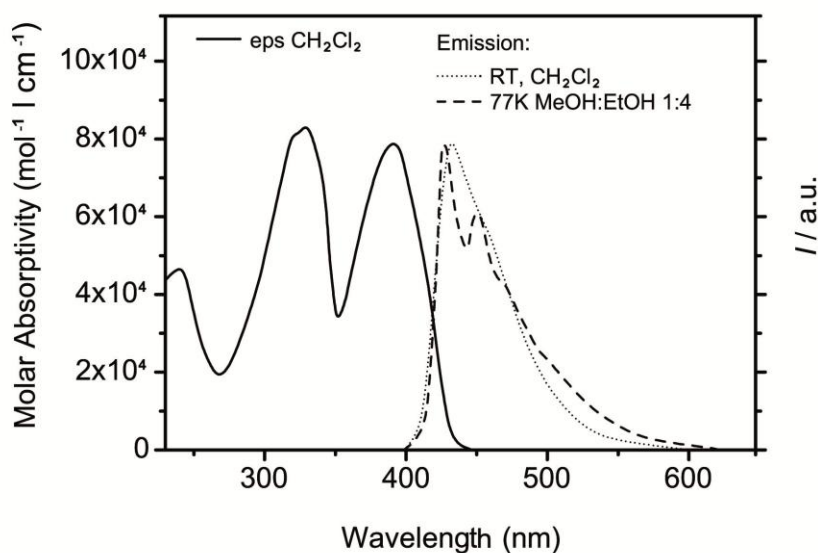


Figure 39. Absorption and emission spectra of **47**. Room temperature absorption (black line) and emission (dotted line) in CH₂Cl₂; fluorescence (dashed line) at 77 K in MeOH:EtOH frozen glass mixture. Excitation 330 nm. Emission spectra are normalized to the intensity of the lowest energy absorption band.

As reported in section 2.1.2, to be employed into the PET scanner, the wavelength shifter has to be embedded into a solid matrix. In particular, amongst different matrices, STRING focused the research on the sol-gel glasses, wherein alcohols are used as solvents. Therefore, the organic shifter has to show a good dispersability in polar solvents. The insertion of the alkoxy lateral chains on the central ring in **47** revealed to be a good strategy to increase

the solubility in alcohols and to permit the fabrication of a scintillator stack for the PET machine. Figure 40 displays the scintillator stack comprising several components prepared by the partners of STRING research network. The ceramic scintillator combined with the wavelength shifter (round disk) is sandwiched between two interference filters, prepared by *Philips Lighting*. This device was fully characterized. However, its preparation and the related results are part of confidential information, and they will not be reported in this dissertation.

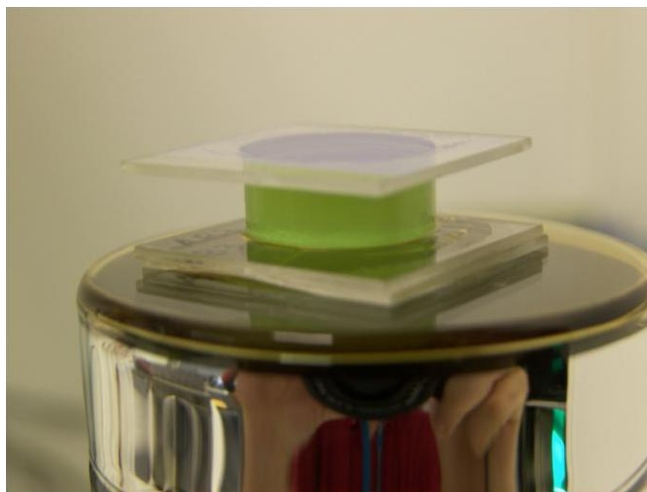


Figure 40. Scintillator stack engineered by STRING network, featuring two interference filters (squared plates) combined with the scintillator material mixed and the wavelength shifter embedded into a solid matrix (round disk).

2.5. Conclusions

This chapter focused on the design of organic UV to Visible wavelength shifters for Positron Emission Tomography applications. The chosen strategy for achieving novel organic wavelength shifters involved the selection of two main approaches based on the push-pull and the heteroatom effects. To exploit the first approach, unsymmetrical donor-acceptor modules separated by a π -conjugated linker (D- π -A) and symmetrical D- π -D/A- π -A structures (**34-42**) were synthesized *via* the Pd-catalyzed *Sonogashira* cross-coupling as main synthetic reaction. The heteroatom effect was instead applied in a new series of O-, S-, and Se-doped bisbenzazole derivatives (**43-45**), where two hetero-doped benzazoles moieties were linked through a 1,4-diethynyl phenyl core. The photophysical properties of systems **34-42** have been investigated in solvents of different polarity and in PMMA thin films (for dyes **34-40**) by steady-state absorption and fluorescence measurements. The spectral results in solution show that increasing the electron donating and accepting strength of the substituents, as well as the solvent polarity, a small solvatochromic shift in the absorption maxima but a large bathochromic shift in the fluorescence maxima are observed, accounting for a larger dipole moment in the excited-state with respect to the ground state. The lowest energy transition is attributed to an intramolecular charge transfer (ICT) state populated upon photoexcitation. All compounds revealed to be highly luminescent in condensed media, *e.g.* in frozen solutions at 77 K and in PMMA films at rt, with a hypsochromic shift of the emission band maxima, according to the ICT nature of the emitting state. A neat increase of the quantum yield, when the push-pull dyes were embedded in the rigid environment with respect to solution, was obtained. In some cases, the increase was higher than one order of magnitude (for **38@** and **40@PMMA**), and mono-exponential luminescence decays with excited state lifetimes shorter than 3 ns. Therefore, the push-pull approach revealed to be a powerful strategy to prepare UV to Visible wavelength shifters for the PET imaging technique. In particular, the preparation of solid matrices is a promising methodology for the design of new generations of organic-based devices with good conversion performances ($\Phi = 1$ and $\tau < 3$ ns).

Heterodoped bisbenzazoles **43-45** and alkoxyated bisbenzoxazole **47**, envisaged to exploit the solubility in polar solvents, showed very high room temperature photoluminescence quantum yields in solution (Φ : 0.53-0.79), coupled with short lifetimes of the excited state (τ : 0.5-2.0 ns). Amongst all, the O-doped bisbenzazoles **43** and **47** were found the most promising derivatives exhibiting outstanding properties for the role of wavelength shifters in PET scanners (**43**: $\Phi = 0.75$, $\tau = 0.78$ ns; **47**: $\Phi = 0.79$, $\tau = 2.0$ ns). In particular, module **47** was implemented into a first wavelength converting device designed to improve the performances of the PET instrument.

The heteroatom substitution in bisbenzazoles, **43-45**, allowed the photophysical investigation of the internal heavy atom effect. Luminescent measurements were performed on the **43-45** series exhibiting a pronounced fluorescence decrease going from **43** to **45**. Phosphorescent emissions were detected for the S-derivative, **44**, and more intense for its Se-analogue, **45**, witnessing the effect of the heavy atom in promoting the excited state deactivation through intersystem crossing ($S_1 \rightarrow T_1$) processes. In summary, the heteroatom effect may be a useful strategy to generate novel phosphorescent organic emitters.

The effect of the heteroatom substitution in the series **43-45** was also investigated at the solid state by means of X-Ray chrystallography analysis. All modules arranged according to the same symmetry group (P21/c). The effect of the progressively heavier atom, from O to Se, was clearly retrieved in the crystal packing mainly on the π - π stacking and offset distances. In particular, a periodic trend was observed for the π - π stacking distances going from the O- to the Se-doped derivative (from 3.46 to 3.67 Å). The same periodic trend was instead not observed in the offset distances, where larger distances were calculated for **43** and **44** (3.26 and 3.54 Å, respectively) and a shorter one for the Se-derivative **45** (2.15 Å). Theoretical calculations were found to be important tools to explain the solid state results. Hence, geometry optimizations and single point energy calculations were carried out to evaluate structural parameters, such as atomic partial charges, surface electrostatic potential (ESP) maps, dipole moments and quadrupole moment tensors, for each derivative. In general, a good overlap was found between experimental and theoretical data. The values obtained from the geometry optimizations permitted to associate the periodic increase of the π -stacking distance in the series **43-45** with the increase of the atomic van der Waals radius going from O to Se. The parameters computed by means of single point energy calculations allowed to find preliminary rationals for the observed offset distance values. While the large offset in crystallized **43** was justified considering the *Hirshfeld* charge distribution, the offset in **44** was explained by means of the calculated quadrupole moment tensor.

3. Self-Assembly of Porphyrin-Derivatives at Interfaces: from Architectures towards Applications

This chapter describes the different types of supramolecular interactions between porphyrin derivatives and hybrid surfaces. The first part addresses the synthesis of pyridyl-substituted porphyrins and the formation, upon deposition on metallic surfaces, of highly organized non-covalent assemblies. The second part sets out the synthesis and the photophysical properties of porphyrin functionalized carbon nanotubes. In particular, porphyrin-based Double Wall Carbon Nanotubes (DWCNTs) were synthesized and characterized as donor-acceptor systems to be exploited as active components in photovoltaic devices.

The chapter has two main sections: *i)* sections 3.1 and 3.2 include a general introduction on the self-assembly properties of porphyrin modules on surfaces imagined by Scanning Tunneling Microscopy (STM) technique, followed by the results obtained on the synthesis and the Ultra-High-Vacuum (UHV) STM analysis of pyridyl-substituted derivatives; *ii)* section 3.3 deals with the design of porphyrin-based donor-acceptor systems for photovoltaic devices and it includes a brief overview on the chemistry and properties of carbon nanotubes, together with the synthesis of the targeted porphyrin-functionalized carbon nanotubes and their photophysical and conductive properties.

The research in sections 3.1 and 3.2 is a collaborative work done with *Daniel Heim, Knud Seufert, Dr. David Écija, and Dr. Willi Auwärter* from the group of *Prof. Dr. Johannes Barth* at the *Technische Universität München (TUM), Munich, Germany*.

The research work in section 3.3 has been carried out jointly with *John Mohanraj* from the group of *Dr. Nicola Armaroli* at the *Istituto per la Sintesi Organica e la Fotoreattività (CNR - ISOF), Bologna, Italy*, *Dr. Sorin Melinte* at the *Université Catholique de Louvain (UCL), Louvain-La-Neuve, Belgium*, and *Dr. Andrea Minoia* from the group of *Prof. Dr. Roberto Lazzaroni* at the *Université de Mons, Mons, Belgium*. Furthermore, *Dr. Riccardo Marega, Daphné Stassen, Valentina Corvaglia* and *Silvia Forensi* from the University F.U.N.D.P. of Namur are kindly acknowledged for their collaboration.

3.1. Porphyrin Scaffolds for Engineering Nanostructured Surfaces

Tetrapyrrolic macrocycles, such as chlorins, bacteriochlorins, porphyrinogens, and protoporphyrins, belong to a class of distinctively multifunctional biomolecules playing a central role in events such as electron transfer, oxygen transfer, and light-harvesting.^[145-149] They are generally present as metallocomplexes in which the four nitrogen atoms are coordinated to a metal ion such as iron(III) or magnesium(II). Two representative examples are: *i)* heme, an iron(III)-containing complex bound to various proteins, which is a central structure in all biological mechanisms involving oxidation and/or oxygen carriage, and *ii)* chlorophylls which are magnesium(II)-chlorin complexes having a central function in the natural photosynthesis. Among the biological processes based on the mentioned macrocycles, the natural solar energy transduction pathways are, without any doubt, the most investigated and mimicked processes.^[150]

Although the π -conjugation is maintained over the central 16-membered ring, in the large majority of natural tetrapyrrolic macrocycles, the electron delocalization does not extend over all C-atoms of the core skeletons because of the saturation of one or two double bonds (Figures 41a-c). Due to the presence of two or more saturated C-atoms, the chemical synthesis and modification of such macrocyclic scaffolds were found to be tedious, low-yielding and, thus, less convenient for investigations in artificial photosynthetic systems, although several fullerene-chlorin

conjugates have been reported in the literature.^[151] Therefore, it is fundamental to produce synthetically accessible structures with the electronic properties similar to those of chlorophylls. Fully conjugated tetrapyrrolic macrocycles, such as porphyrins (Figure 41d) and their derivatives proved to have similar excitation energies, quantum yields, and electron transfer properties as chlorophylls, *i.e.*, the uptake and release of electrons produce only minimal structural changes upon electron transfer.^[152] As a result, they are by far the most used molecular scaffolds to replace chlorins and their congeners for mimicking natural photosynthesis.

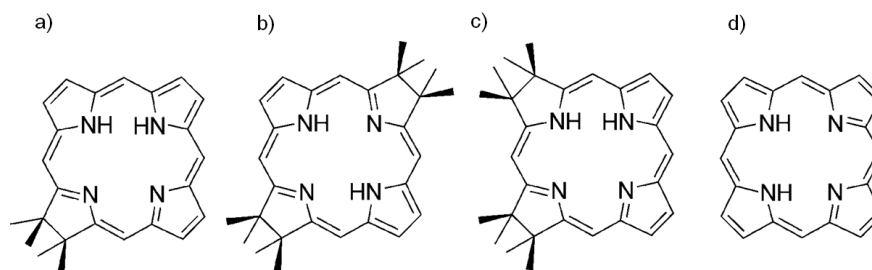


Figure 41. Skeleton of porphyrin-related compounds. a) chlorins (precursor of *chlorophylls*); b-c) bacteriochlorins (precursors of *bacteriochlorophyll-a* and *b* respectively); d) π -conjugated porphyrin core.

The term ‘porphyrin’ derives from the Greek “πορφύρεος” (*porphuros*), purple, due to their intense color. The basic porphyrin skeleton consists of four pyrrole-type heterocycles interconnected by four methine groups. This conjugated macrocycle includes a perimeter with 18 π -electrons which is aromatic according to *Hückel’s* rule ($4n + 2$ delocalized π -electrons, with $n = 4$).^[153] The robust structure and the extended conjugation are responsible for the outstanding optical and electrochemical properties of porphyrin molecules. For this reason, porphyrins have been extensively studied to mimic biological functions.^[154, 155] However, control over structural organization at the molecular level is an essential requirement for molecular electronics applications or for assembling new materials mimicking the photosynthetic processes.^[156, 157] Consequently, not only their peculiar photophysical properties but also the arrangement and their relative orientation play an important role for the efficiency of porphyrin-based molecular nanoscale devices.

Electronic devices were initially composed of inorganic semiconductors and fabricated according to the “top-down” process. In the “top down” approach nano-objects are constructed from larger entities without atomic-level control. It is generally believed that there are limitations to this approach for construction of small devices, particularly with sizes in the nanometer range. Thus, an obligatory transition from this type of electronic devices to molecular electronic devices built with organic molecules is occurring. To accomplish that, the research is mainly focused on the development of organic structures capable of meeting the specific structural requirements needed for molecular electronics. In order to construct such molecular-based nanoscale devices, it is necessary to develop methods for the controlled fabrication of well-defined organic nanostructures.^[158-160] In this respect, one of the most promising methods is the “bottom up” approach, by which it is possible to form ordered structures with nanometer precision. Supramolecular chemistry has developed the tools for self-assembly and self-organization of molecular materials for nanotechnologies, as well as the general rules for the controlled design of molecular electronic functions such as logic operators or switches. The concept of this approach is to exploit multiple non-covalent interactions between pre-organized organic molecules, which through their selective recognitions are able to form convergent assemblies. The great advantage of this methodology consists in the dynamic equilibrium that exists between the molecular components and the whole assembly, responsible of the system reversibility.

Figure 42 presents a schematic diagram illustrating how research activities are directed towards the goal of molecular electronics, following the “bottom up” approach. In order to be consistent with the general topic of this

chapter porphyrins as considered as the main components. The first step consists of an assessment of the electronic properties of the single molecule and consequently, an investigation of the structures of the assemblies formed by the single components. Subsequently, to have a good electronic communication between the single components a higher ordered of organization has to be achieved. This can be done by analyzing the correlation between the structures of components, substrates and those of the whole assembly. At this stage it is important to master the art of molecular design to create surface patterns by judicious choice of different structures with specific molecular shapes, polarities, distribution of hydrophilic/hydrophobic sites, as well as introducing directional forces such as hydrogen bonding or coordination interactions. In this way, it is possible to achieve a modulation of the electronic communication within the ordered assemblies, which is the general aim of an intelligent electronic device.

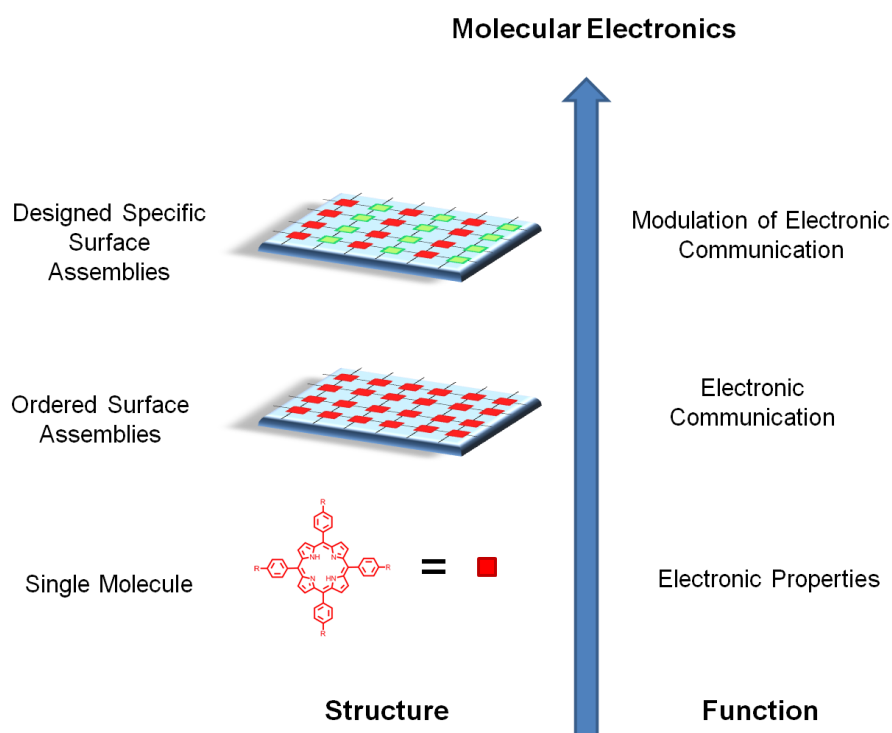


Figure 42. Map towards molecular electronics. At each step the structural feature is related to the corresponding function.

As anticipated in Figure 42, especially relevant are the assemblies on surfaces. This is because the connection between the molecular and the macroscopic worlds can be achieved through conventional electronic circuitry constructed on solid surfaces. Moreover, the intrinsic advantage of the surfaces is that molecules can be easily addressed at the nanoscale level. This does not occur, instead, in solution experiments or at the crystalline state, even though some examples of supramolecular assemblies have been reported in these cases.^[161-163] To be implemented in electronic devices, organic structures must also be able to show durability and functionality under the extreme conditions that are normally used in operating practical devices.^[164] Scanning Probe Microscopies (SPMs) have emerged as powerful tools to solve these problems.^[165, 166] These techniques, in particular the Scanning Tunneling Microscopy (STM), are in fact, largely employed to achieve a precise nanoscale characterization of assemblies formed by depositing functional organic materials on surfaces. Despite the large scientific output describing the organization of molecules on surfaces,^[167-181] the development of hybrid devices in which surfaces are modified with molecular assemblies^[167, 182-184] is becoming the key to bring forth applications in many fields ranging from electronics^[185-194] to nanomedicine.^[195, 196]

In this respect, porous two-dimensional (2D) arrays are of particular interest since their cavities (potentially controllable both in size and shape) can be used to host functional molecules that can be remotely controlled, bringing functionality at the nanoscale level to material. The main strategies for the preparation of well-defined self-assembled architectures featuring pores on surfaces, involve H-bonding interactions,^[197-209] dipole-dipole interactions and van der Waals contacts^[210-218] and metal-ligand coordination.^[219-226]

Most of the synthetic work described in the following sections of this thesis deals with the preparation of porphyrin derivatives to study the formation of 2D arrays on surface by means of STM technique. Therefore, this part sets out the recent developments related to supramolecular assemblies of porphyrin molecules on surfaces, at the solid-liquid interface and under Ultra-High-Vacuum (UHV) conditions, by means of key examples from the literature.

3.1.1. Introduction on Surface-Confined Discrete Assemblies and Bidimensional Networks

3.1.1.1. General Introduction on Scanning Tunneling Microscopy (STM)

The invention of Scanning Tunneling Microscopy (STM) by *Binnig* and *Rohrer* (Nobel Prize in Physics in 1986) in the early 1980's represented a breakthrough in nanoscale science and nanotechnology.^[227] STM allowed for the first time to produce real-space images of electrically conductive surfaces with sub-nanometer scale resolution. This invention was quickly followed by the development of a whole family of related techniques, which together with STM, can be classified in the general category of Scanning Probe Microscopy (SPM) techniques. A major advantage of Scanning Probe Microscopies (SPMs) is that they can operate under different media such as air, liquid, gas streams and ultra-high vacuum (UHV).^[165] UHV conditions, in particular, provide a well defined environment with control of the substrate coverage. In addition, temperature control gives a handle to regulate the molecular mobility and as such individual molecules, clusters, one dimensional (1D) rows and 2D patterns can be deposited. However, not all species can be adapted to UHV conditions, such as those with relatively low thermal stability and high molecular weight (71500 Da).

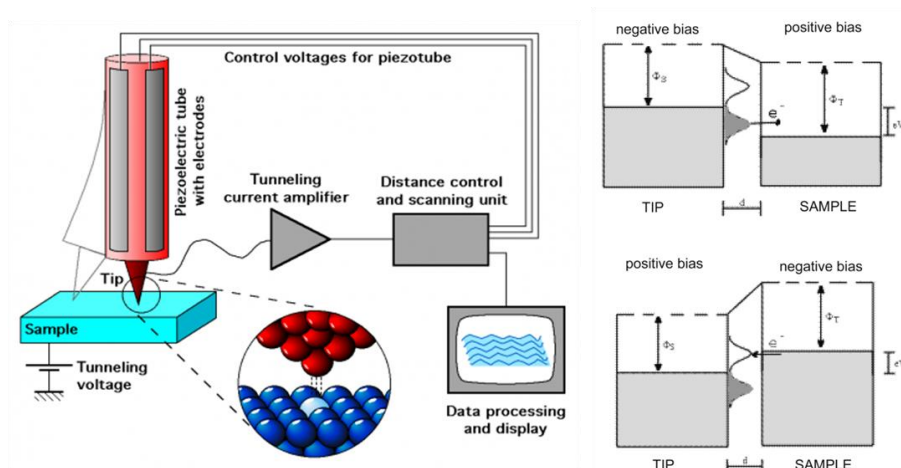


Figure 43. Left: schematic representation of a STM microscope (<http://wikipedia.org>); right: negatively biased tip (electrons tunnel from the tip to the sample) and positively biased tip (electrons tunnel from the sample to the tip).

The basic principle of STM is based on the tunneling current between a metallic tip, which is sharpened to a single atom point, and a conducting material. If the STM tip is close enough to the surface ($\leq 10 \text{ \AA}$) the presence of a

bias voltage (pA to nA) between the tip and sample will cause the electrons to tunnel through the vacuum barrier separating the tip and sample (Figure 43). The tunneling current is then the result of the overlapping wave-functions between the tip atom and surface atoms. The magnitude of tunneling current is extremely sensitive to the gap distance between the tip and sample, the local density of electronic states of the sample and the local barrier height. The Local Density of States (LDOS) represents the amount of electrons that exist at a specific energy level. By keeping the gap distance constant, a measure on the current change with respect to the bias voltage can probe the LDOS of the sample. Moreover, changing the polarity of bias voltage it is possible get local occupied and unoccupied states. As it is shown in the right side of Figure 43 when the tip is negatively biased, electrons tunnel from the occupied states of the tip to the unoccupied states of the sample. If the tip is positively biased, electrons tunnel from the occupied states of sample to the unoccupied states of the tip. STM microscopy therefore does not probe the nuclear position directly, but rather it is a probe of the electron density.

The most common setups to study adsorbed molecules on conductive substrates in the STM involve experiments under atmospheric conditions at room temperature by imaging at the solid liquid interface or measurements under ultra-high vacuum conditions (Figure 44). In the studies performed at the solid-liquid interface the STM tip is immersed in a saturated organic solution of an apolar solvent. Interfacial interactions govern the self-assembly at surfaces, that is in competition with solvation of the molecules with the apolar solvent. Exploiting this method, ordered monolayers can be easily formed and studied with a sub-molecular resolution. This makes possible to gain insight into different types of physico-chemical properties that span from the thermodynamics of physisorption at the solid-liquid interface to the 2D behavior of molecules at surfaces. Due to the presence of the solvents, which can interact itself with the tip, the solid-liquid STM sometimes lacks of spatial resolution. This does not occur under ultra-high vacuum environment where operation at cryogenic temperatures (77 K) reduces electronic noise and eliminates free movement of the molecules. Practically, in this case, the sample preparation requires the sublimation of the molecules onto flat and clean conductive substrates. The molecules are evaporated from a quartz crucible and the microscope is placed into an ultra-high vacuum environment (10^{-10} mbar), which allows for controlled surface preparation and to work in a “clean” atmosphere.

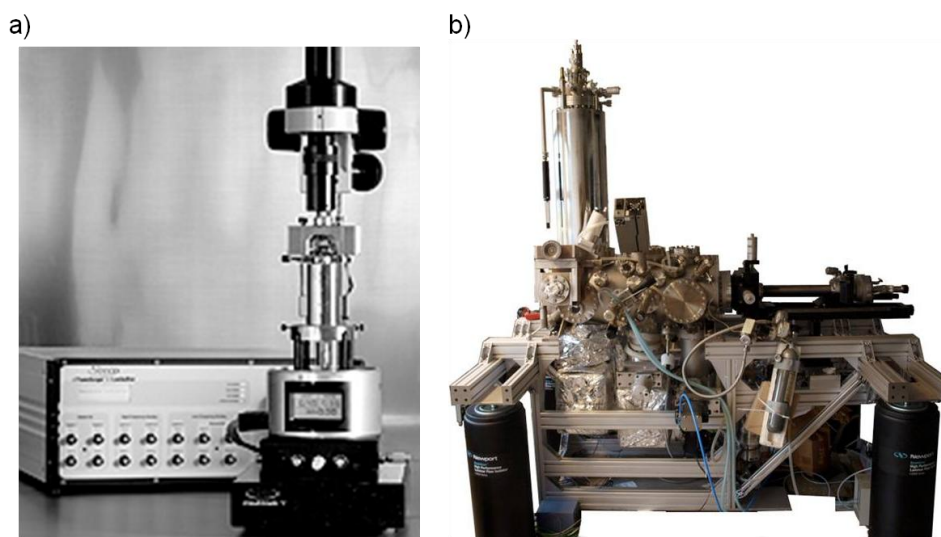


Figure 44. a) Room temperature STM Veeco®; b) home made Low Temperature STM (LT-STM, Physics Department at University of Munich).

3.1.1.2. Porphyrin Architectures at the Solid-Liquid Interface

The development of high quality films of functional molecules such as porphyrins and their derivatives at the nanoscale size in ambient conditions are very important for the engineering of biocompatible materials that might find applications in nanomedicine, for instance, where mild temperatures and ambient pressures are used in common routine experiments. One of the most used surfaces to investigate porphyrin assemblies at the solid-liquid interface, *e.g.* under ambient conditions, is represented by the HOPG. This substrate offers in fact several practical advantages for the characterization of molecular arrays *via* STM: *i*) HOPG has an atomically flat surface, *ii*) to obtain a clean surface is enough a manual cleavage by adhesive tape, *iii*) the HOPG surface is stable at air (in contrast with many metallic surfaces that often require UHV conditions to keep the surface clean).

Since the first observations of molecular arrays from solutions on HOPG surface,^[228-230] the research community has invested many efforts to develop highly ordered assemblies and to investigate their properties by means of the STM technique. In this regard, the most common methodology involves the employment of alkylated compounds by taking advantage of their strong affinity for the HOPG surface. This affinity arises from the packing of the alkyl chains on the surface, in particular from the van der Waals interactions between the chains and the HOPG surface, and the interaction between the alkyl groups themselves. One of the first reported examples applying this strategy deals with the self-assembly of a tetraalkoxy phenyl porphyrin **93**, which was deposited on HOPG from a 1-phenyloctane solution and observed by STM at room temperature (Figures 45a and b).^[231] Porphyrin **93** arranges forming a lamellar array wherein four-lobed structures corresponding to single molecules are discernable. The bright lobes correspond to the phenyl groups, while in the area of dark, alkyl chains extending nearly perpendicular to the molecular rows cover the surface. This dark separation can be easily tuned in the width by changing the number of carbon atoms in the chain.

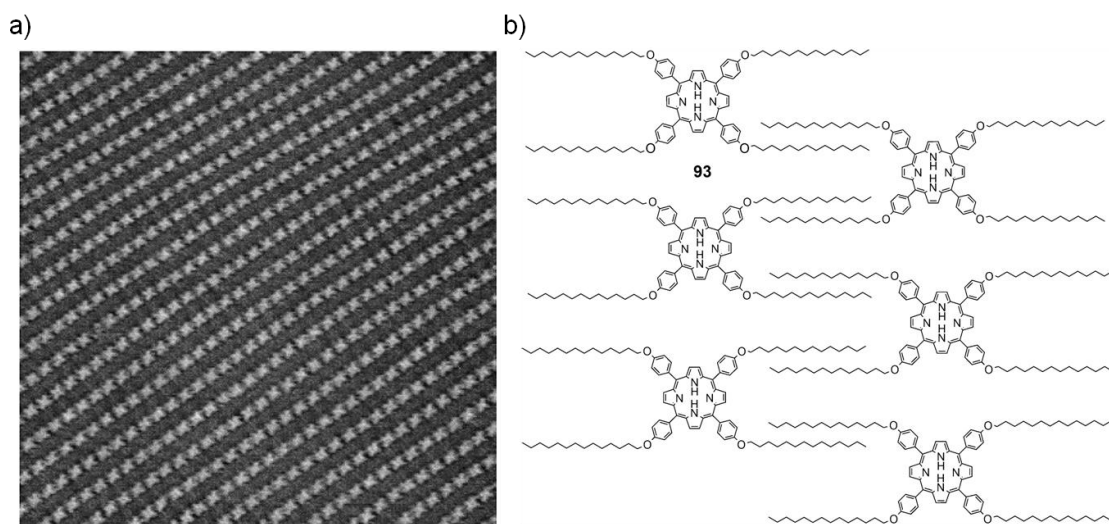


Figure 45. a) STM image of the surface array of porphyrin **93** at the 1-phenyloctane/HOPG interface ($I = 1.12$ nA, $U = 0.68$ V); b) molecular models showing the close packed mode of **93** on surface.^[231]

A similar example was described years later by *Feringa et al.*^[232] After the deposition of 0.1 mM solution of 5,10,15,20-*meso*-tetradodecylporphyrin **94** (Figure 46a) in *n*-tetradecane on HOPG, the STM analysis revealed the formation of highly ordered monolayer (ML) of **94** (Figure 46b). Even in this case, the bright lobes correspond to the macrocycle core lying flat on the substrate, while the alkyl chains are arranged in the darker area. In particular, each porphyrin in the 2D network occupied an average area of 2.2 ± 0.1 nm², which corresponded to the porphyrin

heterocycle ($\sim 0.8 \text{ nm}^2$) and two dodecyl chains ($\sim 0.7 \text{ nm}^2$ each) physisorbed on the surface. The authors then concluded that the two remaining chains were pointing away from the surface into the solution. In the same work, **94** was deposited on a metallic Au(111) surface resulting in a totally diverse arrangement (Figures 46c and d). In this case they observed a well-distributed domain of four-leaf clover, where each lobe corresponded to a pyrrole moiety of the porphyrin core. Two different packing modes were obtained (Figures 46f and g). The first mode presented all the alkylic chains aligned along the (110) axis of the Au(111) substrate. The assembly, however, is not perfect due to the alignment of some alkylic chains to the (112) axis of the Au(111) surface. The second type of packing shown in Figure 46g, featured an alternation of chains alignments between the (110) and (112) axis. Moreover, they also observed that on Au(111) surface the density of porphyrin molecules was considerably higher than that on HOPG. This was probably due to a favorable interaction between the Au substrate and the aromatic core of the porphyrin, which caused a conformational distortion of the heterocycle bringing it out of plane. This behavior also explains why on HOPG porphyrin **94** is visualized as a single bright spot, while on Au(111) as a four-lobed leaf with two brighter and two darker lobes, suggesting a distortion of the cycle caused by a coordinative interaction between the pyrrolic nitrogen atoms and the Au surface. The authors corroborated these observations with X-ray Photoelectron Spectroscopy (XPS) experiments, which indicated the presence of three types of nitrogen species in the monolayer, the pyrrolic nitrogen ($>\text{NH}$) free imininc nitrogen atoms ($-\text{C}=\text{N}-$) and coordinated imininc nitrogen atoms as well.

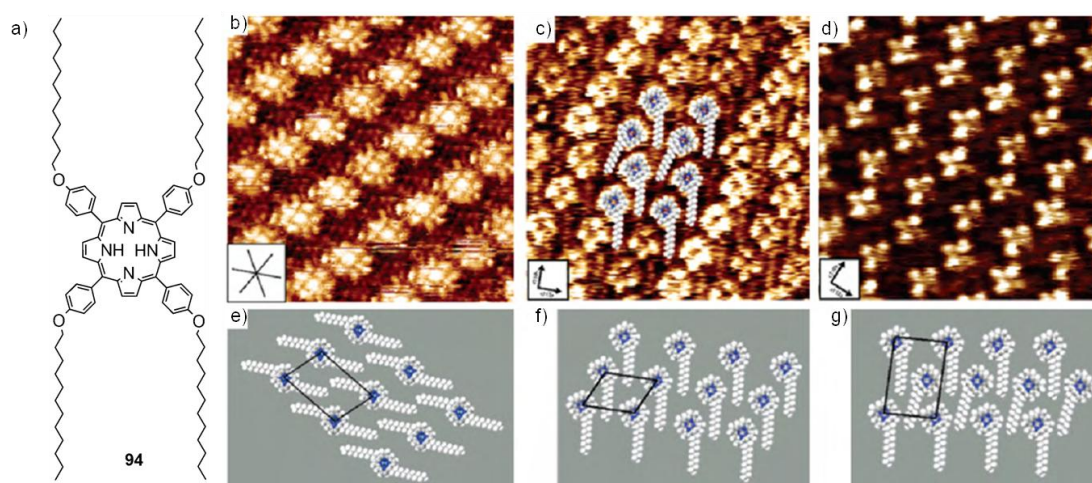


Figure 46. a) Structure of investigated porphyrin **94**; b) STM image of the self-assembly of **94** on HOPG interface. The orientations of the main axis is presented on the inset ($8.1 \times 8.1 \text{ nm}^2$, $I = 17 \text{ pA}$, $U = 0.35 \text{ V}$); c-d) STM images of the two assemblies formed by **2** on Au(111) substrate (c: $9.5 \times 9.5 \text{ nm}^2$, $I = 42 \text{ pA}$, $U = 0.57 \text{ V}$; d: $8.4 \times 8.4 \text{ nm}^2$, $I = 7 \text{ pA}$, $U = 0.58 \text{ V}$); e-g) proposed packing models for the assemblies shown in the corresponding STM images.^[232]

It is important to point out that it is possible to design surface patterns other than close-packed by incorporating sites for directional interaction into the molecular structures, such as hydrogen bonding and coordination motifs. Effects of the hydrogen bonding on the structure of surface assemblies were investigated with a series of porphyrin derivatives bearing carboxyl groups on the phenyl moieties. The deposition of tetrabenzoyloxy porphyrin derivative **95** co-adsorbed with stearic acid on HOPG at ambient conditions, gave rise to a highly ordered domain where porphyrin modules were joined together through cyclic hydrogen bonds provided by four carboxyl groups (Figures 47a and b).^[233] The disk-shaped structure of molecules **95** in Figure 47a is attributed to the porphyrin ring, and the four extending wings are attributed to the four phenyl groups. This arrangement was found to be totally different from the close packing structure obtained in the X-ray crystal of the porphyrin several years before.^[234] The crystals in fact consisted in two-dimensional sheets stacked together through hydrogen bonded carboxylic acid cyclic dimers. The

authors attributed this difference to the minimization of surface free energy in the adsorption process, considering that the surface density is higher in the tetrameric hydrogen bonding motif rather than in the sheet in the bulk crystal.

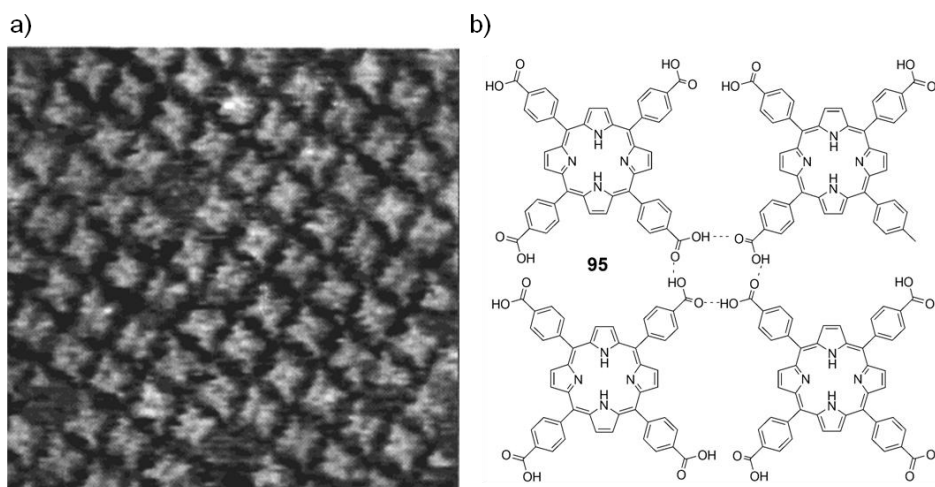


Figure 47. a) STM image of the self-assembly of **95** on the stearic acid/HOPG interface ($I = 1.089$ nA, $U = 0.85$ V); b) proposed packing model for the assemblies shown in the corresponding STM image.^[233]

3.1.1.3. Porphyrin Architectures under Ultra-High Vacuum (UHV)

In contrast to the room temperature measurements, the ultra high vacuum conditions provide extremely clean surfaces, which cannot be obtained at ambient conditions because of surface oxidations and related undesired processes. In addition, by means of UHV-STM wide temperature ranges can also be achieved, which allow experiments at very low temperatures, affording stable and high-resolution measurements. Therefore, the electronic structures of molecules and electronic processes occurring at the surface level are nowadays mostly probed *via* UHV-STM.

3.1.1.3.1. 2D Discrete Assemblies

Several discrete assemblies have been investigated by means of UHV-STM. The first was developed by Yokoyama *et al.*,^[218] who studied the spontaneous self-assembly of four different porphyrin modules **96-99** bearing cyanophenyl substituents at the *meso* positions (Figures 48 a-d) on Au(111) surface. Three types of intermolecular interactions have been invoked between the cyanophenyl groups (Figure 49): antiparallel dipolar $C\equiv N\cdots C\equiv N$ interactions (Figure 49a), a trimeric bonding which involves the cyano groups and positive polarized hydrogen atoms in the *ortho* position to the cyano group, $C\equiv N\cdots H-C_{ortho}$ (Figure 49b) and a H-bonding type interaction between the cyano groups and a hydrogen atom linked to a sp^2 carbon of the phenyl moiety (Figure 49c).

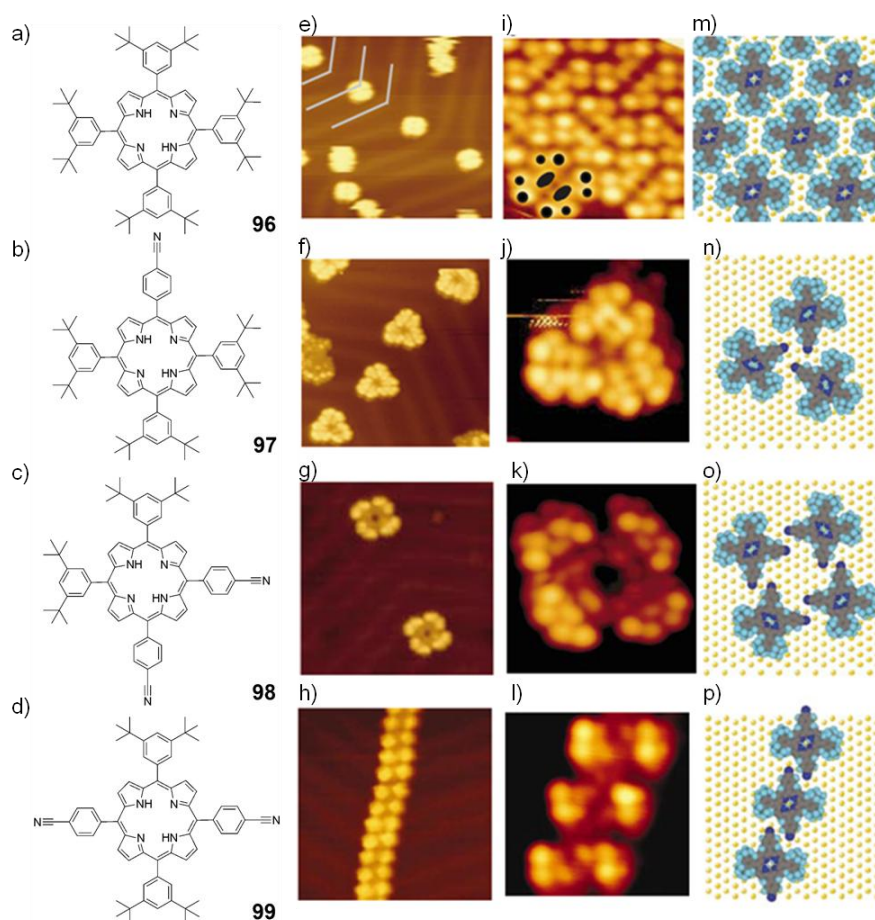


Figure 48. a-d) Molecular structures of the porphyrins investigated by Yokoyama *et al.*; e-h) STM images ($20 \times 20 \text{ nm}^2$) taken at 63 K of the supramolecular assemblies formed by the corresponding porphyrin **96-99** on Au(111). The herringbone patterns of Au(111) are displayed in (e); i-l) high-resolution STM images ($5.3 \times 5.3 \text{ nm}^2$) of the same porphyrin assemblies; m-p) molecular models of the observed assemblies.^[218]

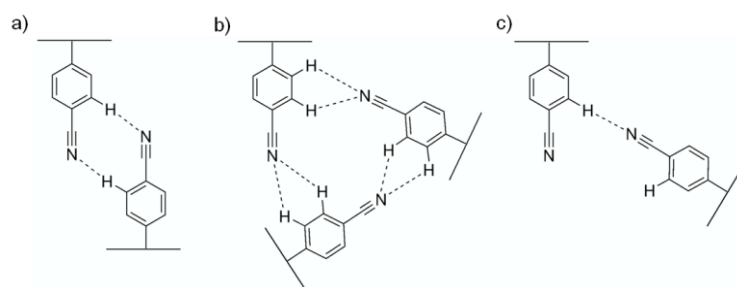


Figure 49. Interactions of cyanophenyl groups described by Yokoyama *et al.* a) antiparallel dipole-dipole; b) trimeric bonding; c) hydrogen-bond type association.

Porphyrin **96**, which does not bear any cyanophenyl groups, did not aggregate at low coverage (Figure 48e), however, upon further deposition, a close-packed arrangement of **96** molecules could be observed (Figures 48i and m). Porphyrin **97**, with a single cyanophenyl group formed trimers upon deposition onto the Au surface (Figures 48f, j and n). These structures were obtained due to the cyclic configuration assumed by the cyanophenyl groups' trimeric bonding interactions. In order to probe the system further, two other porphyrins were synthesized bearing two cyanophenyl substituents: *cis*-like and *trans*-like isomers **98** and **99**, respectively. Molecule **98** formed a supramolecular tetramer on the surface (Figures 48g, k and o), guided by the antiparallel dipolar interactions of the adjacent cyano groups. In contrast with this, *trans*-like isomer **99** formed supramolecular wires with lengths over 100

nm (Figures 48h, l and p). In all these assemblies, the Au(111) surface did not only act as a substrate, but also interacted with the porphyrins guiding the initiation positions of the discrete assemblies and supramolecular wires; the Au surface is characterized, in fact, by ‘herringbone’ patterns (see the reconstructed pattern shown in Figure 48e), and in all cases, the porphyrins were mainly located at the apices of the pattern since these are ideal nucleation points.

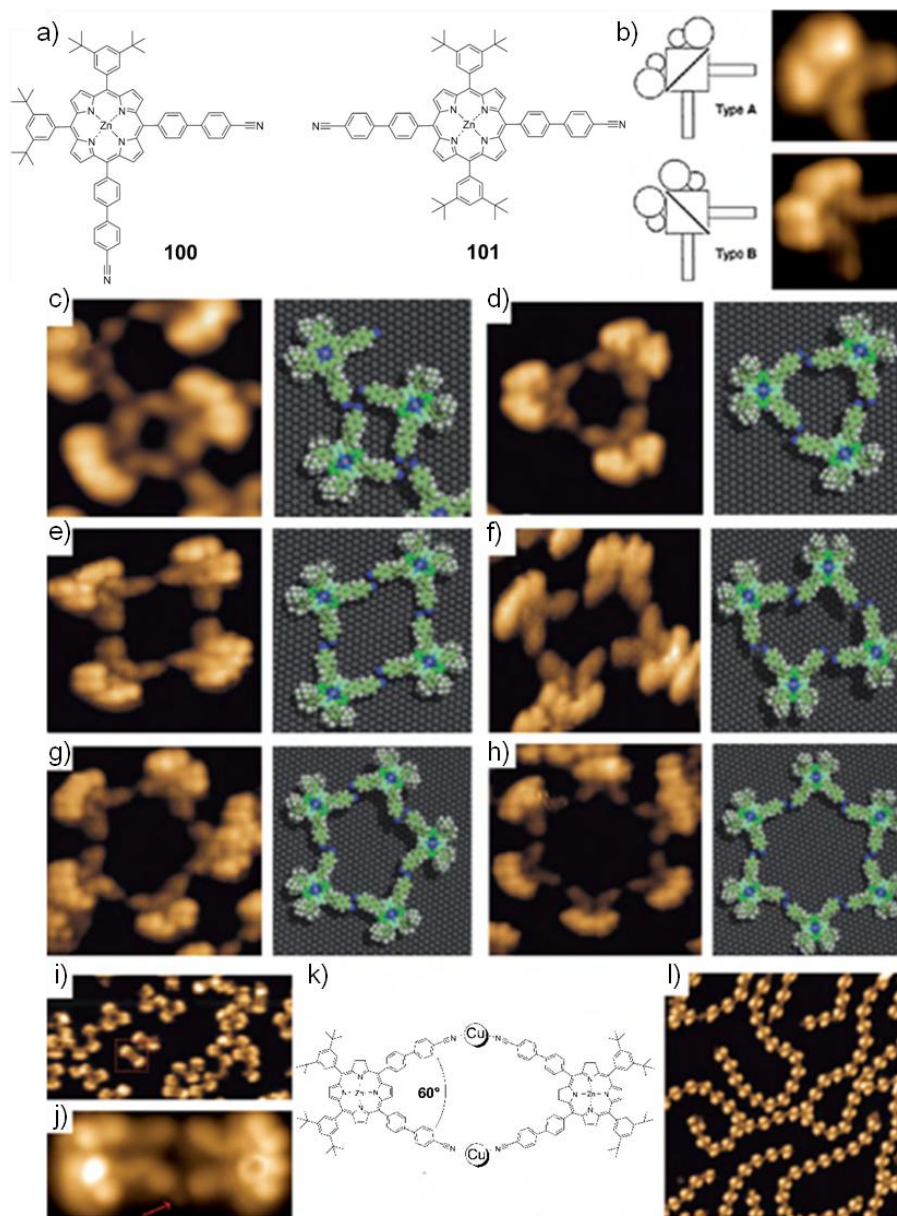


Figure 50. a) Molecular structures of the porphyrins **100** and **101** investigated by *Diederich et al*; b) schematic models representing the conformational isomers, type A and type B; c-h) STM images with the corresponding molecular models of the various assemblies (c: dimers $5.0 \times 5.0 \text{ nm}^2$; d: all type A trimer $6.3 \times 6.3 \text{ nm}^2$; e: mixed type tetramer $6.4 \times 6.4 \text{ nm}^2$; f: all type B tetramer $6.2 \times 6.2 \text{ nm}^2$; g: pentamer $7.6 \times 7.6 \text{ nm}^2$; h: hexamers $8.2 \times 8.2 \text{ nm}^2$); i) STM image of a submonolayer of **100** on Cu(111) annealed at 150°C ($50 \times 26 \text{ nm}^2$); j) zoom of the STM image in (i) showing the dimer of **100** ($5.5 \times 2.5 \text{ nm}^2$); k) proposed model for the dimer showing the 4'-cyanobiphenyl groups bending together, enabling the Cu adatoms coordination; l) STM image of the long polymeric chains formed after the deposition of **101** on Cu(111) ($50 \times 50 \text{ nm}^2$).^[235]

Contemporary to our investigations, *Diederich* and co-workers expanded the work of *Yokoyama* reporting the self-assembly of two bis-cyanobiphenyl porphyrin derivatives (bearing two 4'-cyanobiphenyl and two 3,5-di(*tert*-butyl)phenyl substituents in *cis*-like **100** and *trans*-like **101** configurations, respectively, Figure 50a) on a Cu(111)

surface under UHV conditions.^[235] Surprisingly, the *cis*-like isomer gave rise on the surface to various discrete supramolecular assemblies formed by single oligomers, ranging from dimers to hexamers (Figures 50 c-h). This large variety of assemblies has been attributed to two facts: *i*) the presence of contributions other than dipolar bonding interactions which guide the formation of other favorable geometries and *ii*) Cu(111) surface has a stronger interaction with large aromatic systems in comparison to Au(111). The porphyrins adsorbed on Au surface tend, in fact, to align to principle directions of the substrate, altering the balance in strength between the adsorbate–adsorbate and adsorbate–substrate interactions. Despite the large variety of the observed architectures, the most common assemblies were trimers and tetramers. In the trimeric species (Figure 50d), each of the three porphyrins has its central axis rotated of 120° with respect to the next, and thus each one is favorably aligned to the principle directions of the Cu(111) surface. As no bending of the cyanobiphenyl moieties is apparent in the STM images and the structural alignment between neighboring cyano groups is estimated at an angle of 150°, the interaction involved is a hybrid between antiparallel dipolar and hydrogen-bonding. Beside the trimers, the authors observed two types of tetramers (Figures 50e and f) due to the fact that porphyrins form conformational enantiomers upon deposition on surfaces. Specifically, the *meso*-phenyl substituents are rotated away from their preferred perpendicular orientation relative to the porphyrin core, causing a saddle shape of the porphyrin core with two opposing pyrrole rings pointing upwards, and the other two pointing downwards. This can occur in two axes (Figure 50b), leading to type A and type B. One of the tetramers is formed by two type A and two type B porphyrins (Figure 48e). The interactions of the CN groups in this case are at 180°, the optimal angle for antiparallel dipolar interactions, and furthermore, all the porphyrins are aligned with the Cu(111) surface axes. In the second type of tetramer (Figure 50f), the porphyrins are all of the B type, and in order to maintain their alignment on the Cu substrate's axes, the 4'-cyanobiphenyl substituents bend (inwards in two of the porphyrins and outwards in the other two) to be able to interact intermolecularly. Going a step forward in complexity, the deposition of these porphyrin derivatives on Cu(111) also gave rise to pentamers (Figure 50g), but very rarely because the formation does not correctly fit the Cu(111) lattice. Hexameric structures due to the large cavities are generally less favored and very infrequently observed (Figure 50h). The most interesting result obtained with porphyrin **100** was related to the dimer formation. The bonding interaction for the dimer was expected to be similar to that of the trimeric arrangement, where the CN group of one porphyrin would interact with the phenyl hydrogen atoms of the neighboring porphyrin macrocycle. In this way, in fact, the arrangement would conform to the geometry of molecule **100** (Figure 50c). However, the annealing of the surface above 150 °C, led to the formation of another dimeric system characterized by a distortion of the 4'-cyanobiphenyl substituents, closing to approximately 60° (Figures 50 i-k). This extreme distortion was probably caused, firstly, by the aforementioned Cu-substrate-induced saddle shape of the tetrapyrrolic core permitting the *meso*-substituents to move laterally, an effect that is even more pronounced at elevated temperatures; and secondly, and more significantly, the elevated temperatures allow for the mobilization of Cu adatoms from the Cu step edges making them available for the coordination of two cyano groups, and hence the formation of dimers. The number of such dimers increased further upon heating to 200 °C. Lastly, in the case of *trans*-enantiomer, **101**, the deposition on the Cu(111) surface at low coverage gave rise to linear chains formed by the antiparallel dipolar interactions of the cyanophenyl moieties (Figure 50l).

Similar geometrical assemblies were observed by Yokoyama *et al.* upon deposition of carboxyphenyl substituted porphyrins on Au(111) surface, investigated by means of UHV-STM.^[236] The H-bonding interactions between the carboxyphenyl substituents were responsible of the formation of surface-supported supramolecular clusters or wires of porphyrins. Specifically, they reported the investigation of three porphyrin derivatives, a mono-substituted carboxyphenyl porphyrin **102** and two disubstituted carboxyphenyl porphyrins, in a *cis*-like, **103**, and in *trans*-like, **104**, orientations (Figure 51). The monocarboxylic acid derivative appeared chiral upon adsorption on the surface.

This chirality arose, according to the authors, from the twist angle between the macrocycle plane and the phenyl plane, which upon deposition reduces to $\sim 20^\circ$ from the values of 60° or 90° in the ground state conformations. Due to this angle variation, steric repulsion between the hydrogen atoms in β position of the pyrrole and the phenyl *ortho* hydrogen atoms caused the chiral saddle-like distortion of the porphyrin ring. The chirality aspect of the porphyrin molecules can be easily distinguished from high-resolution STM images, wherein the appearance of a dark line across the core is clearly discernable (Figure 51a). Hence, module **102** formed dimer units on Au through the formation of optimal coplanar H-bonds between the carboxylic acid groups (Figure 51a). The chirality issue also emerged upon sublimation of the *trans*-isomer **104** (Figure 51b). **104**, in fact, formed wire-like structures, where the orientation of the macrocycle distortion alternates along the one-dimensional assembly in order to maintain the coplanarity of the carboxylic H-bonds. As in the previously described example reported by *Diederich et al.*, the *cis*-like isomer derivative **103** formed tetrameric aggregates (Figure 51c). The assemblies were obtained due to optimal coplanarity of the H-bonds within the tetramer. The high resolution STM of Figure 51c revealed the formation of two different tetrameric assemblies, containing a diverse alternation of the chiral isomers.

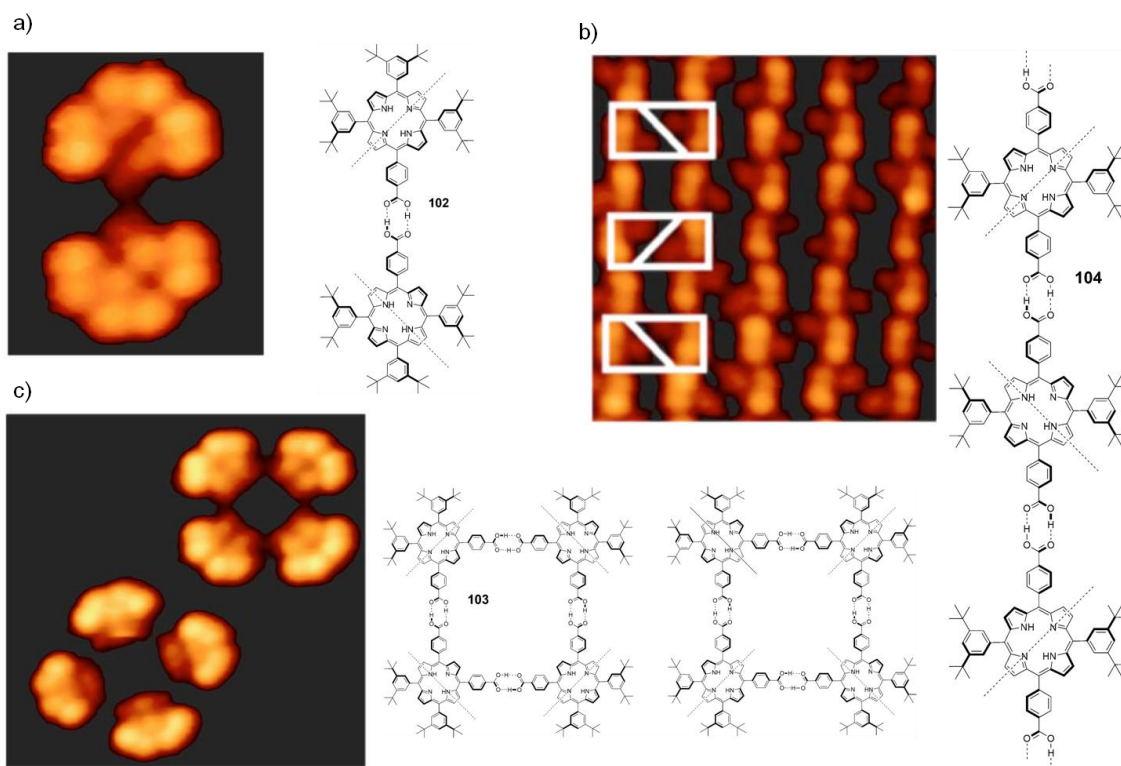


Figure 51. a) STM image of a dimer of **102** on Au(111) surface formed *via* coplanar H-bonds with corresponding schematic model; b) H-bonding driven chains of **103** on Au(111) with corresponding schematic model; c) STM image of tetramers formed upon deposition of **104** on Au(111). There are two conformational isomers with regards to distortion as displayed in the corresponding schematic models.^[236]

3.1.1.3.2. Infinite 2D Porous Networks

As an extension of a precedent work, *Wintjes et al.* recently reported a systematic study on the influence of different alkoxyphenyl substituents on the porosity of porphyrin-based assemblies on Cu(111) under UHV conditions.^[217] They investigated the self-organization of three different porphyrin derivatives, **105-107**, (Figure 52). Each porphyrin features two 4-cyanophenyl substituents in opposing *meso*-positions of the porphyrin core; the remaining *meso*-substituents bear various types of alkoxyphenyl substituents. The variation of the alkoxyphenyl

moieties controls the dimensionality of the resultant porous networks, altering the pore-to-pore distance in each assembly (3.09 ± 0.2 nm, 3.35 ± 0.12 nm and 4.80 ± 0.14 nm for assemblies of **105**, **106** and **107** respectively). Despite the changes in the pore-to-pore distances, the dimensions of individual pores remained unchanged in all the assemblies. At coverage below 0.8 ML, only porphyrin **105** self-assembled into a nanoporous hexagonal network (Figure 52a), whereas porphyrins **106** and **107** formed long chains with branching at random intervals. At higher coverage, as shown in Figures 52b and c, porphyrins **106** and **107** also assembled into 2D porous networks. The arrays of porphyrins **105** and **106** (Figures 52a and b) consisted of dimeric and trimeric supramolecular modules produced *via* dipolar interactions of two or three cyanophenyl groups, as previously described, while porphyrin **107**, bearing the isopentyloxy substituents assembled through a different trimeric asymmetric non-covalent motif (Figure 52c). One of two cyanophenyl groups of adjacent porphyrins formed a $C\equiv N \cdots H-C$ hydrogen-bond with the *ortho*-polarized C-H residue belonging to the phenyl bearing two electronegative alkoxy groups in a third neighboring porphyrin.

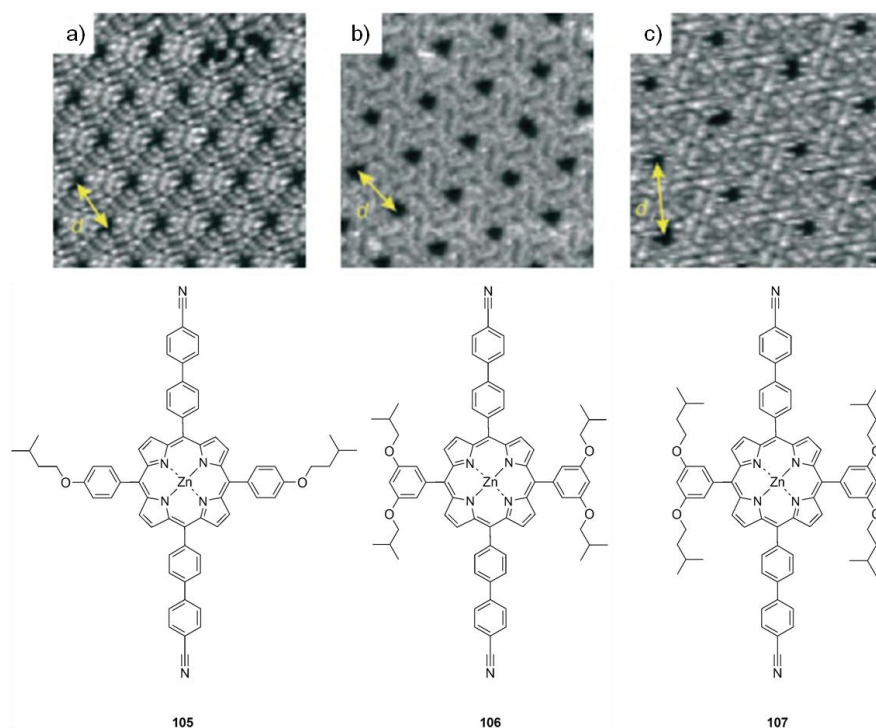


Figure 52. a-c) STM images of nanoporous networks, exhibiting different pore-to-pore distances, formed by the corresponding porphyrin **105-107** on Cu(111) under UHV (a: $I = 24$ pA, $U = -1.3$ V; b: $I = 20$ pA, $U = -1.5$ V; c: $I = 17$ pA, $U = -0.4$ V).^[217]

These porous domains formed *via* the self-assembly of organic components are of particular interest also in view of future applications. They are in fact capable of recognizing^[237, 238] and hosting molecular guests. C_{60} , having the appropriate geometry, has been one of the first guest organic molecules that has been introduced within 2D porous networks.^[168, 214, 239]

Following this trend, with the aim of exploiting 2D porous networks to host suitable organic molecules, *Spillmann et al.* studied the surface arrays formed by a *trans*-dicyanophenyl porphyrin, **108**, deposited on Ag(111) under UHV conditions (Figures 53a and b).^[214] Some years before this study, the same group reported the formation of ordered porphyrin patterns on Ag(100) where C_{60} molecule were co-deposited. They demonstrated that fullerenes were accommodating onto the porphyrin ML, specifically onto the cyano substituents, in well organized manners.^[168] In the present work, the deposition of **108** on Ag(111) yielded a highly ordered porous domain. The primary driving

forces for the formation of the porous networks were the previously described interactions between the cyanophenyl moieties (Figure 49): dipole-dipole and van der Waals. Figure 53c shows porous networks composed by trimeric units with a central cavity diameter of about 1.2 nm. In addition to the intermolecular interactions discussed above, the Ag(111) substrate is thought to play a role in the formation of the hexagonal pores since the cyano functional groups can act as donating ligands coordinating to Ag ions, a well-known and strong interaction. Following the formation of the cavities in this self-assembly, C_{60} guests were introduced in different concentrations. Fullerenes appeared to be spherical bright spots on the surface, mainly hosted at the pore sites (Figure 53d). They were also mobile, hopping from pore to pore at a rate of 10^{-3} s^{-1} at room temperature. Gradually increasing the coverage of C_{60} led to formation of supramolecular islands of guests, including linear hosted fullerene chains at 0.02 ML, branched chains and large islands at 0.07 ML (as displayed in Figure 53d), saturation of all the pores at 0.1 ML and finally the irreversible collapse of the 2D porous network of porphyrin at monolayer coverage greater than 0.1 ML. These changes were also accompanied by a gradual reduction in the mobility of the guest molecules.

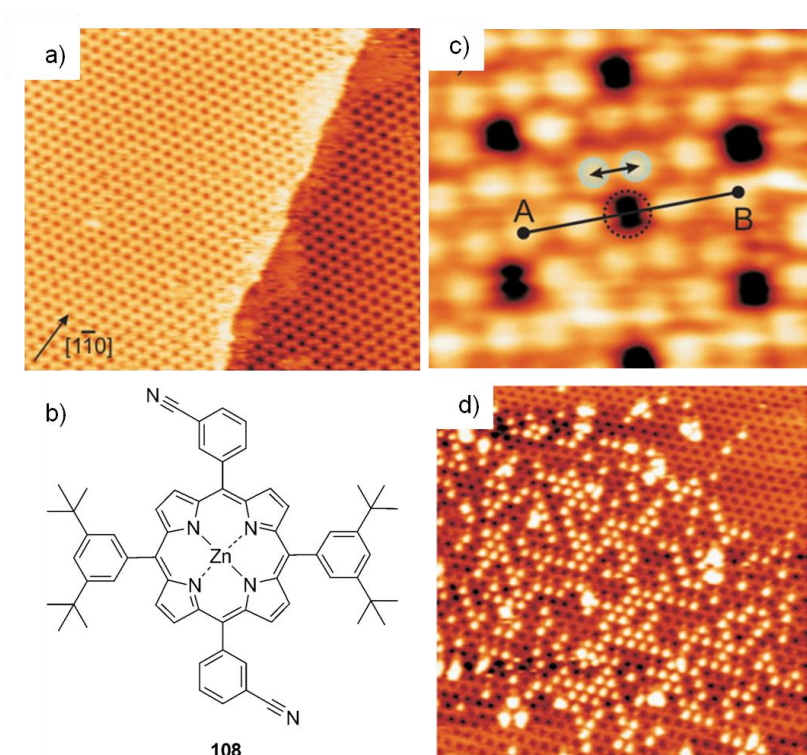


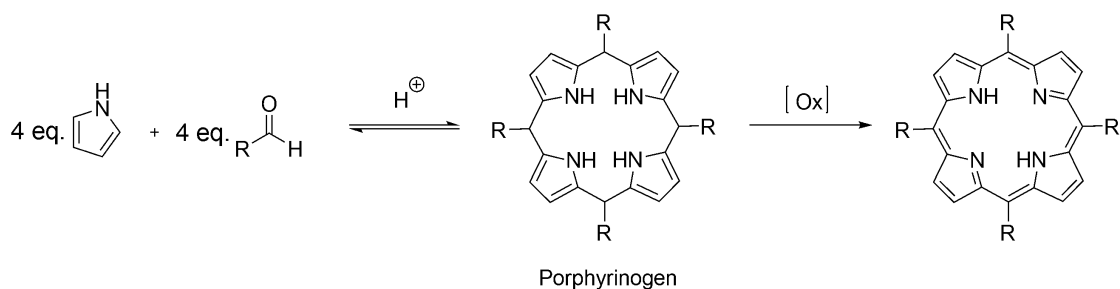
Figure 53. a) STM images of nanoporous networks formed upon UHV deposition of module **108** on Ag(111) ($I = 15 \text{ pA}$, $U = 3 \text{ V}$); b) structure of porphyrin **108**; c) detailed STM image exhibiting the size of the pore ($I = 25 \text{ pA}$, $U = 2.9 \text{ V}$); d) STM image obtained after sublimation of 0.07 MLs of C_{60} ($I = 9 \text{ pA}$, $U = 3 \text{ V}$).^[214]

3.1.2. Synthesis of Porphyrin Scaffolds for Engineering Nanostructured Surfaces

The derivatives investigated in this work include symmetrically and unsymmetrically substituted porphyrins. Symmetrically substituted pyridyl porphyrins were synthesized to form infinite supramolecular porous arrays on surfaces, characterized by means of STM technique. Unsymmetric porphyrins were instead synthesized for a double goal: to produce discrete assemblies on metallic surfaces, and to explore their interactions once covalently grafted on DWCNTs.

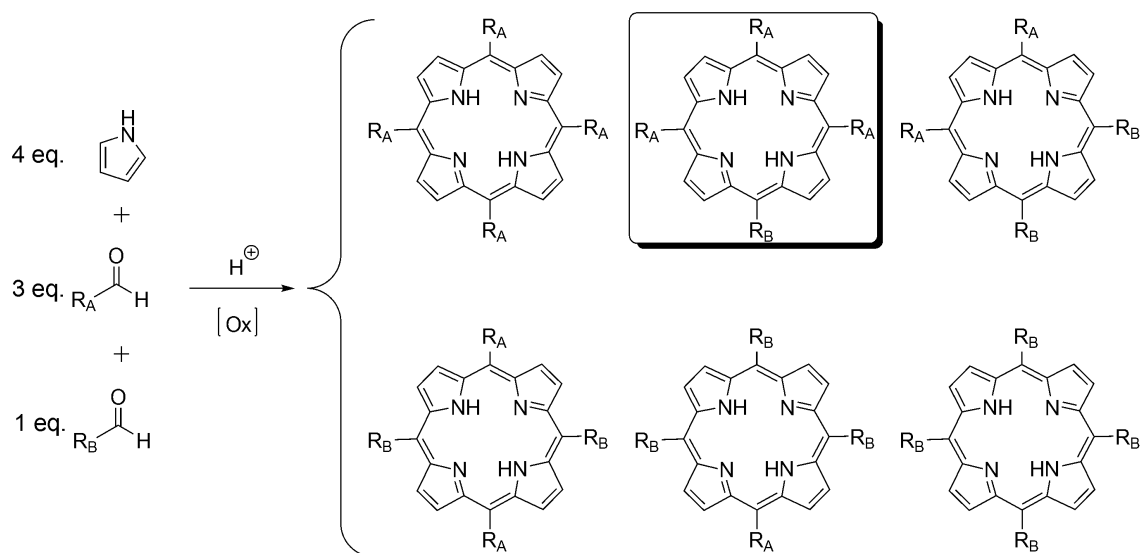
Chapter 3

Synthetically speaking, symmetrical porphyrins are accessible by two main methodologies. An easy pathway, originally developed by *Adler and Longo*, takes into account the acid-catalyzed condensation reaction of pyrrole with the suitable aldehyde at around 140 °C, followed by air-oxidation of the following porphyrinogen (Scheme 20).^[240] This method, applied for the first time in the early 60's, was a practical version of the sealed-bomb method of *Rothemund* developed in the 1940's.^[241-243] Despite the modest yields, the simplicity of this approach allows the synthesis of symmetrical porphyrins at large scale. A very powerful modification of this protocol has been achieved several years later by the *Lindsey's* methodology.^[244, 245] This approach applied milder reaction conditions reaching higher reaction yields.^[246] Diverse variations of this protocol allowing higher reactant concentration conditions were also developed by the same group, in subsequent years.^[247]



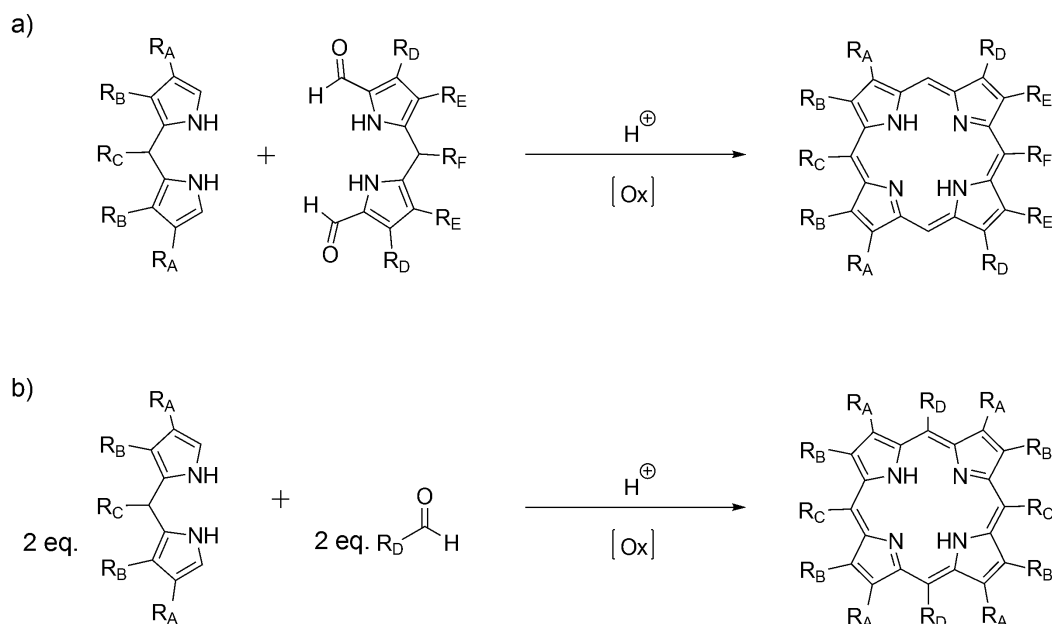
Scheme 20. Synthetic pathway towards symmetrical porphyrins, developed by *Rothemund and Menotti*.^[241-243]

The synthesis of unsymmetrically substituted porphyrins is by far considered more delicate than the corresponding tetrasubstituted porphyrins and in general it can be achieved following two strategies.^[248] The first method to prepare unsymmetrically substituted porphyrins involves the mixed aldehyde condensation reaction protocol. This procedure, firstly reported by *Lindsey*, involves the reaction of two different aldehydes and the pyrrole leading to a statistical mixture of products (Scheme 21).^[249] The desired porphyrin can be then isolated by extensive chromatography.



Scheme 21. Synthetic pathway towards asymmetrically substituted porphyrins using the mixed condensation procedure developed by *Lindsey et al.*^[249]

The alternative route towards unsymmetric porphyrins employs dipyrrolic starting materials, which are opportunely combined to form the tetrapyrrolic macrocycle. These are defined [2 + 2] condensation reactions and were firstly reported in early 60's by *MacDonald* and coworkers.^[250] Over the years they were improved by several research groups (Scheme 22a).^[251] They were promoted by acidic catalysis followed by an oxidation through air exposure to afford the desired specie. A similar approach involves the acid catalyzed condensation of free dipyrromethanes with aldehydes to form porphyrinogens, which are then chemically oxidized to give porphyrins (Scheme 22b). Porphyrins are also produced through a [3 + 1] condensation, in which tripyrrolic species are condensed with 2,5-diformylpyrroles to form a cyclic tetrapyrrole.^[251] The dipyrrolic-based methodology is considerably more versatile to prepare unsymmetrically substituted porphyrins, in particular to build multiporphyrin arrays. However it presents several drawbacks, such as the time and the resources required to synthesize the dipyrromethane precursors whose purification is not always straightforward. For these reasons in this work we opted for the mixed condensation route following the procedures reported by *Lindsey's* research group.



Scheme 22. a) Examples of synthetic pathways towards unsymmetrically substituted porphyrins using the dipyrrolic condensation methodologies. a) [2 + 2] Condensations of dipyrromethanes according to the *MacDonald* method; b) [2 + 2] condensations of dipyrromethanes with aldehydes.^[250, 251]

3.1.2.1. AB_3 Mono- and A_2B_2 Bis-functionalized Pyridyl-Porphyrins

The unsymmetrically substituted porphyrin derivatives considered in this section are depicted in Figure 54. These were employed to study the self-assembly processes on copper, Cu(111), and silver, Ag(111) surfaces, by means of UHV-STM (section 3.1.4). The three porphyrin modules investigated in this work are based on a tetrapyrrolic core differently substituted at the four *meso*-positions: porphyrin **109** features three 3,5-di-*tert*butyl substituents and one phen-1,4-diyl-ethynyl-pyridyl functions, and was used as main reference compound. Porphyrins **110** and **111**, instead, bear two 3,5-di-*tert*butyl and two phen-1,4-diyl-ethynyl-pyridyl substituents at the 5,10 (*cis*-like) and 5,15 (*trans*-like) positions, respectively.

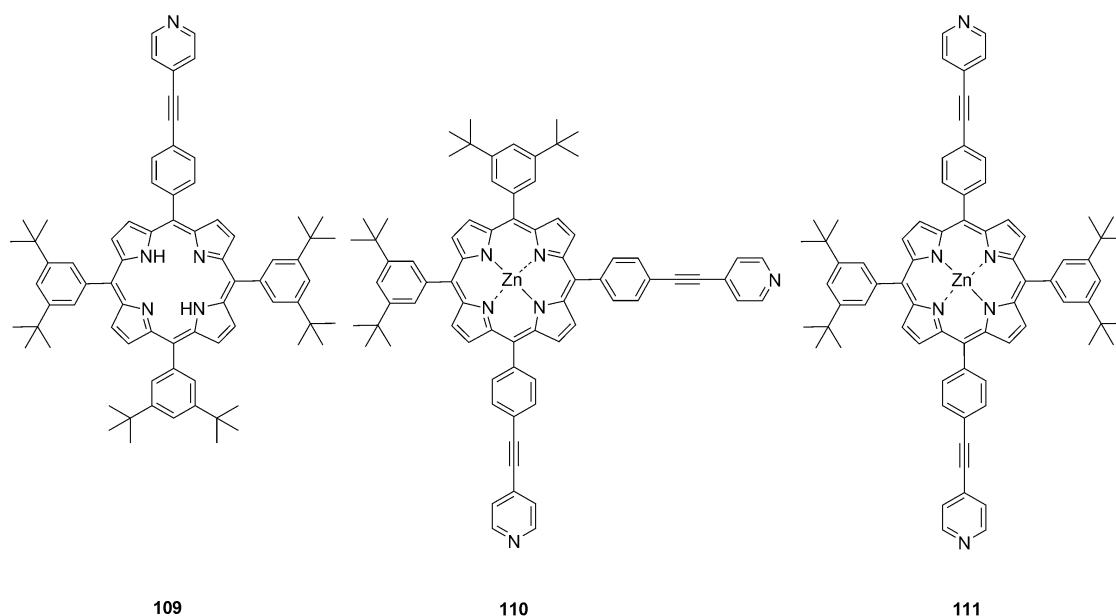
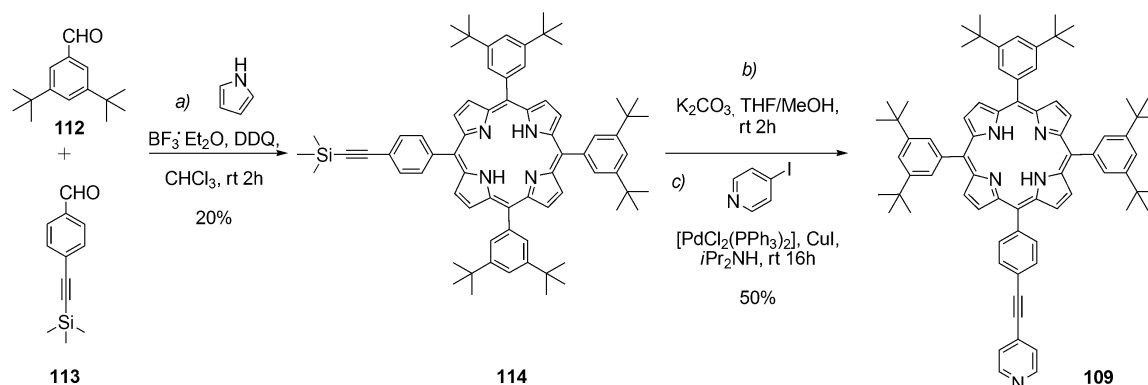


Figure 54. Unsymmetrically substituted pyridyl-porphyrins **109–111** investigated in this thesis.

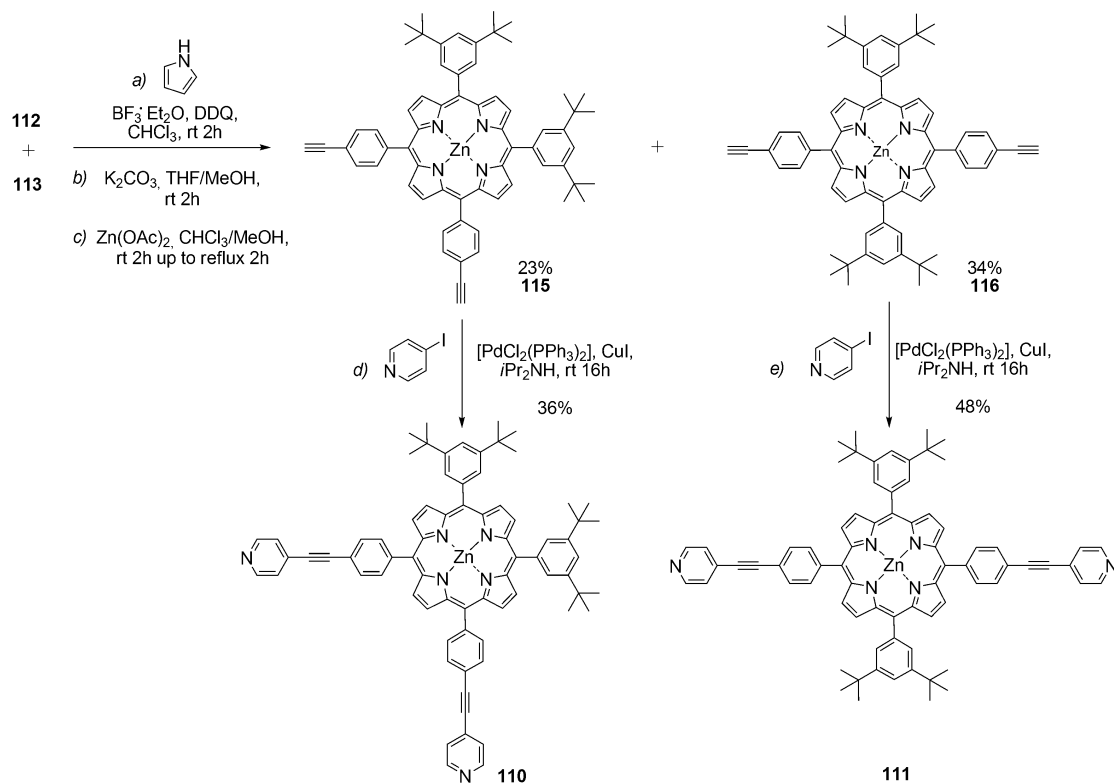
The synthesis of the mono-substituted porphyrin **109** is depicted in Scheme 23. The pathway which involves three steps commences with the statistical macrocyclization of pyrrole in the presence of 3,5-bis-*t*-butylbenzaldehyde, **112**, and 4-[(trimethylsilyl)ethynyl] benzaldehyde, **113**, in a 3:1 ratio and catalyzed by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in CHCl_3 . The porphyrinogen formed was then oxidized *in situ* by DDQ, affording desired porphyrin **114** in 20% yield (Scheme 23, path *a*). The latter was then deprotected of the TMS group under mild basic conditions (Scheme 23, path *b*). The so formed free terminal alkyne porphyrin was immediately reacted using a *Sonogashira*-type cross-coupling reaction^[107] with 4-iodopyridine in the presence of catalytic amounts of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI in $i\text{Pr}_2\text{NH}$ affording targeted porphyrin **109** in a good overall yield of 50 % (Scheme 23, path *c*).



Scheme 23. Synthetic pathway towards mono-substituted pyridyl porphyrin **109**.

In parallel the synthesis of the two disubstituted pyridyl-porphyrin modules **110** and **111** bearing two pyridyl groups at the 5,10 (*cis*-like) and 5,15 (*trans*-like) positions, respectively, was carried out (Scheme 24). In this case, following a procedure that was adapted from the literature,^[252] the statistical condensation by means of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and DDQ between **112** and **113** in a 1:1 ratio with four equivalents of pyrrole, gave rise to an isomeric mixture of disubstituted porphyrins. These were not immediately separated, but subjected to a metalation reaction with $\text{Zn}(\text{OAc})_2$ in a mixture of THF and MeOH (Scheme 24, path *a*), followed by the removal of the TMS group in basic

media (Scheme 24, path *b*). The isomeric combination of porphyrin derivatives **115** and **116** were finally isolated by extensive column chromatography (Scheme 24, path *c*). Subsequently, **115** and **116** were reacted separately with 4-iodopyridine under *Sonogashira*-type reaction conditions^[107] producing targeted molecules **110** and **111** in 36% and 48% yield respectively (Scheme 24, paths *d* and *e*).



Scheme 24. Synthetic pathways towards disubstituted pyridyl porphyrin **110** and **111**.

3.1.2.2. *A₄ Tetra-functionalized Pyridyl-Porphyrins*

In view of organizing infinite 2D porous networks exploiting the metal-ligand coordinative interaction driven by the presence of the pyridyl groups on metallic surfaces, we addressed the synthesis of tetrasubstituted Zn-porphyrins bearing at each *meso* position identical pyridyl-based moieties. The three porphyrins studied in this thesis are reported in Figure 55. With the interest of forming ordered arrays, linear and rigid moieties were chosen as *meso*-substituents. Porphyrin **117** features four ethynylpyridyl “legs” connected to the macrocycle *meso* positions. Four phenylethynylpyridyl functions decorate the *meso* carbon atoms of porphyrins **118**, while four (2,5-dimethylphenyl)ethynylpyridyl moieties were inserted into porphyrin **119**.

The diverse substitution on these molecules was designed with different goals. On one side the idea was to exploit the flatness of the tetrapyrrolic cycle and of its substituents to form very well ordered assemblies on the surfaces with porous of constant sizes and shapes. The structural features of tetrapyrrolic porphyrin **117** perfectly match this first objective, as also demonstrated by the flat model obtained after a geometry optimization performed with PM3 semiempirical calculations as implemented in the Mopac2009³ molecular modeling package (Figure 56a). The modeled geometry displayed that the porphyrin should adopt a fully planar arrangement with the ethynylpyridyl moieties lying on the same plane of the macrocycle.

³ MOPAC2009, James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, [HTTP://OpenMOPAC.net](http://OpenMOPAC.net) (2008).

In parallel, with porphyrins **118** and **119** the effect induced by the phenyl and the 2,5-dimethylphenyl groups was addressed in view of the formation of infinite surfaces assemblies. In general, the conformations of the “legs” are determined by two angles (θ and ϕ). The angle θ describes the rotation of a *meso* substituent, in our case the phenyl group, around the C-C bond connecting it to the porphyrin core, while the angle ϕ indicates the bending of the same C-C bond out of the macrocycle plane.^[253] To some extent these angles depend on the steric repulsion between hydrogen atoms of the ring and of the macrocycle.

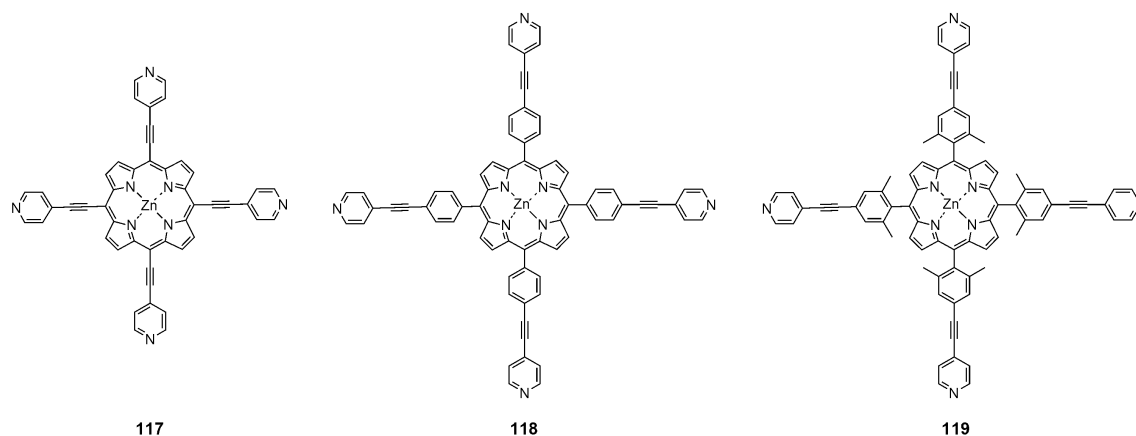


Figure 55. Symmetrically tetrasubstituted pyridyl-porphyrins **117-119** investigated in this thesis.

Relatively to our investigations, the presence of a phenyl ring directly linked to the *meso* position of the core contributes to the formation of a dihedral angle θ with macrocycle plane.^[253] To visualize θ , Figure 55b reports the modeled geometry of porphyrin **118** (PM3 method). Similarly to this case, the bulkier 2,5-dimethylphenyl groups of porphyrin **119** should adopt an out-of-the-plane conformation due to steric repulsion between the methyl groups and the hydrogen atoms on the pyrrole β -positions. Indeed, this situation was obtained after the geometry optimization run on module **119** as displayed in Figure 56c.

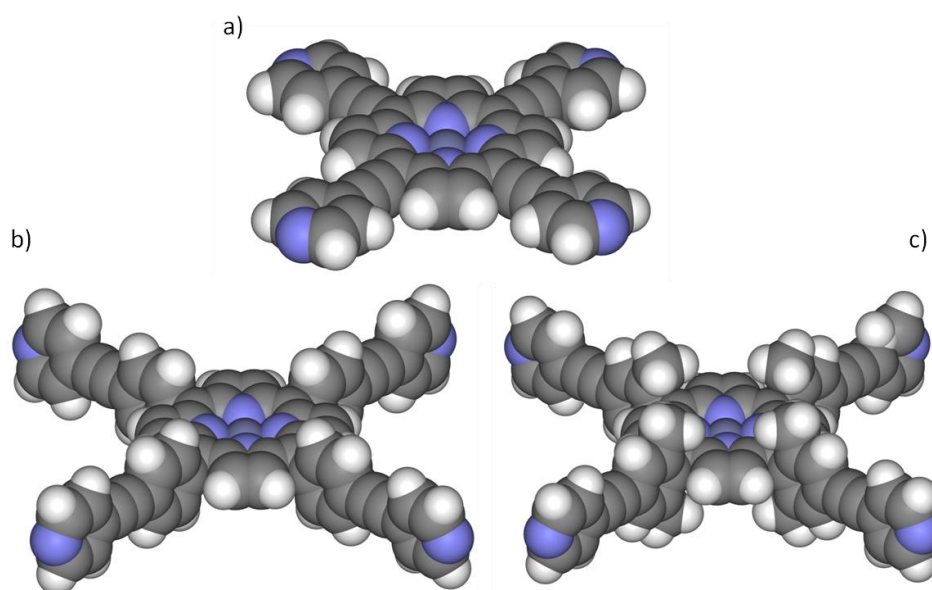
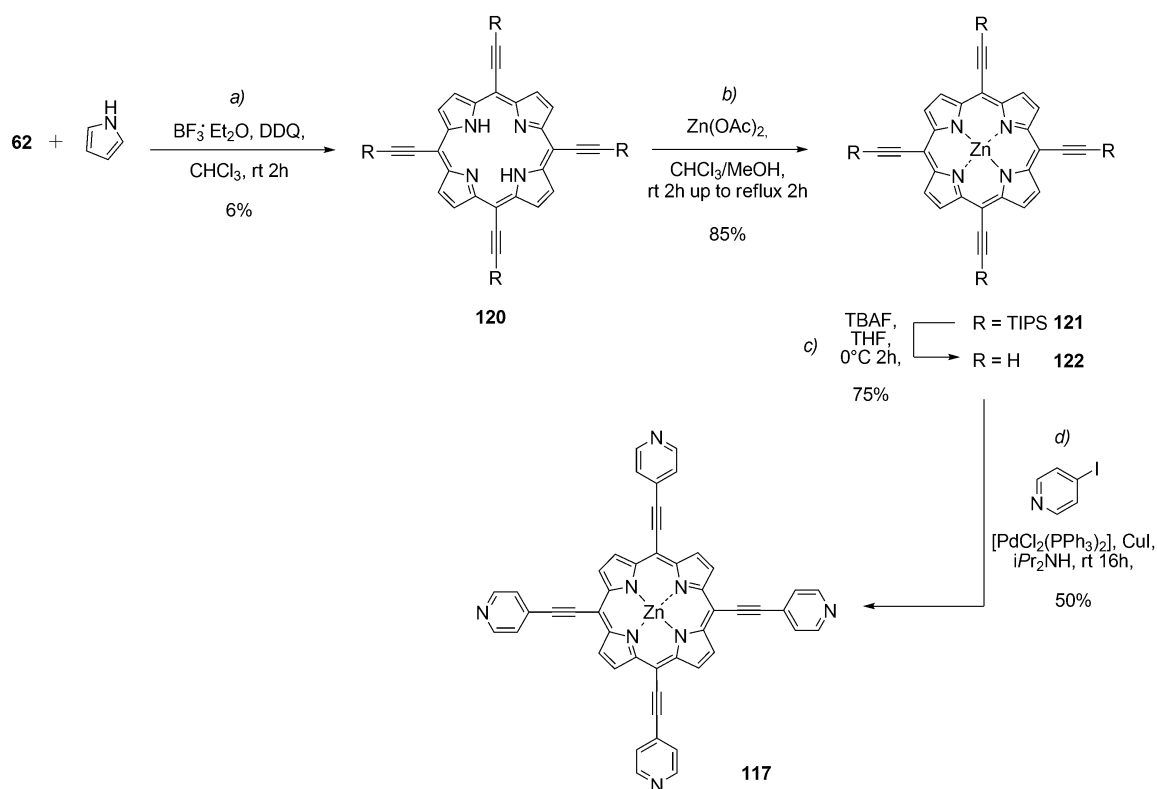


Figure 56. Predicted geometries for tetrasubstituted pyridyl-porphyrins a) **117**, b) **118** and c) **119**, investigated in this thesis. Geometries were optimized by means of semiempirical PM3 calculations as implemented in Mopac2009.³

3.1.2.2.1. Synthesis of A₄ Tetra-Functionalized Pyridyl-Porphyrin **117**

As described before, we opted for the mixed condensation methodology as the synthetic protocol to prepare the porphyrin core. Therefore, in the synthesis of porphyrin module **117**, the statistical macrocyclization of four equivalents of pyrrole and TIPS-protected 2-propionic aldehyde **62** (Scheme 11, section 2.3.2) gave rise in poor yield to intermediate **120** (Scheme 25, path a).^[254] The low yield obtained in this step is due to the considerably low solubility of porphyrin **120** in most of the common organic solvents. In the successive step porphyrin **120** was reacted with Zn(OAc)₂ in a mixture of CHCl₃ and MeOH, affording Zn-porphyrin **121** with 85% yield (Scheme 25, path b). After the cleavage of the triisopropyl silyl group, performed by means of TBAF in anhydrous THF (Scheme 25, path c), free ethynyl porphyrin **122** was cross-coupled four times with 4-iodopyridine under a slightly modified *Sonogashira* protocol.^[107] Tetrasubstituted pyridyl porphyrin **117** was, thus, formed in very good yield, 50% (Scheme 25, path d). However, final molecule **117** was found to be insoluble in organic solvents. The addition of pyridine drops to a solution of **117** in CH₂Cl₂ favored its solubilization allowing the ¹H-NMR, IR and UV-Vis characterizations (Chapter 4). On the other hand, the improved solubility of the molecule in organic solvents was not enough for its ¹³C-NMR analysis. In Figure 57 the ¹H-NMR spectrum of about 10 mg of **117** solubilized in deuterated pyridine supports the chemical structure of the porphyrin showing only three peaks (δ: 9.92, 8.97 and 7.97 ppm) due to the O_h space group symmetry of the molecule. The low intensities of the peaks account for the poor solubility of the porphyrin in the chosen solvent. Further confirmation for the structure of molecule **117** came from the MALDI-HRMS analysis (Figure 58). The spectrum displays the molecular ion, [M]⁺, of **117** at 776.1402 *m/z* and at the same time, other peaks (251.1 and 501.1 *m/z*) relative to the matrix used for the analysis, the *trans*-2-[3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB).^[255]

Porphyrin **117** has been investigated through UHV-STM and the results are reported in section 3.1.5.



Scheme 25. Synthetic pathway towards tetrasubstituted pyridyl porphyrin **117**.

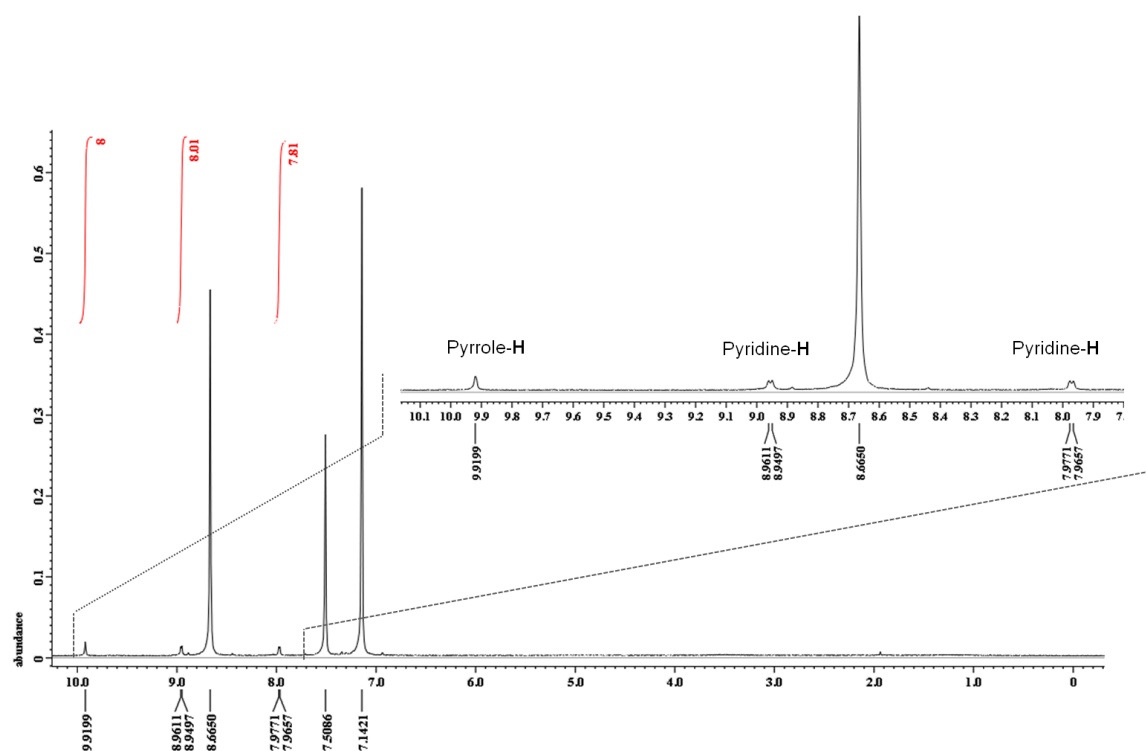


Figure 57. ^1H -NMR spectrum (400 MHz, pyridine- d_5) of tetrasubstituted pyridyl porphyrin **117**. Inset: zoom of the 10.0-7.0 ppm area.

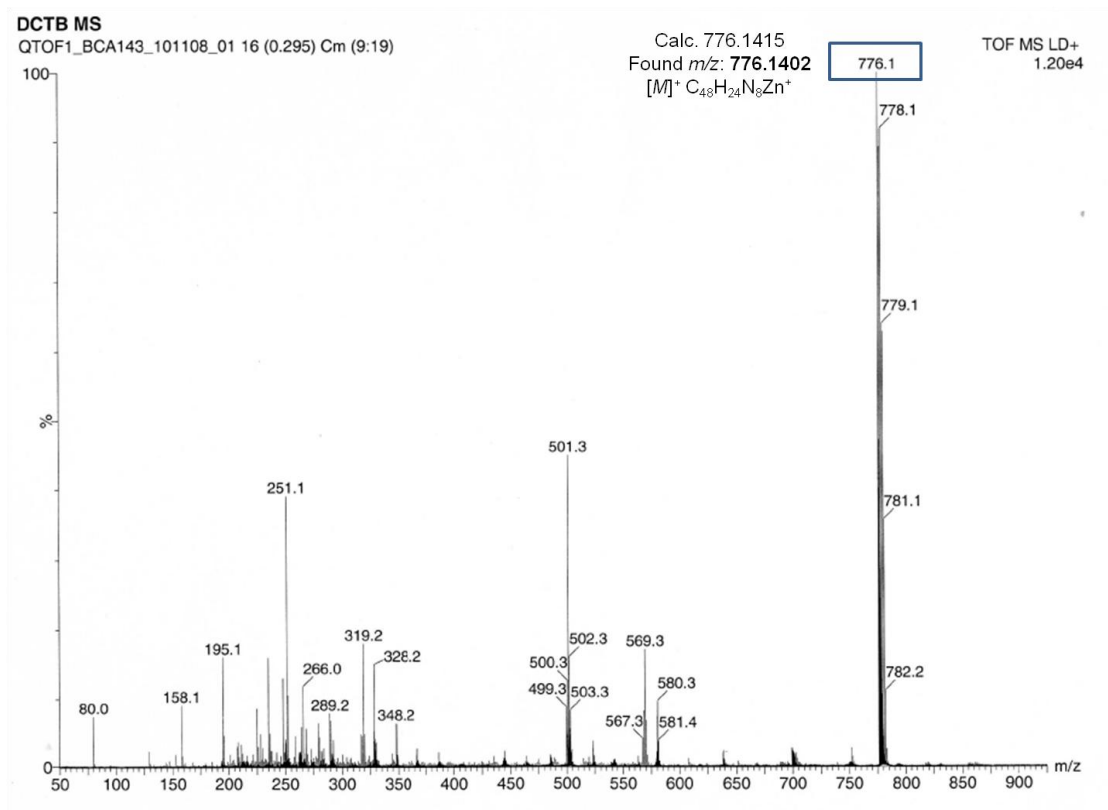
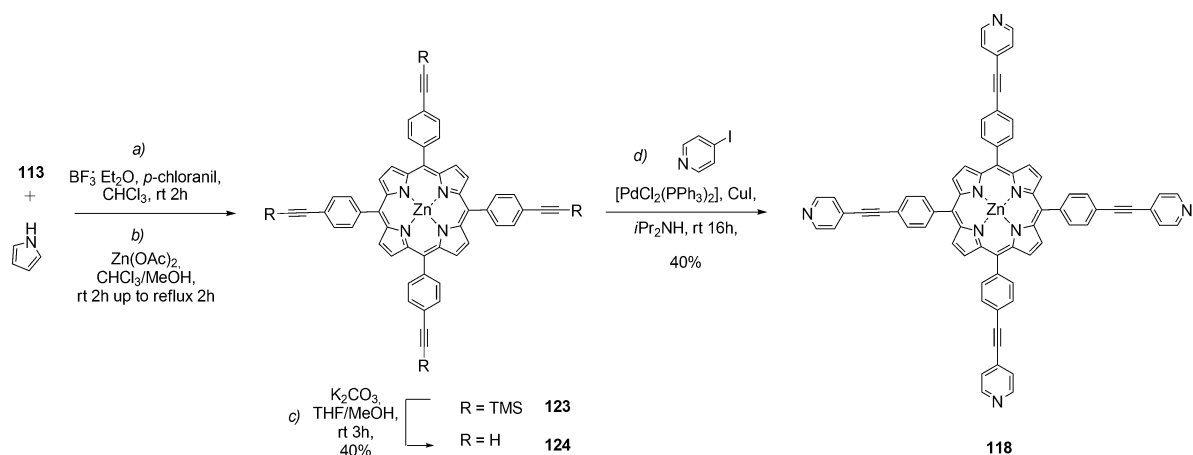


Figure 58. MALDI-HRMS spectrum of tetrasubstituted pyridyl porphyrin **117** in the positive mode (matrix: DCTB MW: 250.12 g/mol). The other m/z values at 251.1 and 501.1 are ascribed to matrix adducts, $[M+1]^+$ and $[2M+1]^+$, respectively.

3.1.2.2.2. Synthesis of A₄ Tetra-Functionalized Pyridyl-Porphyrin **118**

The core of porphyrin **118** was prepared by the BF₃-catalyzed reaction between aldehyde **113** and freshly distilled pyrrole, followed by treatment with *p*-chloranil to oxidize the resultant porphyrinogen macrocycle (Scheme 26, path *a*). The so formed TMS-protected tetra-acetylene porphyrin was immediately used for the following metalation reaction (Zn(OAc)₂, THF/MeOH). The Zn-porphyrin derivative obtained, **123** (Scheme 26, path *b*), was then deprotected of its TMS-group (K₂CO₃, THF/MeOH) affording the free acetylene porphyrin intermediate **124** in 40% yield (Scheme 26, path *c*). Similarly to the previous case 4-iodopyridine was then inserted on **124**, precedently dissolved in *i*Pr₂NH, via a modified *Sonogashira* reaction in the presence of catalytic amounts of [PdCl₂(PPh₃)₂] and CuI, yielding the desired tetradecorated pyridyl porphyrin **118** in 40% (Scheme 26, path *d*). As observed for pyridyl-porphyrin **117**, the final molecule was barely soluble in the common organic solvents and, in this case too, pyridine was necessary to favor its solubilization. Therefore, the ¹H-NMR was performed adding few drops of deuterated pyridine into a CD₂Cl₂ solution of **118** (Figure 59). The spectrum is relatively easy to interpretate and is characterized by a singlet signal (8.90 ppm) for the pyrrole-H, two coupled doublets (8.60 and 7.47 ppm) given by the hydrogen atoms on the pyridine groups (Py-H) and two additional doublets (8.20 and 7.90 ppm) for the hydrogen atoms on the phenyls (Ar-H). A further proof was adducted by MALDI-HRMS spectrum displayed in Figure 60. Herein, the analysis revealed the presence of the most abundant [M]⁺ mass peak assigned to the molecular ion of **118**. At lower values of *m/z* the ion mass of the corresponding non-metalated porphyrin at 1019.3090 *m/z* [(M-Zn)+1]⁺ was also observed with minor abundance.

Porphyrin **118** has been investigated through UHV-STM and the results are reported in section 3.1.5.



Scheme 26. Synthetic pathway towards tetrasubstituted pyridyl porphyrin **118**.

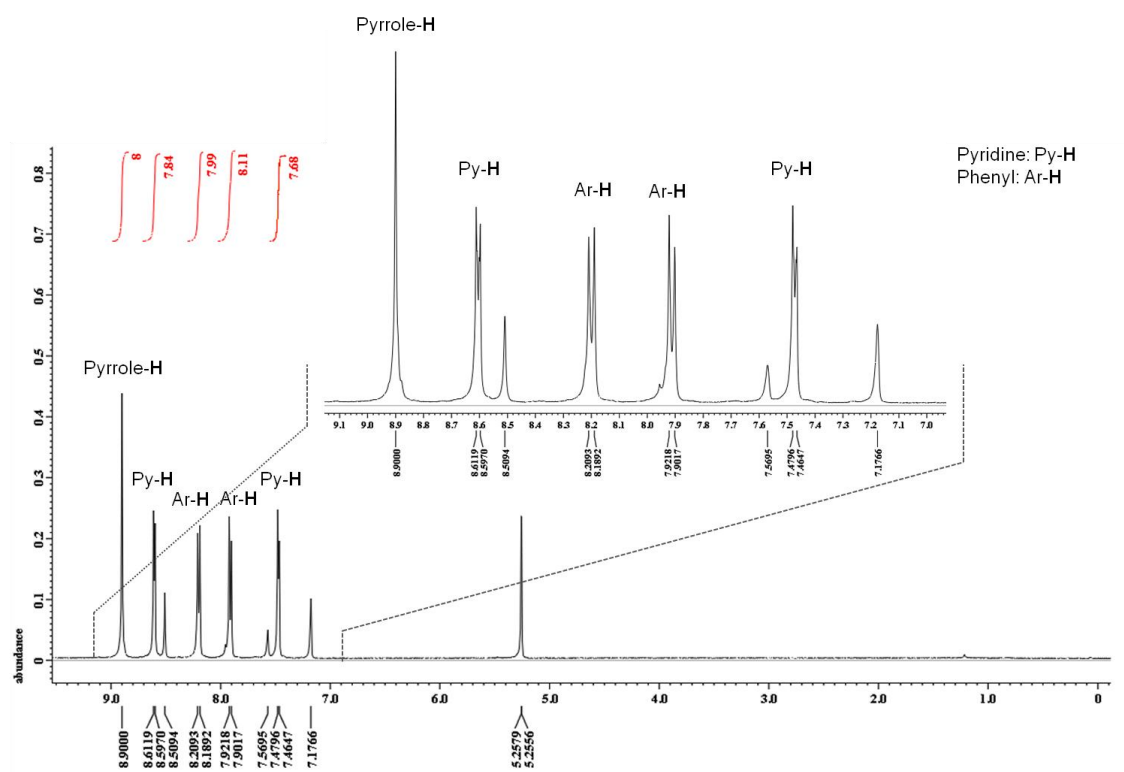


Figure 59. ^1H -NMR spectrum (400 MHz, $\text{CD}_2\text{Cl}_2/\text{pyridine-}d_5$) of tetrasubstituted pyridyl porphyrin **118**.

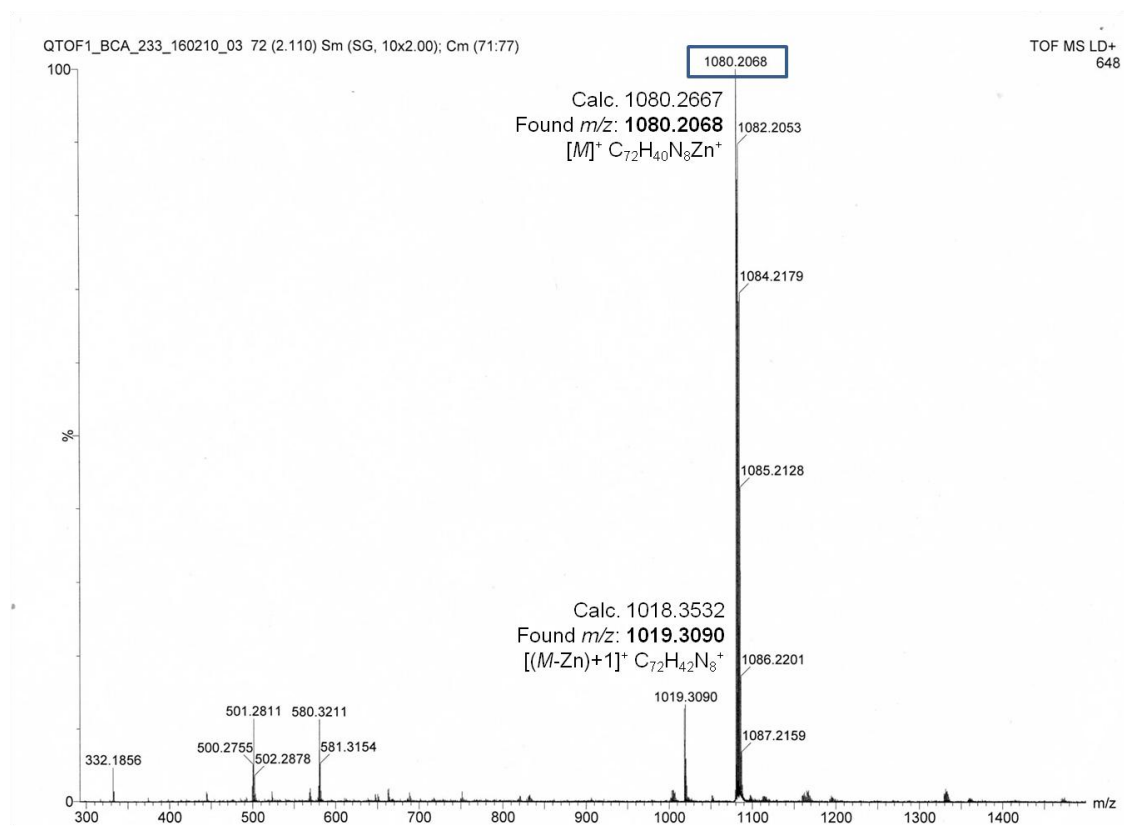


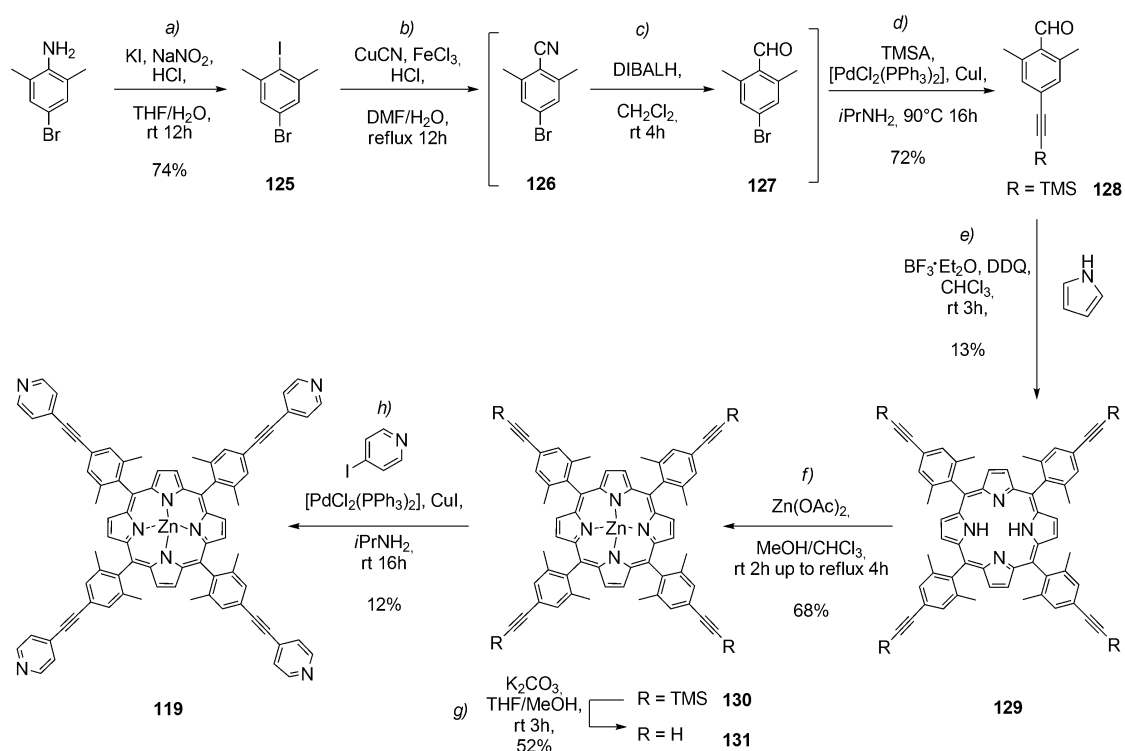
Figure 60. MALDI-HRMS spectrum of tetrasubstituted pyridyl porphyrin **118** in the positive mode (matrix: DCTB MW: 250.12 g/mol). The value at 1019.3090 m/z is assigned to the non-metalated porphyrin.

3.1.2.2.3. Synthesis of A₄ Tetra-Functionalized Pyridyl-Porphyrin **119**

The synthesis of porphyrin **119**, featuring 2,5-dimethylphenyl moieties attached to the four *meso*-positions of the macrocycle, is reported in Scheme 27. Starting from 2,6-dimethyl-4-bromoaniline, 4-iodobromobenzene derivative **125** was synthesized through a diazotation reaction in 74% yield (Scheme 27, path *a*). Subsequently, after the replacement of iodine with a nitrile group by means of a Lewis acid in acidic media (Scheme 27, path *b*, **126**), the reduction with DIBALH led to the 2,6-dimethyl-4-bromobenzaldehyde **127** (Scheme 27, path *c*). Unfortunately, the introduction of the nitrile group in step *b* led to a mixture of two compounds, the desired molecule **126** and the side product bearing two nitrile substituents in *para* positions. Although lower reactive, the bromide of derivative **125** reacts, in fact, with CuCN affording a bis-ciano byproduct. The latter was not immediately separated from the desired **126** due to the similar *rf* values on the TLC plate. The same problem occurred in the following step *c*, as the reduction worked on the mono-ciano derivative **126** and on the bis-ciano side product as well, giving rise to the targeted aldehyde **127** and to the byproduct having two aldehyde groups in *para* positions. The introduction of a protected acetylene on the crude obtained from path *c*, via a *Sonogashira*-type reaction,^[107] made possible the separation of the crude leading to the desired benzaldehyde **128** in 72% yield (Scheme 27, path *d*). The latter was, then, reacted with commercial pyrrole according to the typical *Lindsey's* procedure, producing the TMS-protected tetra-acetylene intermediate **129** (Scheme 27, path *e*). Porphyrin **129** was then metalated with Zn(OAc)₂ producing Zn-porphyrin **130** in 68% yield (Scheme 27, path *f*), which was successively deprotected by means of K₂CO₃ in a mixture of THF and MeOH producing 52% of terminal ethynyl porphyrin **131** (Scheme 27, path *g*). The coupling between **131** and 4-iodopyridine in the presence of catalytic [PdCl₂(PPh₃)₂] and CuI gave rise to final tetrapyrrolyl-porphyrin **119** in 12% yield (Scheme 27, path *h*). As observed for parent Zn-porphyrins **117-118**, the use of deuterated pyridine was essential to perform the ¹H- and ¹³C-NMR of the product. Figure 61 reports the ¹H-NMR spectrum of a CDCl₃ solution of **119** with few μ l of pyridine-*d*₅. Specifically, with respect to the previous spectra (Figures 57 and 59) the singlet peak relative to the the hydrogen atoms on the pyrrole β -positions (Pyrrole-**H**) shielded from 9.99 and 8.90 (for **117-118**) to 8.55 ppm, probably due to the electron donating effect of the methyl groups in the *meso*-phenyl moieties. The MALDI-HRMS analysis also supports the formation of porphyrin **119** (Figure 62), displaying the [M]⁺ molecular ion at 1192.3931 *m/z* of **119** and the [(M-Zn)+1]⁺ ion at 1131.5 *m/z* of the corresponding free-base porphyrin.

The UHV-STM characterization of this molecule is reported in section 3.1.5.

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Scheme 27. Synthetic pathway of the tetrasubstituted pyridyl porphyrin **119**.

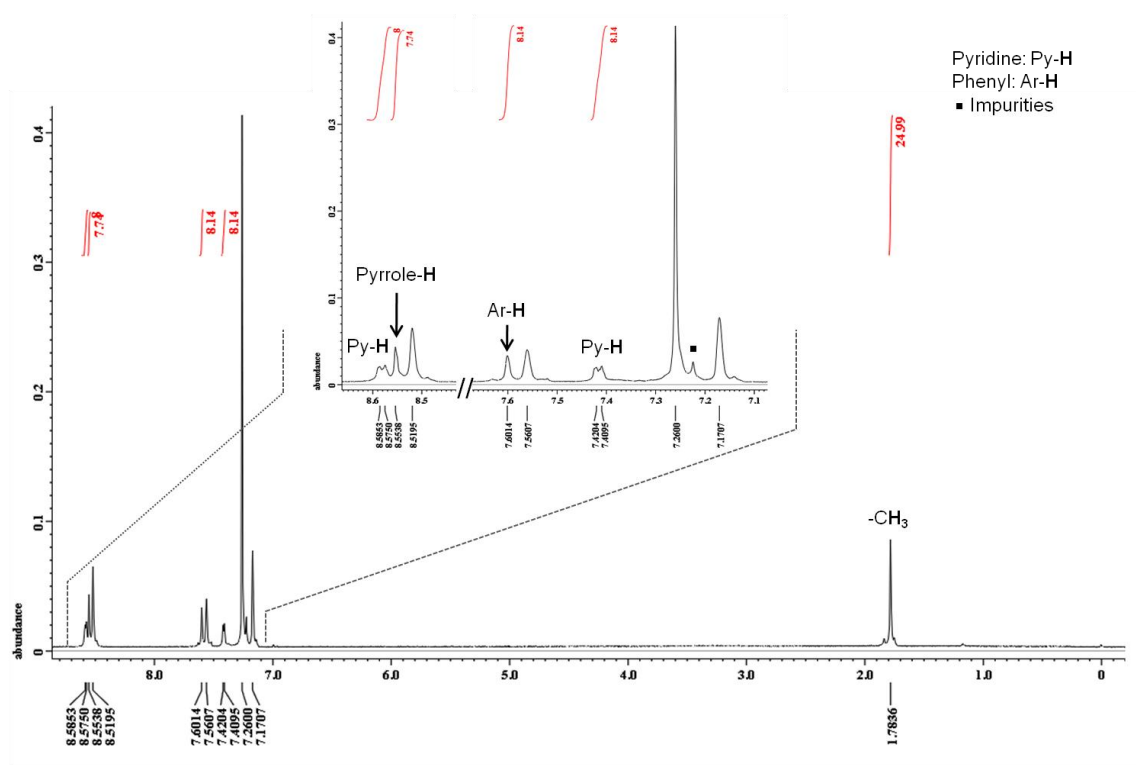


Figure 61. ¹H-NMR spectrum (400 MHz, CDCl₃/pyridine-*d*₅) of tetrasubstituted pyridyl porphyrin **119**. Inset: zoom of the 9.0-7.2 ppm area.

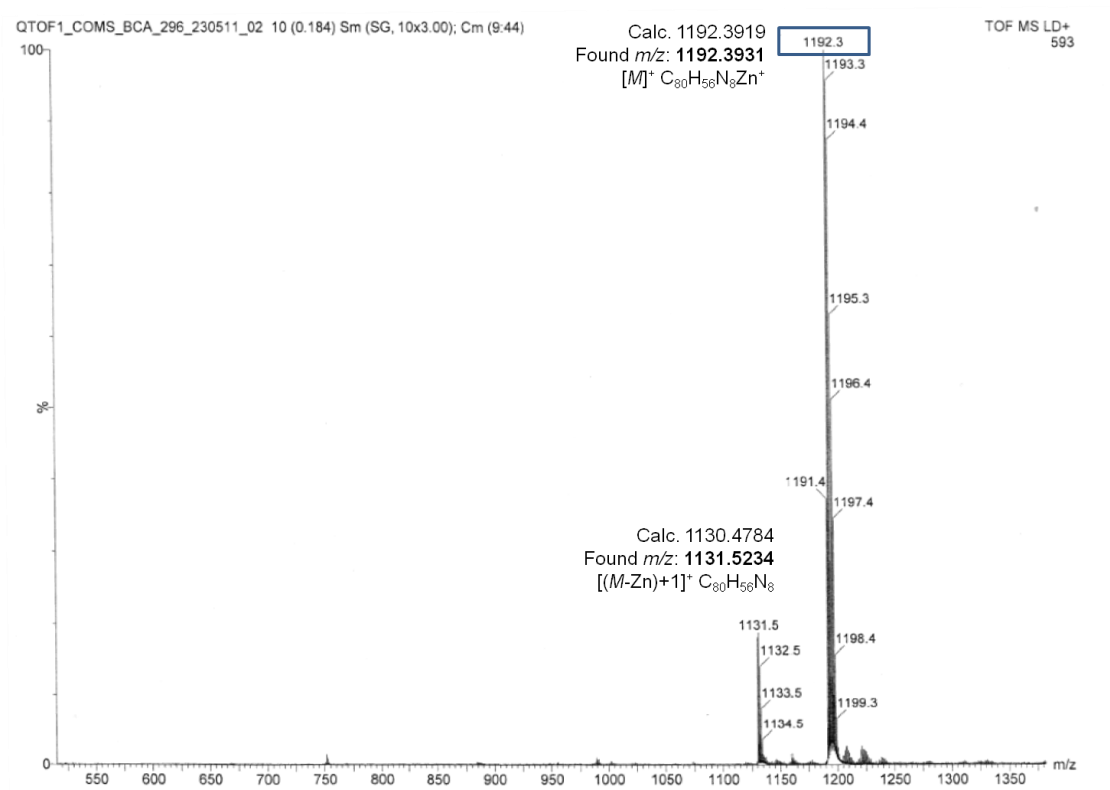


Figure 62. MALDI-HRMS spectrum of tetrasubstituted pyridyl porphyrin **119** in the positive mode (matrix: DCTB MW: 250.12 g/mol). The value at m/z 1031.5 is assigned to the free-base porphyrin.

3.1.3. UHV-STM Characterization of Unsymmetric Porphyrins 109-111

3.1.3.1. Discrete Assemblies on Cu(111) Surface

STM measurements have been performed in order to provide the formation of porphyrin-based discrete assemblies on atomically flat Cu(111) surface through metal-ligand coordination motifs. Molecular modules **109**, **110** and **111** (Figure 54), bearing specific 3,5-di-*tert*butylphenyl (*t*-Bu₂Ph) groups and pyridyl sites, have been designed to undergo physisorption on Cu(111) into highly ordered ML under ultra-high-vacuum experimental conditions. After a detailed description of each molecule's arrangement, this part will report the investigation on the formation of the assemblies. These results have been the object of two recent publications.^[256-258]

3.1.3.1.1. UHV-deposition of module **109**

The first step in our study is the deposition of a submonolayer of porphyrin module **109** onto a Cu(111) surface. While very few single protrusions corresponding to individual porphyrin molecules are observed in the resulting STM images (Figure 63b), the surface mainly hosts larger units characterized by two bright terminations and a dimeric central connection. Specifically, high-resolution images (Figure 63c) reveal that each assembly consists of two molecules **109** interconnected through their pyridyl substituents and thus resulting into dimeric (**109**)₂ species. This structural assignment is based on the molecular dimensions and on previous STM work on 5,10,15,20-tetra(*t*-Bu₂Ph) porphyrin molecule^[218, 259] in which each double-lobed features corresponds to the *t*-Bu₂Ph groups. Besides

the six bright $t\text{-Bu}_2\text{Ph}$ groups, the two pyridyl substituents are clearly resolved. They align in an anti-parallel head-on configuration, where the pyridyl groups face each other. Importantly, the combination of the six-fold symmetry of the first Cu layer with the C_{2h} symmetry of the porphyrin core in the gas phase, together with a considerable molecule-substrate interaction, leads to a conformational adaptation of the molecules upon adsorption. A rotation of the $t\text{-Bu}$ groups results in an alignment of the double-lobed features with the dense-packed substrate directions. Accordingly, the double-lobes representing the $t\text{-Bu}_2\text{Ph}$ substituents are not perpendicular to each other, but enclose an angle of either 60° or 120° (Figures 63c).

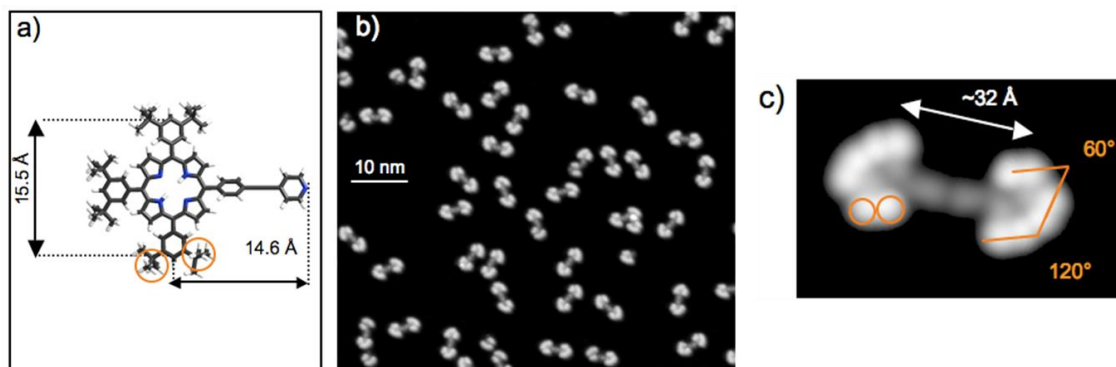


Figure 63. a) Molecular structure of porphyrin **109** showing the three $t\text{-Bu}_2\text{Ph}$ groups and the pyridyl substituent. The molecular dimensions are extracted from PM3 calculations as implemented in the HyperChem molecular modeling package and are consistent with values^[260] reported in literature; b) STM image of self-assembled dimers (**109**)₂ on a Cu(111) surface (data acquired with $I = 0.12$ nA, $U = -1$ V); c) detailed view of a single (**109**)₂ dimer exhibiting the three double-lobes representing the $t\text{-Bu}_2\text{Ph}$ groups of each molecular module and the head-on aligned pyridyl substituents ($I = 0.4$ nA, $U = -0.9$ V).

3.1.3.1.2. UHV-deposition of module **110**

To further explore the controlled aggregation of porphyrins guided by their pyridyl substituents, we investigated a porphyrin module bearing two functional pyridyl moieties in a *cis*-like configuration, molecule **110**. The large-scale image in Figure 64b shows that different aggregates of well-defined shape and orientation coexist on the surface after deposition of molecule **110**. Triangular and rhombic architectures (Figures 64c and d) consisting of three and four molecular modules **110**, (**110**)₃ and (**110**)₄, are clearly resolved. Again, the molecular modules are interacting *via* the head-on pyridyl functions as observed for dimers (**109**)₂. While the trimeric species (**110**)₃ dominate at low coverage, the tetrameric (**110**)₄ assemblies prevail at higher surface coverage where additionally pentameric (Figure 64e) and hexameric (Figure 64f) assemblies occur. This trend indicates that the spontaneous self-assembly of the supramolecules is based on a statistical process related to the probability that a given number n ($n = 3, 4, 5$, etc.) of molecules meet while diffusing on the surface and not solely induced by an energy difference favoring either triangular or rhombic architectures.

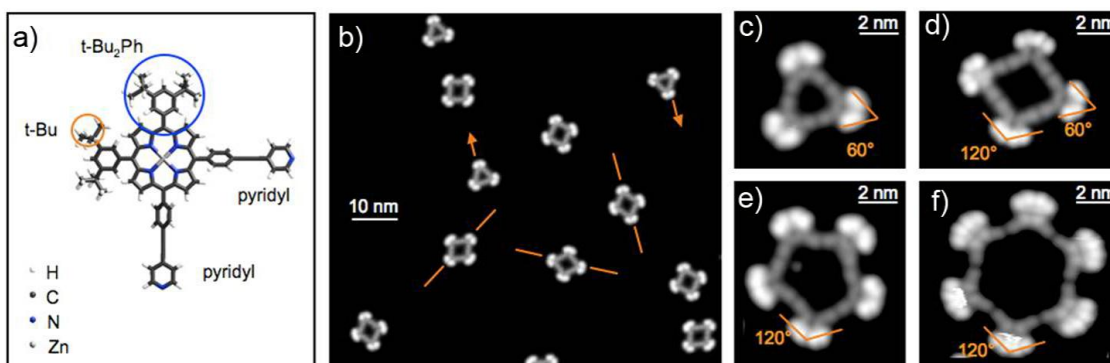


Figure 64. a) Molecular structure of porphyrin **110**. The molecular dimensions are extracted from PM3 calculations as implemented in the HyperChem molecular modeling package and are consistent with values^[260] reported in literature; b) coexistence of triangular and rhombic supramolecules after deposition of porphyrin **110** ($I = 0.1$ nA, $U = -0.5$ V). The arrows and lines mark the distinguishable azimuthal orientations of the supramolecules; c-f) detailed view and structural properties of supramolecular cycles (**110**)_n (c: $n = 3$, d: $n = 4$, e: $n = 5$, f: $n = 6$). The two possible opening angles of the *t*-Bu₂Ph groups are indicated (b: $I = 0.2$ nA, $U = -0.22$ V, c: $I = 0.1$ nA, $U = -1$ V, e: $I = 0.2$ nA, $U = -1$ V, f: $I = 0.1$ nA, $U = 1$ V).

Together with the pyridyl-to-pyridyl coupling, the conformational flexibility of the macrocyclic structure and thus its adaptability and interaction with the underlying surface governs the geometrical properties of the supramolecules. Notably, the different interactions between the porphyrin and the Cu(111) surface induces marked changes in the conformation of the central tetrapyrrolic core strongly affecting the opening angles of both *t*-Bu₂Ph and pyridyl groups. This results in opening angles of the *t*-Bu₂Ph groups of either 60° or 120°. In addition, the pyridyl substituents can also laterally bend.^[261] Besides the intrinsic opening angle of 90° rarely observed on the surface, we determined opening angles of either $80 \pm 5^\circ$ or $100 \pm 5^\circ$. The small *t*-Bu₂Ph angles imply the small pyridyl angle and vice versa. As a consequence, to assemble a supramolecular trimeric cycle by a nearly straight head-on coupling of the pyridyl groups, the molecules have to adapt to the *t*-Bu₂Ph opening angle of 60° and as a result, trimeric species can only exist in two distinguishable azimuthal orientations on the surface, rotated by 180° towards each other. This is visualized in Figure 64b, where trimeric supramolecules (**110**)₃ are observed exclusively in two orientations with respect to the substrate atomic lattice. Exceptions constituted by triangles exhibiting *t*-Bu₂Ph opening angles of 120° were rarely spotted. Their assembly follows the same empirical rules, but they exhibit a more complex, chiral structure. The area of the regular triangular cavities amounts to ~ 6 nm².

Following these rules, the only possible geometry for symmetric and quadrangular supramolecules coupled by the pyridyl groups is a rhombic shape, where two opposing corner molecules exhibit a *t*-Bu₂Ph angle of 60°, whereas the other pair has a *t*-Bu₂Ph opening angle of 120°. Consequently, the rhombic (**110**)₄ supramolecule exists exclusively in three distinguishable azimuthal orientations on the surface (compare Figure 64b and Figure A2 in the *Appendix*) and regular square or pentagonal structures are more rare. Over 95% of the observed quadrangular supramolecules (**110**)₄ are regular rhombs exhibiting 60°/120° *t*-Bu₂Ph opening angles and a cavity area of 10.5 nm². For the pentagons and the hexagons the area amounts to 15 and 19 nm², respectively.

3.1.3.1.3. UHV-deposition of module **111**: from polymeric assemblies to larger cyclic supramolecules

To complete the characterization of the self-assembly of our basic building blocks we proceed to the *trans*-like isomer **111** depicted in Figure 65a. As expected from the head-on coupling of the pyridyl groups, molecules **111** align in extended chains, whereby straight segments have a stride of 32.7 ± 0.5 Å (Figures 65b and c). Figure 65d shows a large-scale STM image of the Cu(111) surface after the deposition of 0.4 ML of module **111** at a substrate

temperature of 350 K. The surface steps appear completely covered with molecules. Porphyrin derivative **111** self-assembles into one-dimensional chains, presenting a striking flexibility as linear and curved segments can be distinguished. In addition, most of the chains do not interconnect to each other, even at higher coverage, which testifies the presence of repulsive forces between the chains, similarly encountered for H-bonded 1D surface-confined polymers.^[262, 263]

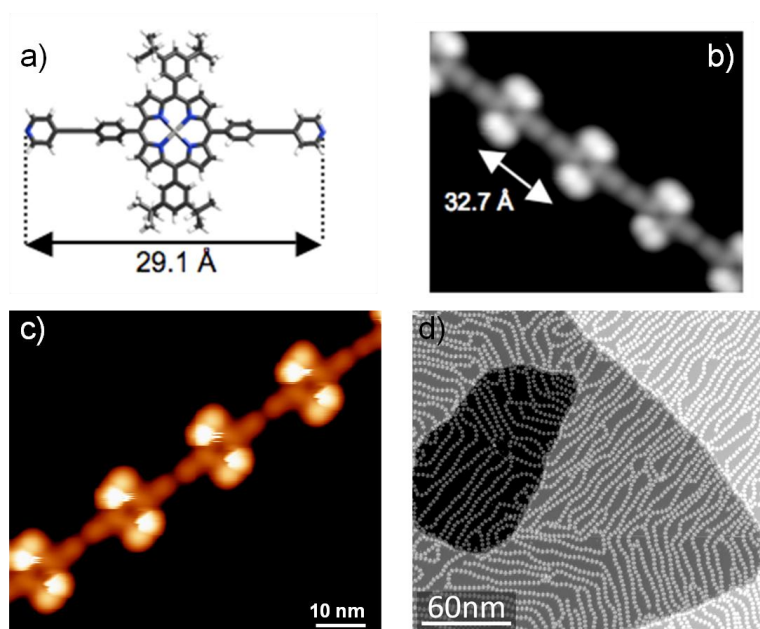


Figure 65. a) Molecular structure of porphyrin **111**. The molecular dimensions are extracted from PM3 calculations as implemented in the HyperChem molecular modeling package and are consistent with values^[260] reported in literature; b) STM image of the one-dimensional supramolecular assembly following deposition of **111** on Cu(111) ($I = 77$ pA, $U = -0.1$ V); c) STM image of the one-dimensional supramolecular assembly formed by molecules of **111** on Cu(111) clearly presenting *t*-Bu groups with opposed different brightness ($I = 77$ pA, $U = -0.1$ V); d) STM image of a Cu(111) surface taken at 6 K after the evaporation of 0.4 ML ($I = 0.1$ nA, $U = -1.0$ V) of porphyrin **50** at a substrate temperature of about 350 K.

A closer look to the images obtained from the deposition of the *trans*-like module revealed that in each *meso*-position one *t*-Bu fragment is brighter than the other (Figure 65c). Such differences are due to height variations between the two protrusions of *t*-Bu₂Ph groups and have already been documented in literature.^[236, 264] In particular, the lower *t*-Bu from each *meso*-position are going to act as legs, interacting through van der Waals forces with the metallic substrate and decoupling the core of the porphyrin macrocycle from the substrate. In Figures 66a and c we reported a schematic illustration of module **111** presenting the rotation of the *t*-Bu₂Ph moieties to match the aspect of the molecule on the surface.

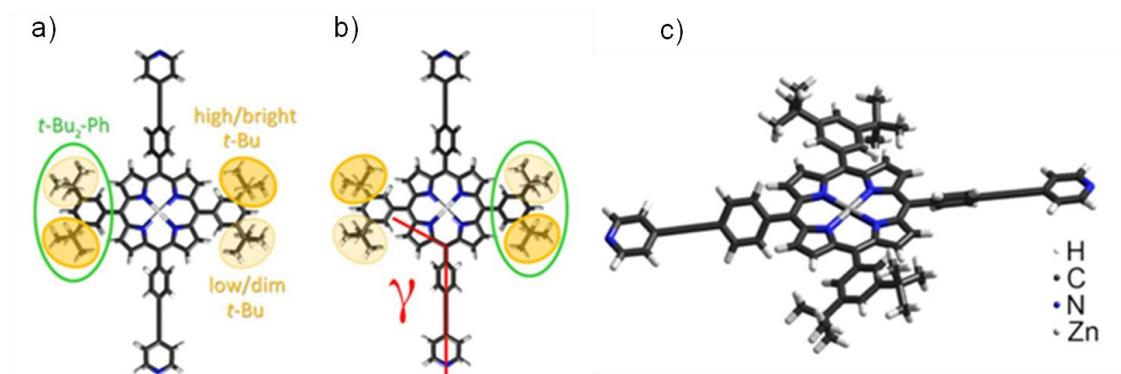


Figure 66. Porphyrin derivative **111** used as building block for the coordination polymers. a-b) Schematic illustration of adsorption-induced molecular deformations resulting in conformational surface enantiomers β (a) and α (b). A rotation of the $t\text{-Bu}_2\text{Ph}$ group results in one $t\text{-Bu}$ constituent being higher than its counterpart. The angle γ of the phenyl-ethynyl-pyridyl leg can deviate from the intrinsic value of 118° ; c) 3D view showing the converse rotation of opposite $t\text{-Bu}_2\text{Ph}$ substituents upon surface deposition.

Due to these conformational properties, *i.e.*, the flexibility of the phenyl-ethynyl-pyridyl substituents and the rotability of all *meso*-substituents, $t\text{-Bu}_2\text{Ph}$ groups included, module **111** deconvolutes into two stereoisomers upon surface confinement (enantiomers α and β , Figures 66a and b),^[236] which play a major role in the structure of the polymer chains. The two enantiomers are formed due to the interaction of the molecule with the surface, which blocks the rotation of the $t\text{-Bu}_2\text{Ph}$ groups around the axis with the macrocycle in an opposed way. The porphyrin is then forced to adapt in two specific configurations upon surface confinement. Statistical treatments show that enantiomers α and β were adsorbed on the surface in a 1:1 ratio. Furthermore, a detailed analysis of the polymeric chains disclosed the presence of straight and zig-zag chains, formed by the same enantiomers and by an alternate sequence of enantiomers α and β , respectively (Figures 67 g-i and j-l). Together with these chains arrangements, the assembling mode gives also rise to characteristic turns, labeled here U-turns (Figures 67 m-o). It is worthy to point out that as a consequence of the $t\text{-Bu}$ rotations there is a collective macrocycle distortion consisting in two downwards and two upwards twisted pyrroles similar to that observed by *Diederich at al.* for disubstituted porphyrin **100** (section 3.1.1.3.1).^[235] In their case, to form tetramer aggregates the *meso*-phenyl substituents of **100** are rotated away from their preferred perpendicular orientation relative to the porphyrin core, causing a saddle shape of the porphyrin core with two opposing pyrrole rings pointing upwards, and the other two pointing downwards. This occurred in two axes (Figure 50b), leading to type A and type B tetramers.

In our case, very remarkably, the overall intramolecular and molecule-substrate interactions favor the exclusive existence of two conformers, in which the dihedral angle of opposing substituents is converse. The possible conformer, where the opposite $t\text{-Bu}_2\text{Ph}$ groups are rotated towards the same direction was not detected.

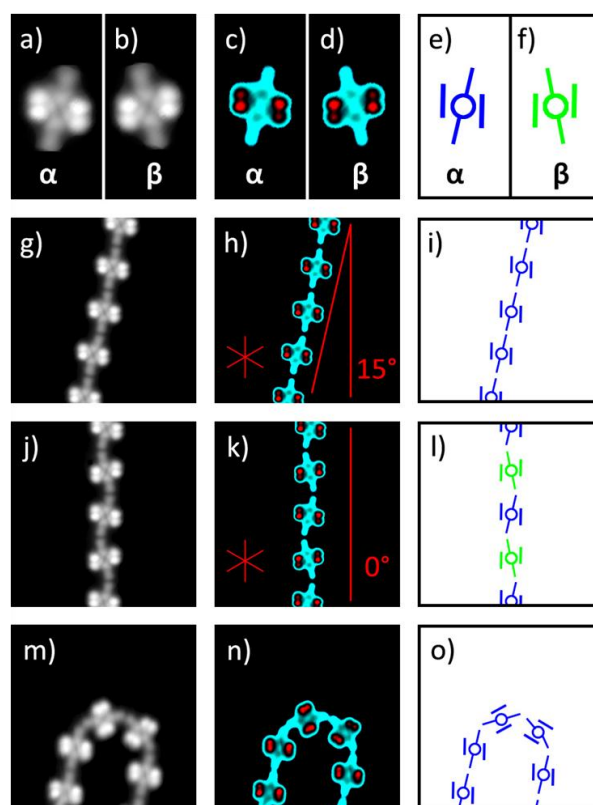


Figure 67. a-b) STM images of the two conformational isomers α and β of porphyrin derivative **111** on Cu(111); c-d) images a) and b) reproduced in enhanced contrast to visualize the different apparent height of the *t*-Bu groups. The vertical line represents a dense-packed substrate direction and thus a projection of the mirror plane; e-f) schematic representation of both isomers; g-i) portion of straight chain constituted only by α enantiomers. The chain direction includes an angle of 15° with a dense-packed Cu(111) direction (red vertical line, the red star indicates all dense-packed directions; j-l) zig-zag chains constituted by alternating enantiomers α and β , the overall segment orientation is aligned with a dense-packed Cu(111) direction; m-o) example of a U-turn. Tunneling parameters: a-d), g-h), j-k) $I = 0.2$ nA, $U = 1.0$ V; m-n) $I = 0.36$ nA, $U = 0.94$ V.

After characterizing the homomolecular supramolecular architectures we proceeded to the construction of larger supramolecular cavities by mixing building blocks with different symmetry. In order to probe the recognition properties of the different molecular modules, we thus studied bicomponent assemblies. In Figure 68a a schematic model of the possible larger cyclic supramolecule formed by the two isomers **110** and **111** and the STM-measured distances between the pyridyl moieties are reported (for details on the coupling motif interaction see section 3.1.3.1.4). As an example, Figure 68b shows the nanoarchitectures evolving after subsequent deposition of **110** and **111** with a 3.6:1 ratio. Besides the homomolecular triangles (**110**)₃ and rhombs (**110**)₄ discussed before, unprecedentedly large cyclic architectures incorporating modules **111** are also clearly discernible. Figure 68c shows a cyclic assembly (**110**·**111**·**110**)₂ with a 2:1 ratio of **110**:**111** and a cavity area of 20.6 nm². Accordingly, when passing from assembly (**110**·**111**·**110**)₂ to (**110**·**111**)₄ (Figure 68d) the area of the cavities is markedly extended to 41.2 nm². Again, the statistical assembly process inhibits a uniform size distribution of the supramolecules. This is the first observation of individual supramolecular cavities at surfaces formed by multiple molecular modules.

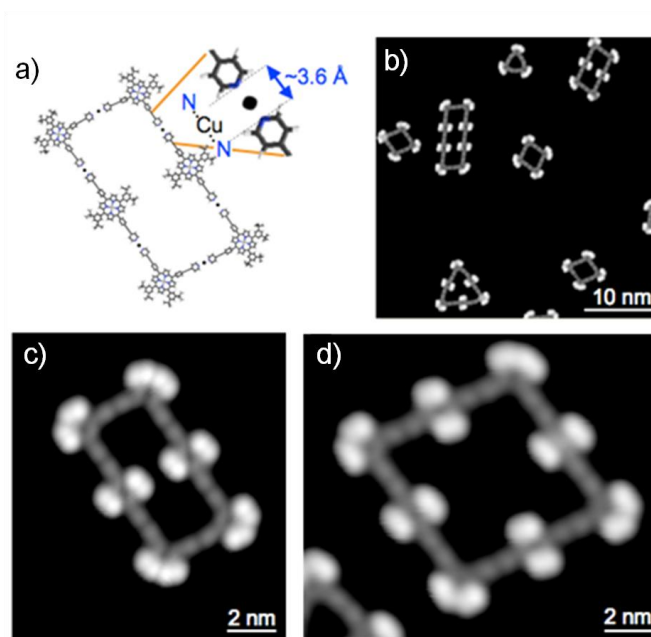


Figure 68. a) Schematic model of the $(110\cdot111\cdot110)_2$ binary cyclic assembly. The black dots represent Cu adatoms embedded in between the terminal pyridyl N atoms; b) STM image showing the coexistence of homomolecular assemblies $(110)_3$ and $(110)_4$ with bicomponent rhombic $(110\cdot111\cdot110)_2$ and $(110\cdot111)_4$ triangular $(110\cdot111)_3$ architectures formed upon mixing of the respective modules; c-d) detailed view of the bicomponent cyclic architectures: e) $(110\cdot111\cdot110)_2$ and f) $(110\cdot111)_4$. (b, d: $I = 0.1$ nA, $U = -1$ V, c: $I = 0.2$ nA, $U = -1$ V).

3.1.3.1.4. Molecular Manipulation Experiments and Mechanistic Aspects

In order to obtain insight into the flexibility of both the porphyrin modules and the cyclic supramolecules as well as the strength of the intermolecular coupling, we performed molecular manipulation experiments. In these experiments, the STM tip was approached to the surface by decreasing the tunneling resistance and laterally moved across the supramolecules in constant current mode. A similar procedure has been applied previously to translate individual porphyrins substituted by four identical *t*-Bu₂Ph substituents on a Cu(100) surface.^[261] Figure 69 compares states prior and after such manipulation steps. Figures 69 a-c indicate that the shape of $(110)_4$ supramolecules can be completely changed without breaking the intermolecular bonds, evidencing a conformational deformation of the cyclic assembly without apparent disruption of the non-covalent intermolecular recognition site. The yellow color in Figure 69b originates from a superposition of the initial state (green) and the final state (red) and highlights regions very molecules overlap prior and after the manipulation step. Nevertheless, it is possible by STM manipulation to rupture the non-covalent interactions and to transfer molecules to the STM tip: Figure 69d shows an example where a transformation from a rhombic to a triangular assembly was induced by the extraction of one module.

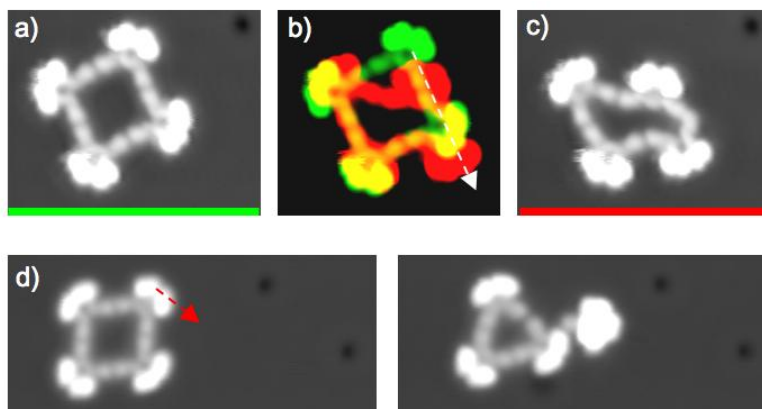


Figure 69. Molecular manipulation experiments with **(110)₄** assemblies. Between the initial (a, green) and final state (c, red) the STM tip was laterally moved at low tunneling resistance across the supramolecule following the path indicated by the arrow in b). The experiments indicate a high flexibility of both the molecular building blocks and the supramolecular assemblies combined with stable intermolecular bonds and show that it is possible to induce a conformational change of the supramolecules without breaking them (a-c: imaging: $I = 0.1$ nA, $U = -0.5$ V, manipulation: $I = 10$ nA, $U = -50$ mV); d) transition of a rhombic to a triangular structure by extraction of one molecule by STM manipulation (imaging: $I = 0.1$ nA, $U = -0.5$ V, manipulation: $I = 8$ nA, $U = -50$ mV). The dark dots representing adsorbed gas molecules can be used as markers.

From the STM images we observed an intermolecular distance of 32.7 ± 0.5 Å for straight **111** chain segments, where the distance measurement and calibration is the most precise and thus it has been considered as our reference module. The measured value is consistent with the center-to-center spacing in the other aggregates. Subtracting the length of molecule **111** of 29.1 Å as determined from a PM3 optimization and preliminary crystallographic data of the molecular structure and in agreement with a previous work,^[260] yields an intermolecular N–N separation of 3.6 ± 0.5 Å between the two terminal pyridyl groups. From electrostatic considerations, a straight head-on coupling of the two opposite pyridyl groups is energetically highly unfavorable, as the terminating N atoms carry negative charge.^[265] Accordingly, on noble metal surfaces as Ag(111), the head-on coupling is not observed. Instead, the molecules form dense-packed islands where the pyridyl groups avoid each other even at low submonolayer coverage (Appendix Figure A3). Thus, the Cu surface plays a decisive role in promoting a head-on alignment of the pyridyl groups. In this context, the strong bonding interactions of pyridyl to Cu are well documented both on surfaces^[253, 266, 267] and for the solid-state,^[268] where typical N–Cu bond distances range from 1.9 to 2.2 Å. These attractive interactions were reported to induce a rotation and bending of the terminal pyridyl groups of a porphyrin molecule towards the Cu(111) surface.^[253] Accordingly, a possible explanation of the head-on pyridyl coupling consistent with the determined N–N separation of 3.6 ± 0.5 Å would be that the two N atoms coordinate to a Cu surface atom by bending towards the substrate, possibly inducing a displacement of the Cu atom.^[269] However, this option is excluded because diffusion experiments show that the **(109)₂** dimers translate at 220 K without breaking. It is highly unlikely that two molecules **109** would coherently form and break bonds to underlying Cu atoms embedded in the surface while wandering large distances without drifting apart. On the other hand, it has already been reported that appreciable Cu adatom densities exist on Cu surfaces even at moderate temperatures, enabling stabilization of supramolecular aggregates by metal-ligand bonding between pyridyl (or other) groups and Cu adatoms.^[266, 270–272] The observed N–N distance of 3.6 ± 0.5 Å would yield a N–Cu bond length of $3.6 \text{ Å} / 2 = 1.8 \text{ Å}$, which is slightly shorter than the values reported above, but consistent with calculated values for an pyridyl–Cu–pyridyl complex.^[270] However, this number is a lower limit as it only considers the projection of the pyridyl–Cu bond length onto the surface plane. Geometric effects as the separation of the terminal N atom from the surface dictated by the molecular backbone or a lateral offset of the coupling adatom can sensitively increase the real pyridyl–Cu distance. Furthermore, the fact that metal atoms coordinating organic ligands are hardly seen in STM images because of electronic effects is well documented in the

literature.^[273-275] The two-fold pyridyl–Cu–pyridyl coordination motif suggested here indicates that the terminal pyridyl rings are rotated towards the surface plane. As a consequence, steric repulsions between H atoms of neighboring pyridyl rings prevents the three-fold coordination motif observed for a related metal-carbonitrile 2D metal-organic networks.^[222]

3.1.3.2. Self-Assembled Hierarchic Nanoporous Surfaces: Porphyrin-based Chiral Networks on Ag(111)

In many cases the surface confinement of molecular modules leads to a simultaneous expression of chirality phenomena, notably formation of organized chiral surfaces with achiral, prochiral or chiral molecular species.^[276, 277] In this respect, very important is the role of the chiral induction that originates from the conformational adaptation of the adsorbed molecules, giving rise to the formation of surface enantiomers,^[235, 236] which effects were recently designated as “conformational chirality”.^[278] Porphyrins represent appealing systems to improve these studies as they can provide novel catalytic properties based on chirality features.

In order to study the porphyrin-based hierarchic design of chiral 2D porous networks on surfaces, we addressed the investigation of porphyrin **111** on Ag(111). To visualize and characterize the formation of the chiral arrays we performed UHV-STM measurements. These results have been the object of a recent publication.^[256]

Differently from Cu-, Ag-surfaces are known to be extremely atomically flat and inert surfaces. For this reason it is quite impossible to find silver atoms free of moving on it, as in the case of Cu-surface discussed above.^[279-281] As previously described, the *trans*-like isomer **111** appears to be very flexible and pliable. Thus, it lends itself perfectly to the construction of chiral networks upon adsorption on a surface exploiting its intrinsic conformational adaptation. Specifically, *meso*-substituents can rotate around the macrocycle-phenyl axis, and the phenyl-ethynyl-pyridyl legs are quite flexible, as they can deviate from the straight equilibrium position towards the *t*-Bu₂Ph substituents. Thus, upon adsorption on Ag(111), module **111** deconvolutes into two chiral conformers, labeled as α and β , as a consequence of their conformational flexibility, which were investigated by STM following cool down to temperatures below 10 K (Figure 70). The deposition of **111**, at very low concentrations, resulted also in the decoration of the step edges and the formation of small molecular aggregates and some isolated molecules. Because of the inherent achirality of the gas-phase molecule (*i.e.* once sublimed), there is an equal probability for each enantiomer to be found on the surface. Similarly to the α - β enantiomers observed on Cu(111), the surface chiral conformational adaptation of module **111** results in an angle of $\pm 15^\circ$ between the molecular board and the axis connecting the two lobes (*t*-Bu₂Ph) (Figures 70c and d), and the phenyl-ethynyl-pyridyl legs are oriented in a straight fashion for isolated species.

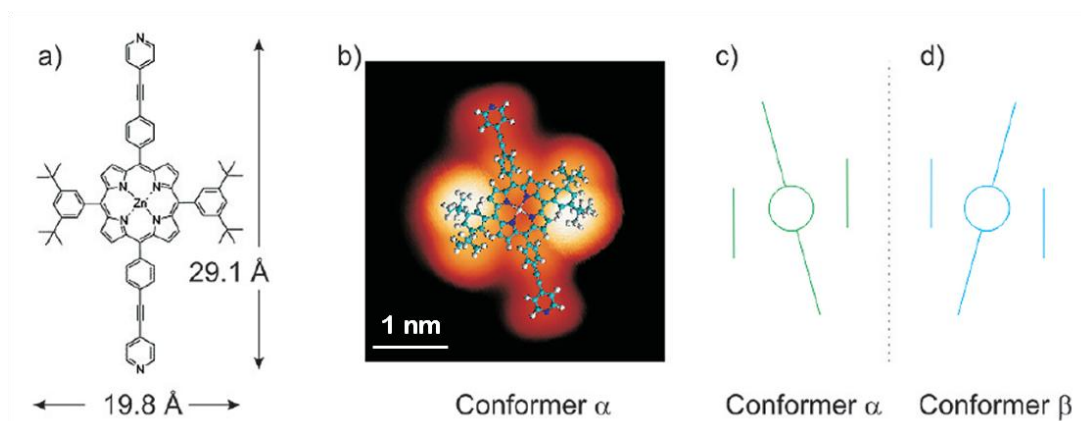


Figure 70. a) Scheme of porphyrin **111**; b) STM image of an isolated molecule adsorbed on Ag(111) with an overlaid model to identify the different subunits ($I = 0.05$ nA, $U = 2$ V); c-d) cartoon representing conformers α and β .

Increasing the coverage of the surface, we observed a novel trimeric aggregate (Figure 71). For clarity reasons we will only consider the aggregates formed by enantiomer α , taking into account that we observed the same arrangements for the other enantiomer. We noted this assembly as α -I. Each of the three bright double-lobes in the corners of the assembly corresponds to one t -Bu₂Ph moiety. Furthermore, the protrusions originating from the phenyl-ethynyl-pyridyl substituents are discernible. If we assign each t -Bu₂Ph moiety to one molecule and superpose a structural model from Figure 71b on the STM image, aligning the t -Bu₂Ph legs with the close-packed directions of the substrate, we obtain three different molecular orientations in the trimeric aggregate: following the substrate symmetry, the modules are rotated by 0, 60, and 120° relative to each other (Figure 71b). The t -Bu₂Ph groups in the model correctly represent the two-lobe structures visible in the STM data. However, the positions of the phenyl-ethynyl-pyridyl substituents deviate from the protrusions in the STM image, as clearly seen for the three outer groups in Figure 71b. Thus, the structural model, which perfectly describes an individual module, does not fit the molecular structure in the trimeric assembly. To achieve structural agreement for the trimeric unit, we have to introduce a bending of $\sim 20^\circ$ of the phenyl-ethynyl-pyridyl moieties (Figure 71c). This distortion is a consequence from the intermolecular steric hindrance between the phenyl-ethynyl-pyridyl and the t -Bu₂Ph substituents in the supramolecular assemblies. Importantly, the trimer is an enantiopure arrangement consisting exclusively of the same conformers; that is, its assembly implies a chiral recognition process.^[282]

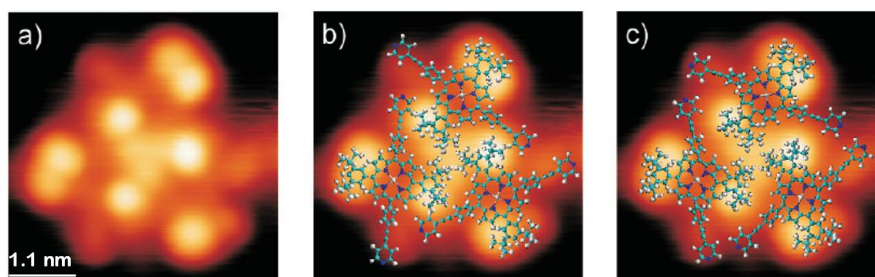


Figure 71. a) STM image of the supramolecular trimeric aggregate of porphyrin **111** on Ag(111); b-c) STM image of the trimeric aggregate with overlaid models of the straight-leg (b), and the bent-leg (c) positions, revealing a flexure of the phenyl-ethynyl-pyridyl legs ($I = 0.2$ nA, $U = 1$ V).

The three-molecules assembly represents a secondary supramolecular unit with two distinct surface orientations (α -I and α -II, Figure 72) related by a 60° rotation, reflecting the symmetry of the surface. The combined assembly of these supramolecular units to a larger aggregate is illustrated by the STM data in Figure 72a. Comparing the STM

images of a trimeric aggregate (Figure 72a) with the larger assembly shown, we could observe the appearance of additional brighter protrusions within the latter structure. These bright protrusions originate from the close proximity of the phenyl-ethynyl-pyridyl and *t*-Bu groups (Figure 72b). We related them to the rotation of the *t*-Bu and pyridyl moieties to minimize steric hindrance. In fact, the lock-in mechanism that bonds the α -I and α -II units is based on the van der Waals and weak hydrogen bonding interactions between the phenyl-ethynyl-pyridyl moieties and the *t*-Bu groups, as depicted in Figure 72 (blue circle).

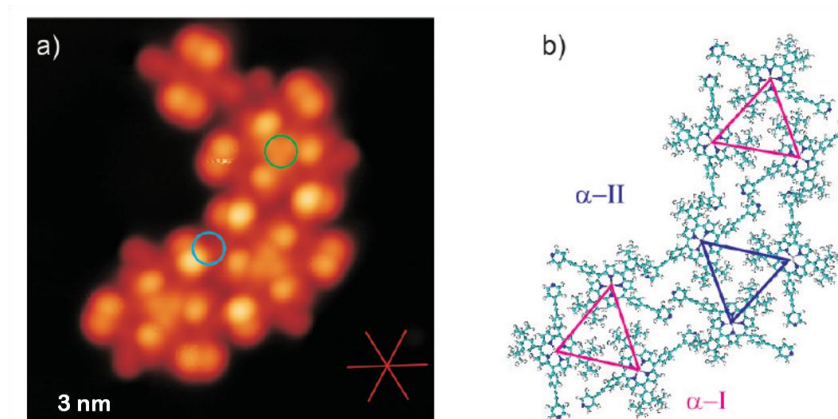


Figure 72. Combination of three trimeric aggregates. a) STM image of the three trimeric units formed by porphyrin **111** on Ag(111), exhibiting the deviation from the isolated trimer ($I = 0.2$ nA, $U = -1$ V). Colored circles emphasize the intermolecular interactions. The units α -I and α -II are depicted by a magenta and purple triangle, respectively. The red star represents the closed-packed directions of Ag(111); b) model of the three trimeric units as displayed in image a, showing the rotated units α -I and α -II.

At higher coverage, extended domains of a highly regular hexagonal supramolecular porous network are created by the alternation of units α -I and α -II (Figure 73). The pores are stabilized by (see circles in Figures 73b and c) i) van der Waals and weak hydrogen-bonding interactions between the $\text{PhC}\equiv\text{CPyr}$ substituent and the adjacent *t*-Bu₂Ph (blue circle) moiety; ii) van der Waals interaction between the *t*-Bu₂Phs groups,^[235, 283] involving three molecules (green circle). As a result, each molecule is connected to four neighbors, and all reactive pyridyl end groups are engaged in noncovalent bonding for the porous network structure. Both mirror-symmetric chiral domains of the hexagonal porous architectures have been observed: α -networks and β -networks made of conformers α and β , respectively.

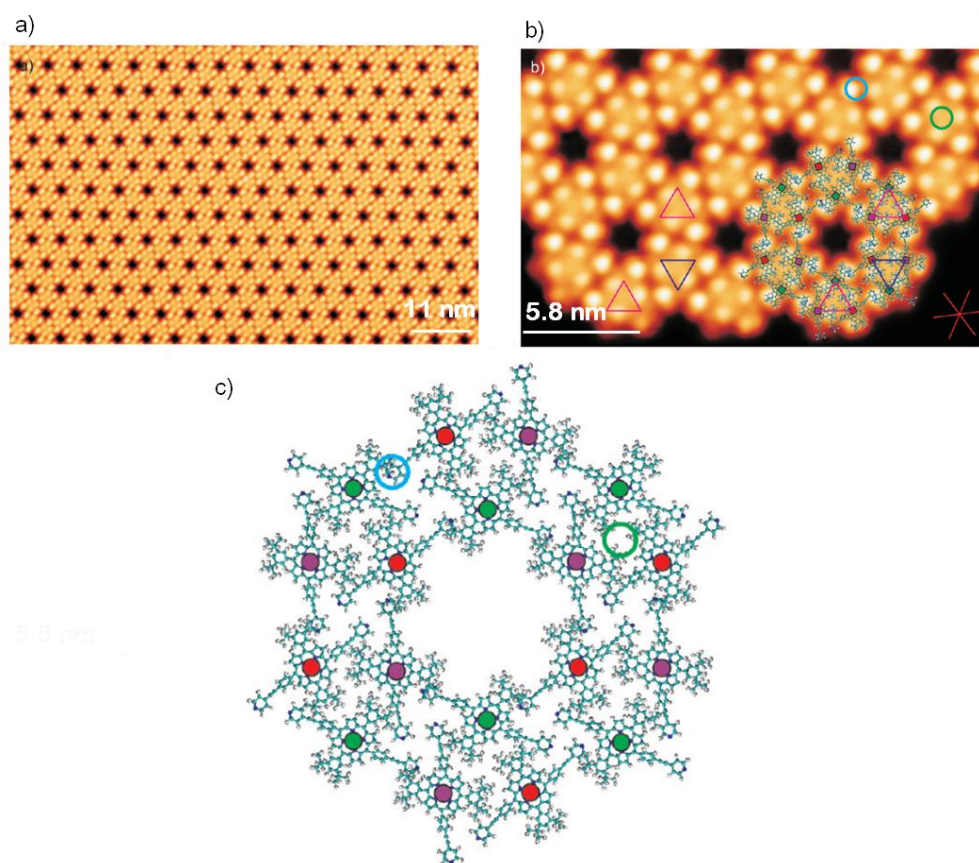


Figure 73. Extended homochiral domains formed by the assembly of trimeric aggregates. a) STM image of the three trimeric units formed by porphyrin **111** on Ag(111), exhibiting the deviation from the isolated trimer ($I = 0.2$ nA, $U = -1$ V). Colored circles emphasize the intermolecular interactions. The units α -I and α -II are depicted by a magenta and purple triangle, respectively. The red star represents the closed-packed directions of Ag(111); b) model of the three trimeric units as displayed in image a, showing the rotated units a-I and a-II.

The transition from the single enantiomer on the surface to the porous chiral domain implied three levels of hierarchy, where strictly the same enantiomers are involved, outlining a chirality transfer: conformer, trimeric unit and porous network (Figure 74). The high mobility of the molecular modules combined with the reported chiral recognition yields exceptionally large homochiral domains, often resulting in only one homochiral domain per terrace (Figure 74g). The α -pattern together with the β -pattern, in fact, could be both recognized on the same portion of surface.

The selection of one chirality might be triggered by the random aggregation of three isomers into a trimeric unit as shown above. We discarded any conformational adaptation of a conformer arriving at the border of a homochiral island made of the opposite conformer since we visualized both conformers at the boundaries of the domains and any manipulation with the STM tip in order to mirror the conformer at the boundary was unsuccessful.^[284] Furthermore, some islands are strictly found on a terrace without any border connected to the steps, which seems to suggest that chiral surface defects are not playing a major role as the starting point for the formation of the chiral supramolecular pattern.

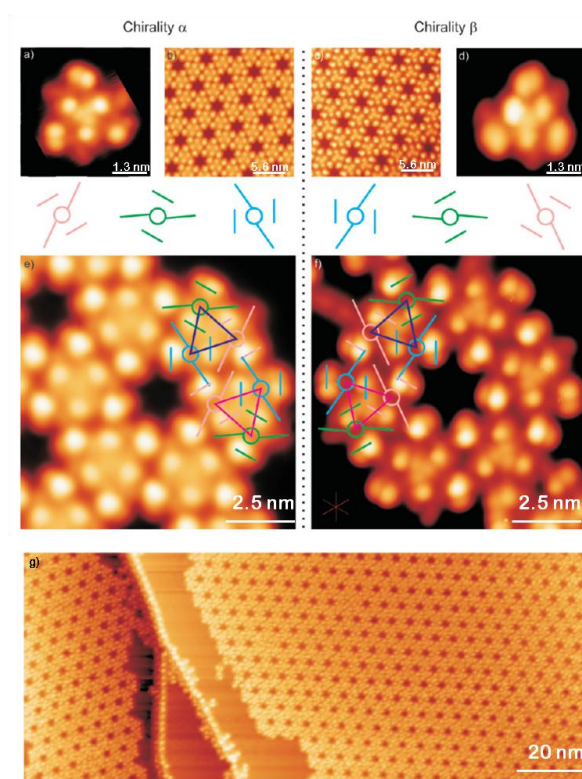


Figure 74. Mirror-symmetric homochiral networks from conformational surface enantiomers showing the transfer of homochirality. a-b, e) STM image showing the hierarchic formation of the α -chirality on Ag(111) (a, e: $I = 0.2$ nA, $U = 1$ V; b: $I = 0.2$ nA, $U = -1$ V); c-d, f) STM image showing the hierarchic formation of the β -chirality on Ag(111) (c-d, f: $I = 0.2$ nA, $U = -1$ V). Each chiral domain is strictly formed by a single enantiomer. For clarity, the three possible orientations for each conformer are depicted in light pink, green and blue colors, respectively. The units α -I (β -I) and α -II (β -II) are depicted by a magenta and purple triangle, respectively. The red star represents the closed-packed directions of Ag(111). The dotted line represents the mirror plane; g) formation of homochiral domains in adjacent terraces after deposition of porphyrin XX ($I = 0.2$ nA, $U = -1$ V).

3.1.3.2.1. Host-Guest interactions within the pore: towards future applications

The great potentiality of this type of porous network resides in the possibility of selectively accommodating molecular guest species within the pore. The size of the pore formed by the *trans*-like isomer **111** amounts to ~ 3 nm². This feature becomes particularly interesting for functional electron acceptor molecules that could yield an interesting optically active reaction center together with the electronically donating porphyrin molecules. Moreover, the chiral pore could be exploited as asymmetric-nanoreactor to selectively carry out optically active transformations, playing the role of the chiral ligand in the common organic synthesis.

An example of a pore hosting an individual porphyrin guest was observed in the course of our STM characterization of the nanoporous Ag(111) surface. In Figure 75 the settled *trans*-like module is very discernable within one pore. In addition, the size of the pore allows for three different porphyrin orientations (Figures 75 c-e). It is worthy to point out that the molecule is not exactly placed in the centre of the hosting pore but it is laterally shifted, due to the van der Waals interactions between one *t*-Bu₂Ph group of the guest and one of a neighboring molecule from the host pattern. Thus, the porphyrin can be locked in six different configurations: four of them are the one reported in Figures 75a and c-e.

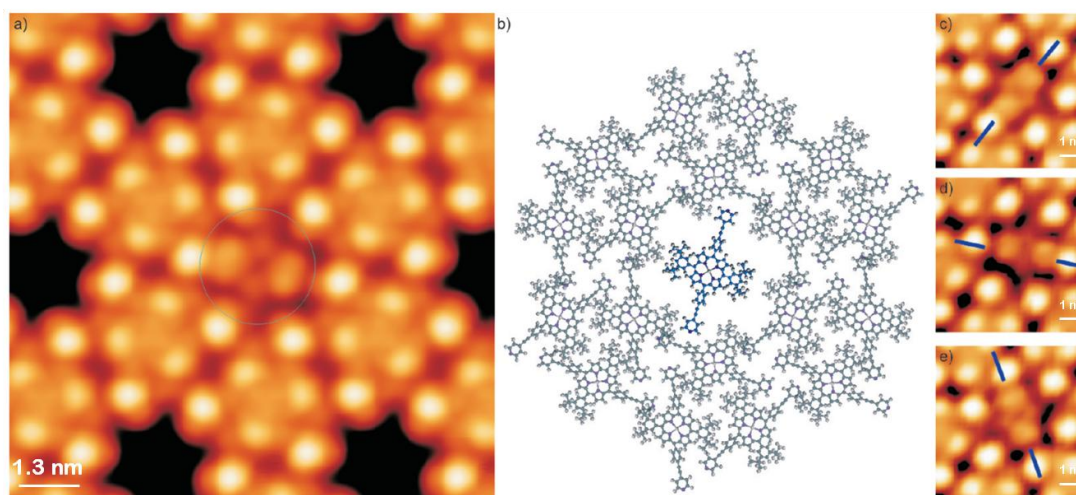


Figure 75. Host-guest interaction in the nanoporous network formed upon deposition of porphyrin **111** on Ag(111). a) STM image showing the pore hosting a porphyrin molecule (blue circle) ($I = 0.2$ nA, $U = 1$ V); b) schematic model representing the asymmetric displacement of the guest porphyrin in the pore; c) three different orientations of the guest within the pore (marked in blue lines) ($I = 0.2$ nA, $U = -1$ V).

3.1.4. UHV-STM Characterization on Cu(111) of Symmetric Porphyrins **117-119**

Tetrasubstituted pyridyl porphyrins **117-119** were deposited on Cu(111) surface and analyzed by STM. The primary goal was to build 2D infinite porous networks by metal-ligand coordination interactions provided by the pyridyl moieties and the Cu atoms present on the surface.

Porphyrin **117** was sublimed starting with an initial temperature of 400°C and then deposited on Cu(111) keeping the substrate temperature at 70°C. However, an increase, up to 500°C, of the sublimation temperature was needed to allow the molecules to reach the surface. In these conditions unrecognizable molecular aggregates of different sizes and shapes were observed on the steps and on the surface. Figure 76 presents a zoomed image of the substrate partly covered with undefined agglomerates. The complete absence of any arranged feature resembling the intact porphyrin molecule but the presence of fragments may induce thinking of a possible degradation of the porphyrin molecules. The decomposition of the porphyrin can be due to the fact that the sublimation temperature is probably higher than that of the porphyrin decomposition. This may be due to the presence of piles of π -stacked aggregates of porphyrin at the solid state, favored by the flat geometry of **117**.

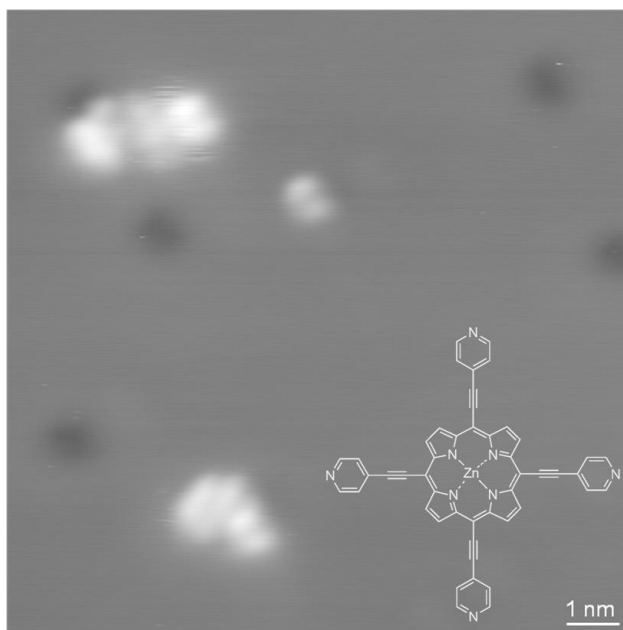


Figure 76. STM image taken after the UHV-deposition of porphyrin **117** on Cu(111) ($I = 0.2$ nA, $U = -0.6$ V) displaying undefined aggregates.

Porphyrin **118** was, subsequently, sublimed on Cu(111) in a various ranges of temperatures, starting from 440°C up to 516°C (Figure 77). The deposition on the metallic substrate afforded large agglomerates in which brightening lobes of different sizes are discernable. Similarly to the previous case, any of these molecular fragments could be referred to to pyridyl porphyrin **118**. Therefore, in this case too a decomposition process might have occurred. Although phenyl rings were here placed between the *meso*-positions and the ethynylpyridyl moieties, also for this molecule at the solid state the sublimation temperature was found to be higher than that of decomposition, leading to degradation phenomena.

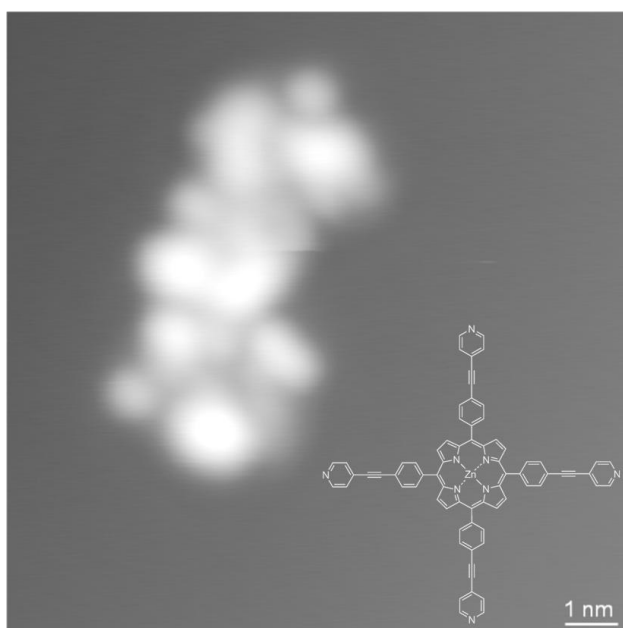


Figure 77. STM image taken after the UHV-deposition of porphyrin **118** on Cu(111) ($I = 0.2$ nA, $U = 1.0$ V) displaying undefined aggregates.

In contrast to previous porphyrins, the sublimation on Cu(111) of the last derivative **119**, performed at different temperatures, afforded the deposition some isolated species at 460°C that might be ascribed to molecules of **119**. In the red circle of Figure 78 an object with tetrafold geometry can be recognized. However, other smaller and bigger sizes species are discernable on the metallic substrate. These may derive from contaminants present in the original sample or it may be possible that a part of molecules decomposed, while only few arrived intact on Cu(111). Although single molecules of **119** were successfully deposited on the surface, the large majority of them decomposed impeding the formation of any ordered assembled patterns.

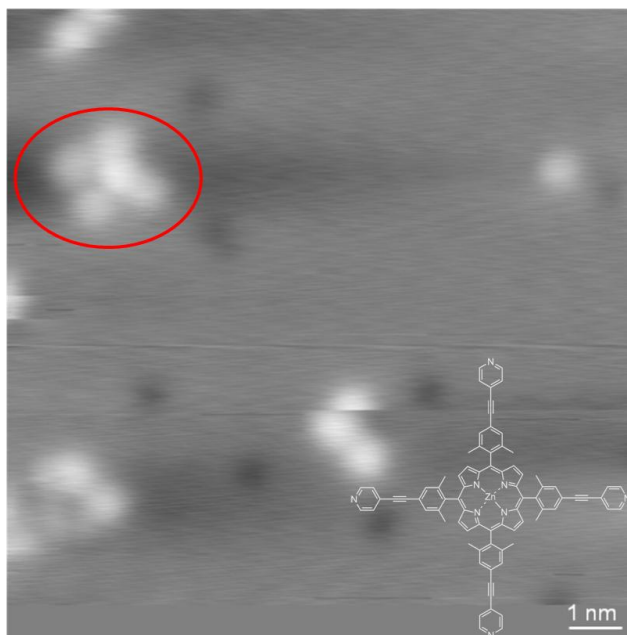


Figure 78. STM image taken after the UHV-deposition of porphyrin **119** on Cu(111) ($I = 0.1$ nA, $U = -0.5$ V). The red circle highlights the tetrafold symmetry object that can be assigned to a single porphyrin molecule.

The promising results obtained with porphyrin **119** induce to believe that the π - π interaction is not the only effect that comes into play in the sublimation of the tetrasubstituted pyridyl porphyrins. The dihedral angle formed by the rotation of the 2,5-dimethyl substituent should in fact impede the formation of these interactions. It might be possible, however, that side effects could provoke the rupture of the molecules, such as collateral reactions that the porphyrin might undergo. For this reason, we are currently inserting structural modifications in the porphyrin backbone in order to prevent these side reactions. However, these results will be reported elsewhere.

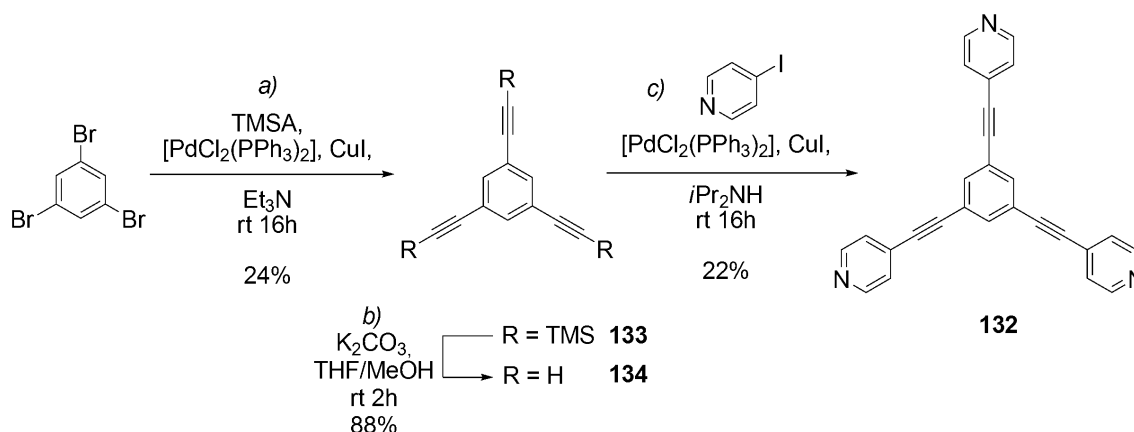
3.2. A Novel Pyridyl-Scaffold for Engineering 2D Glassy Crystals

In parallel with the exploitation of tetrapyrrolyl porphyrins for building 2D infinite porous networks, a novel pyridyl-bearing molecular module was developed with the initial aim to form 2D infinite network featuring different shapes and sizes of the porous. Molecular compound **132** consists of three pyridyl groups connected to a central benzene ring through alkyne moieties (see below). As observed for pyridyl porphyrin derivatives, the functional terminal groups are programmed to steer metal-organic interactions through pyridyl-metal-pyridyl coordination motifs. A key characteristic of this molecular module is the inherent flexibility of the substituents ($\equiv\text{CPyr}$) of the central benzene ring, which can awesomely deviate from the 120° internal angle between two pyridin-4-ylethynyl

peripheries, distorting the expected three-fold symmetry. The results obtained with the STM investigation of module **132** have been object of a work recently submitted.

3.2.1. Synthesis of Module 132

The synthesis of molecule **132** is outlined in Scheme 28. Pd-catalyzed *Sonogashira* cross-coupling reaction was exploited as general procedure for the preparation of tripyridyl derivative **132**.^[107] In the first step, a solution of 1,3,5-tribromobenzene in Et₃N was reacted with three equivalents of trimethylsilylacetylene (TMSA) in the presence of catalytic amounts of [PdCl₂(PPh₃)₂] and CuI affording TMS-protected triethynylbenzene **133** in 24% yield (Scheme 28, path *a*). Successively, the TMS groups were cleaved upon addition of K₂CO₃ in a mixture of THF and MeOH, yielding free triethynylbenzene derivative **134** in 88% (Scheme 28, path *b*). A final Pd-catalyzed *Sonogashira*-type reaction between derivative **134** and 4-iodopyridine in *i*Pr₂NH afforded targeted compound **132** in 22% yield (Scheme 28, path *c*). Molecule **132** was characterized according to a literature procedure (Chapter 4).^[285]



Scheme 28. Synthesis of the 1,3,5-tris(pyridin-4-ylethynyl)benzene **132**.

3.2.2. UHV-STM characterization of module 132

The deposition of compound **132** on Cu(111) at a substrate temperature of 350 K results in an assembly that exhibits polymorphism controlled by the degree of coverage. In particular, upon deposition of molecule **132** onto Cu(111) substrate novel non-crystalline states were formed. For this new system the term *2D glassy crystal* has been created.

In three-dimensional (3D) molecular materials science, an *amorphous solid* is defined as a material that possesses a non-crystalline structure.^[286] In particular, it is called a *glass* if it undergoes a glassy transition when heated to the liquid state.^[286, 287] On the other hand, a *molecular glassy crystal* is a material exhibiting a glassy transition involving a rotational disorder of the constituting molecular units, while their centers of mass form a regular crystalline lattice.^[288-290] Transferring these definitions and concepts to two-dimensional (2D) space, various surface-supported molecular architectures can be created via self-assembly of suitable molecular modules.^[167] Specifically, a few recent reports address 2D amorphous structures.^[291, 292] To simplify terminology (Figure 79), a *2D glass* is a supramolecular structure without spatial long range order, whereas the term *2D glassy crystal* describes a 2D supramolecular structure in which the centers of mass of the molecules form a regular crystalline lattice, but the molecules are disordered regarding their orientational or conformational degrees of freedom.

Regarding the supramolecular approach, for many surface-confined self-assembled nanostructures, the enthalpies of the intermolecular interactions are relatively weak thus implying that a fine interplay of enthalpic and entropic contributions determines the final self-assembled pattern. In particular, upon formation of a nanostructure, freezing conformations of a flexible molecule can make loss of the conformational entropy more significant to the self-assembly process,^[293] even leading to non crystalline condensed matter states.

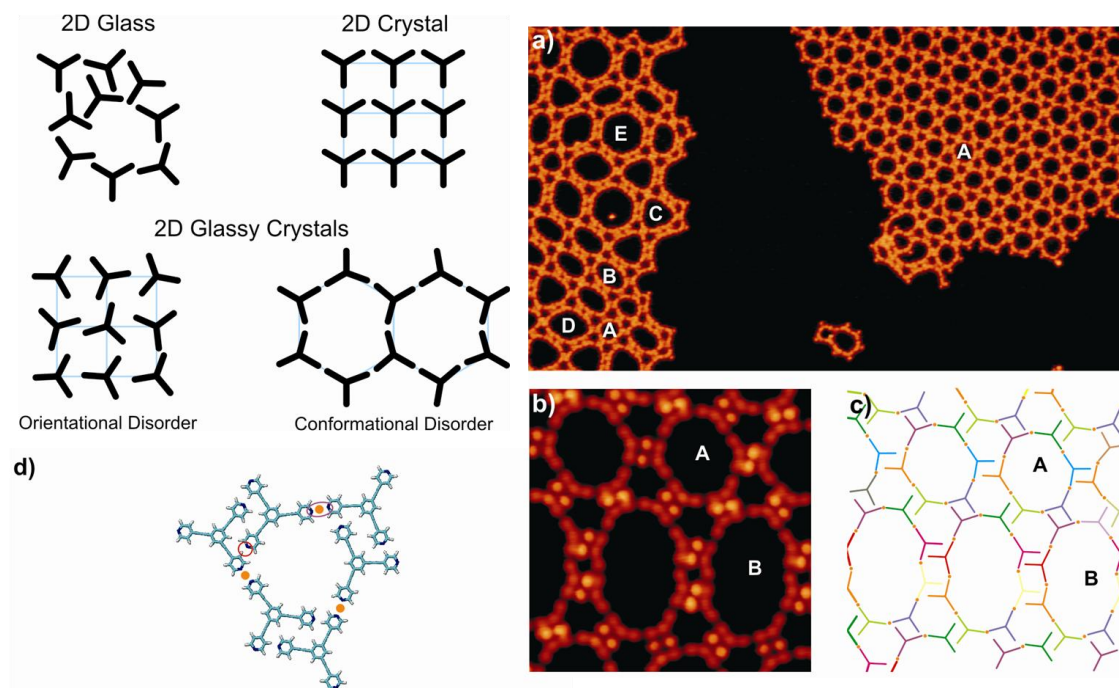


Figure 79. Up left: types of assembly of a 2D supramolecular structure regarding the spatial long range order of the building blocks. Other images: self-assembly of compound **132** on Cu(111) into a glassy crystal (phase α) coexisting with a glassy network, for coverages below 0.2 ML. a) Large scale STM image displaying one glassy island (left side) and one glassy crystalline island (right side); b) high resolution STM image depicting with submolecular resolution pores of type A and B; c) model of Figure 79b in the “stick” representation, in which each stick reflects the angular deviation from the in-gas three-fold molecular symmetry. Molecular units exhibiting the same opening angles are depicted with the same colors. Copper adatoms are represented by an orange circle; d) model of the two bonding motifs stabilizing the network: a two-fold pyridyl-Cu-pyridyl interaction (highlighted by a purple ellipse) and an intermolecular N-H bond between two neighboring pyridyls (highlighted with a red circle). Images sizes: a) 881 x 504 Å²; b) 135 x 135 Å². Tunneling parameters: a) I = 0.3 nA, V_b = 1 V; b) I = 0.2 nA, V_b = -0.2 V.

Therefore, as depicted in Figure 79a, for coverages below 0.2 ML the deposition of compound **132** results in the formation of a porous 2D glassy crystal (phase α) that coexists with a minority porous glassy network. Phase alpha is based on pores formed by six molecules (named as pores A); whereas the glassy network exhibits pores formed by six, eight, nine, ten and twelve molecules (named as pores A, B, C, D and E, respectively). A statistical analysis of the fractional occurrence of the pores at coverages of about 0.2 ML reveals a distribution where pores of type A are clearly the most frequent class (60%), followed by those of type B representing about 20%. With a probability of less than 10%, bigger pores of type C (9%), D (9%) and E (2%) are observed.

High-resolution images (Figure 79b) permit to discriminate individual molecules with submolecular resolution. Each molecule is characterized by four lobes, which correspond to the central benzene and the three peripheral pyridyl groups, respectively. As clearly seen for example in Figure 79b, the networks exhibit two different recognition motifs (Figure 79d): *i*) a head-to-head coupling between two dim pyridyl groups of neighboring molecules exhibiting a projected N-N distance of 3.4 ± 0.4 Å,^[294-298] and *ii*) an interaction of the one bright pyridyl group per molecule with the adjacent pyridyl ring. The latter is assigned to a N··H bond with a bond length of 1.8 ± 0.4 Å as recently reported at the liquid-solid interface.^[299] The pyridyl groups involved in the N··H interaction are

visualized as bright protrusions independent of the applied bias voltage, suggesting a non-parallel orientation of the heteroaromatic ring relative to the surface. Such a tilted conformation could enable π - π interactions between neighboring pyridyl rings and thus further stabilize the assembly. Based on the bond distance and previous reports, the motif is identified as a pyridyl-copper-pyridyl metal-organic interactions, where the mediating copper adatom (supplied by the surface) is not visible. In summary, each molecule is stabilized by two metal-organic coordinations and two N $\cdots$ H links. This demonstrates for the first time a simultaneous expression of these two different interactions, in contrast to previous studies based on the same terminal functional groups, where the metal-organic interaction is reported to dominate.^[294, 296-298] Here, the preference of the system for pores of type A could be related to a more favorable hydrogen-bonded and pyridyl-Cu-pyridyl configuration, as compared to pores of type B and C.^[300]

As mentioned before, for coverages above 0.2 ML a new glassy phase appears, in coexistence with phase α . Figure 80a depicts a high-resolution STM image of the molecular assembly in phase β , in which, as in phase α , the molecular appearance deviates from a three-fold symmetry. Different conformers exhibiting intramolecular opening angles between two legs ranging from 110° to 130° can be identified. The bonding motifs of the assembly are identical to phase α , *i.e.* each molecule engages in two N $\cdots$ H bonds and two pyridyl-Cu-pyridyl links with adjacent molecules (Figure 80b). However, the topology of phase β differs from phase α : in phase β the links between adjacent pores rely on pyridyl-Cu-pyridyl bonds, whereas in phase α the connection between pores is solely based on N $\cdots$ H interactions. The resulting porous network bases on different pores of quasi-hexagonal shape, with a mean area of 184 Å², each one characterized by a particular combination of four conformers. As discussed for phase α , the random component in the assembly is induced by the flexibility of the terminal groups, yielding different molecular conformations at each point of the lattice. Thus, by analogous arguments as those used for the description of phase α , we conclude that the assembly of phase β constitutes a 2D glassy crystal.

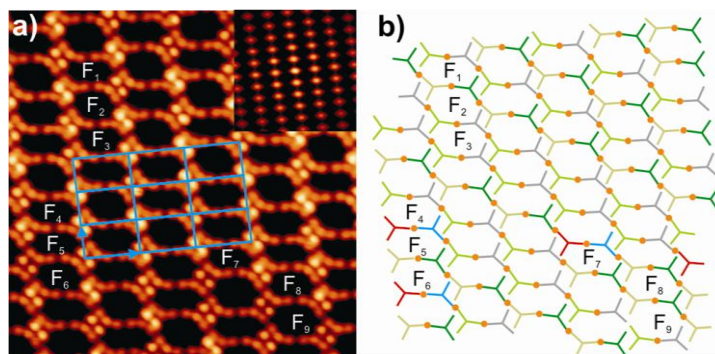


Figure 80. Self-assembly of compound **132** into a 2D glassy crystal (phase β). a) High resolution STM image depicting different types of rectangular pores. Each kind of pore is labeled with the term F_n (from F_1 to F_9). The inset represents the autocorrelation plot of the image. The repeating motif is displayed as a blue lattice (29.5 Å x 17.7 Å). b) Schematic model of Figure 80a highlighting the different conformers characterized by a deviation from a three-fold symmetry. Molecular units exhibiting the same opening angles are depicted with the same colors. Copper adatoms are represented by an orange circle.

3.3. Porphyrin-based Donor Acceptor Systems for Photovoltaic Devices

The photosynthetic system is considered the most elaborate nanobiological machine in nature.^[301] It converts solar energy into chemical energy, which is essential for living organism in the earth. The heart of the photosynthesis is represented by a cascade of photoinduced energy and electron transfers between donors and acceptors in the antenna complexes and reaction centers. For instance, in purple photosynthetic bacteria the light-harvesting antennas, namely chlorophylls and carotenoid polyenes, absorb light and rapidly transfer excitation among various chromophoric components to the reaction center.^[302] This is the place where the absorbed energy is converted to chemical energy in the form of charge separation. In fact, the vectorial electron transfer that occurs along the array of chromophores, produces a charge-separated state across the membrane with a quantum efficiency of nearly 100%. This charge-separated state eventually leads to the production of adenosine triphosphate (ATP) due to the proton gradient generated across the membrane.

The unique nanosized three-dimensional structure of these natural systems and the functions of solar-energy conversion have stimulated the scientific community to mimic such processes in artificially organized systems. Thus, with the final goal of solar-energy conversion and exploitation of suitable molecular devices, donor and acceptor molecules have been organized onto electrode surfaces to obtain details on the relationship between the surface structure and the photo-electrochemical properties.

Several classes of molecules have been tested into the active layers of a photovoltaic cell.^[303] In particular, porphyrins, due to their intrinsic electron-donor character show excellent electron and energy transfer abilities with small reorganization energies.^[152] Furthermore, the rich and extensive absorption features of porphyrins guarantee an increased absorption cross-section and an efficient use of the solar spectrum. For these reasons, they are considered as promising building blocks for molecular-based photovoltaic device.

In this section, porphyrin-based donor-acceptor systems for the construction of molecular photovoltaic devices are described. As acceptor moiety, Carbon Nanotubes (CNTs) were selected. The first sections of this part are dedicated to general introductions on photovoltaic cells, particularly stressing the Organic Photovoltaic Cells (OPV), and on carbon nanotubes structure, properties and chemistry.

3.3.1 General Introduction on Organic Photovoltaic (OPV) Cells

To stress the importance of photovoltaic cells, most commonly called solar cells, in today's society, it must immediately pointed out that every minute the sun delivers more energy to the earth surface than the entire world consumes in one year. This makes solar energy a potential source of virtually unlimited, clean, and free electricity, which is especially important if we take into account that earth's reserves of coal, oil and gas are finite and likely to become resource-depleted in the course of this century.^[304, 305]

Nowadays, solar photovoltaic devices belong to three main classes: inorganic (*e.g.* silicon), organic (*e.g.*, heterojunction cells) and photoelectrochemical cells (*e.g.*, dye sensitized solar cells). However, to a large extent the cells composed of inorganic materials are the most used today. Despite this, the technology based on silicon presents several drawbacks: *i)* the manipulation of these systems require particular precautions, such as atmospherically controlled hoods (better known as gloveboxes); *ii)* the cost of these materials is very high; *iii)* the fabrication of silicon-based cells requires high temperatures; and lastly *iv)* the production of such cells is limited to scarcity of the raw matter.

The ability of a material to produce electric current under illumination is called the *photovoltaic effect*. This process was firstly reported by *Becquerel* in 1839 and constitutes the basis of solar cells. He observed that the action

of light on a silver coated platinum electrode immersed in electrolyte produced an electric current.^[306] This discovery opened the way, forty years later, to the first solid state photovoltaic device, where an electric current was produced by inserting a sample of selenium in close contact with two heated platinum electrodes.^[307]

In general terms, the photovoltaic cell is used to convert the solar light in a flow of electric current. The active layer of the cell is placed between two metallic electrodes of different nature. This layer is constituted by a donor of electrons, characterized by a low electron potential, and an electron acceptor molecule with a high electronic affinity. The generation of electrical power involves three main steps: *i*) the sunlight photons are absorbed within the photoactive layer by the donor and/or the acceptor molecule, favoring the formation of electrons/holes pairs, called excitons, which subsequently start to migrate; *ii*) reaching the interface, the excitons dissociate spontaneously transferring the hole towards the donor and the electron towards the acceptor; *iii*) upon applying an electric field, the free charge carriers reach the electrodes, without recombine during their path. They are, thus, accumulated, collected and taken to an external circuit. Since the appearance of this first photovoltaic dispositive, the research community has made great strides in the developing of novel photovoltaic devices. One of the most important exemplar of PV cell was introduced by Grätzel *et al.*^[308] This dispositive is a hybrid as it involves TiO₂ particles and a dye. These types of cells are in fact called dye-sensitive solar cells. The light is absorbed by the dye immersed into porous TiO₂, in contact with liquid charge-transporter electrolytes, and converted in electric current. In particular, in the prototype described by Grätzel visible light is absorbed by the sensitizer, a Ru(II)(SCN)₂L₂ complex (L = 4,4'-dicarboxyl-2,2'-bipyridyl) which undergoes an electron transfer to the conduction band of TiO₂. The dye is then regenerated by hole injection into the hole-transport medium. The so formed holes and electrons are subsequently transported by electronic conduction to the contact electrodes. With these types of cell the solar energy conversion efficiency, η , (defined as the ratio between the maximum power produced by the cell and the incident light power on the representative area of the cell) reached *ca.* 12%.^[309] Nevertheless, the great limit of the Grätzel-type cell is the short lifetime exhibited, due to the progressive evaporation of the liquid phase. For this reason, PV technology underdevelopment is now completely dedicated at cells composed of solid state materials.

Since mid-1990s the novel technology of organic solar cells (OPV), in which photoactive organic materials are the main constituents of the cell, offered the prospect to make solar power affordable for far broader uses. The advantages presented by the OPV technology are several: *i*) it allows the employment of low quantities of materials; *ii*) it is possible to tune the optoelectronic properties of the organic molecules involved by modifying their chemical structures; *iii*) the OPV cells are composed of materials handy and the fabrication process does not require high temperatures, allowing the generation of very flexible thin films with plastic substrates. One of the most promising examples concerns the fabrication of cells composed of polythiophenes as donor molecules and C₆₀ derivatives as acceptors (in particular the most used is the phenyl-C61-butyric acid methyl ester, PCBM). The efficiency in this case does not exceed the 5%.^[310]

The schematic representation of different organic photovoltaic cells is depicted in Figure 81. The cells consist of a single layer of photovoltaic material sandwiched between two conductive contacts (electrodes) with different work functions. The photovoltaic material, essentially made of electron-donating and an electron-withdrawing species, can be disposed in two manners between the electrodes: two layers placed one on top of the other, one embedding the donor and the other, the acceptor ("heterojunction device", Figure 81a), or a bulk-mixture of both ("bulk-heterojunction device", Figure 81b). To allow the interaction of light with the photovoltaic materials, the device is built onto a transparent substrate (glass, plastic film) and one of the conductive contacts is also transparent, so that the material can absorb the incident sunlight photons and generate excitons. An exciton is an excited state that corresponds to a bound state of an electron, e⁻, and an imaginary particle called an electron hole, h⁺ (Figure 81c). Upon irradiation, an electron of the HOMO is excited to the LUMO orbital of the material leaving behind a hole of

opposite charge (process 1 in Figure 81c). As the promoted electron and hole have opposite electric charge, both remain bounded by a Coulomb force, which makes this state slightly more stable than a dissociated free electron and a hole. When the light-generated exciton reaches (mainly by diffusion) a dissociation site it separates into charges of different sign (process 2 in Figure 81c). The overall electric field between the two electrodes drives separated charge carriers towards the respective contacts (charge transport). This light-triggered transfer of one electron from a molecule to another is the photoinduced electron transfer. Finally, the charges are collected at the electrodes (process 3 in Figure 81c) to generate an electric current. In this way, the flow of absorbed photons is converted into a flow of dc power by the illuminated cell.

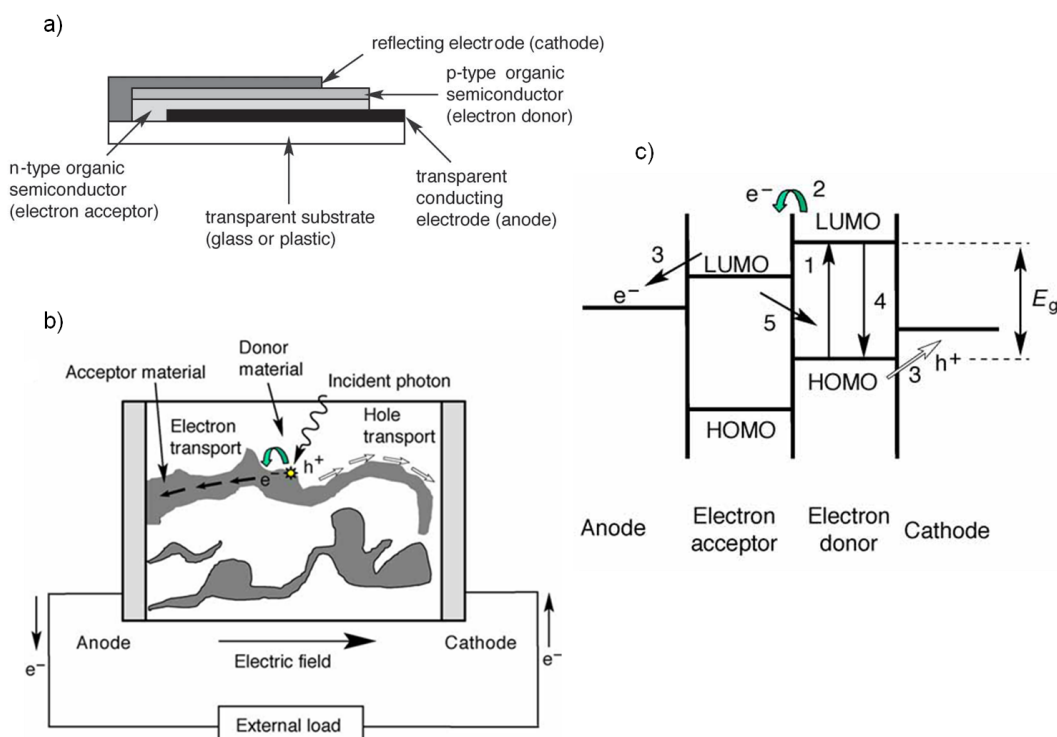


Figure 81. a) Typical heterojunction organic solar cell architecture; b) schematic bulk-heterojunction solar cell. Donor and acceptor materials are mixed together to form a dispersed heterojunction. Arrows denote electrons and holes movement. c) Schematic energy diagram of a donor-acceptor heterojunction.^[311]

In heterojunction and bulk-heterojunction devices, the exciton dissociation takes place at the donor–acceptor (D–A) interface leading to a free electron in the acceptor material and a free hole in the donor. One important limitation to the use of organic materials in this type of solar cells lies in their low intrinsic mobility for hole-transporting materials and are even smaller for electron transporters. One of the possible reasons of this low mobility is the high disorder of most organic solids. Thus, one strategy to enhance the mobility involves the employment of very well ordered molecules, like polymers which might arrange in ordered phases resembling liquid crystals. One of the most exploited polymer is the poly(3-hexylthiophene) (P3HT), employed as an absorber/donor substrate as well as charge-transporter medium. It has been shown that the molecular packing of the P3HT may influence both the optical and electronic properties of the photovoltaic material.^[312]

In order to achieve higher efficiencies, innovative materials as carbon nanotubes have been implemented in OPV cells.^[313, 314] They have been exploited as integrative part of the photoactive layer, and, alternatively, they have been used to construct semitransparent and flexible hole collecting electrode. The most common strategy to implement CNTs into the photoactive layer of an organic solar cells is based on the dispersion of CNTs in a solution of P3HT

based polymers and spin coating these blends onto a transparent conductive electrode. The potentialities of CNTs as integrative specie of OPV reside, not only in the electron-acceptor features, but also in their high aspect ratio which perfectly supports migration of charges along the tubular axis towards the electrodes limiting the undesired charge recombination phenomena. So far, the implementation of pristine CNTs in OPV devices has provided an average of efficiency equal to 0.1%.^[315, 316] Several factors are thought to contribute to the limited efficiency. Firstly, the poor dispersion of carbon nanotubes within the polymeric matrix may induce charge recombination processes. Secondly, incomplete exciton dissociation may occur especially at low CNTs concentrations. On the other hand dissolving higher percentage of CNTs could generate ropes or bundles where appreciable amounts of metallic entities should be considered.

There are several possibilities to improve the efficiency of CNTs/polymer based solar cells, especially with respect to morphology. For instance, very important is the developing of better processing procedures for a fine CNTs debundling in solvents or solvent mixtures. Other parameters to control are the purification, separation and shortening steps, which allow the debundling and processings of nanotubes. On the same line is the chemical derivatization of CNTs which favors the dispersability.

3.3.2. General Account on Carbon Nanotubes

3.3.2.1. Structure of Carbon Nanotubes

As in the case with numerous, important scientific discoveries, Carbon Nanotubes (CNTs) were accidentally discovered. Before nanotubes, however, fullerene was discovered by accident by Kroto, Smalley and Curl.^[317] C₆₀ is a truncated icosahedral cluster of 60 carbon atoms, bonded together in pentagons and hexagons, with 32 faces (Figure 82), 12 of which are pentagonal and 20 hexagonal. Because of the resemblance of the structure with the geodesic domes of the American architect Richard Buckminster Fuller, C₆₀ took his name as homage. Fullerenes was found in the products of the vaporization of graphite by laser irradiation during experiments aimed at understanding the mechanism by which long-chain carbon molecules are formed in interstellar space and circumstellar shells. Since their discovery and their bulk production, fullerenes have been the subject of intense research both for their chemistry and for their technological applications, especially in material science, electronics and nanotechnology. It this, then, from this intense research efforts on, that Smalley in 1990 proposed the existence of tubular shaped fullerenes and, one year later, carbon nanotubes were proved by Iijima in the side products of C₆₀ production.^[318] These observations opened the way to the intense research activity causing the renaissance in the study of carbon and its derivatives.^[319, 320]

Carbon nanotubes as well as fullerenes are considered as additional allotropic forms of carbon, beside the two well known diamond and graphite structures. Diamond is a transparent crystal of sp³ carbon atoms where each carbon is bonded to four others with a tetrahedral arrangement (Figure 82). The sp³ crystalline network gives diamond the unique properties of hardness, excellent heat conduction, electric insulation and optical transparency. Graphite is characterized by layered planar sheets of sp² hybridized carbon atoms, strongly bonded together in a hexagonal network (Figure 82). Each layer, called graphene, is weakly bonded and stacked through Van der Waals forces with other layers forming a pile-like structure. This gives graphite the typical softness and the cleaving properties. Additionally, because of the delocalization of the fourth electron of each atom in a 2p orbital, graphite conducts electricity on the plane of each covalently bonded sheet. The delocalization is also responsible for the higher thermodynamic stability over diamond at room temperature.

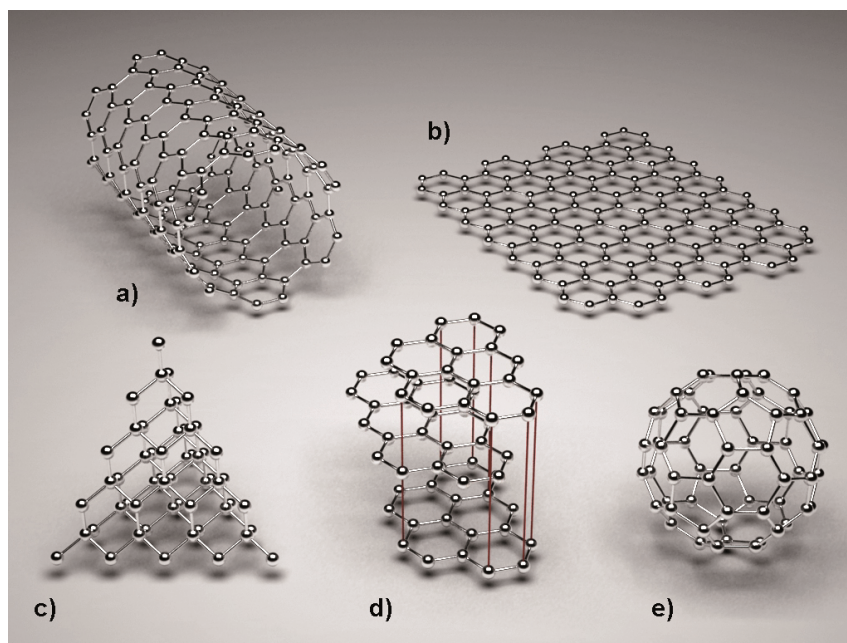


Figure 82. Allotropes of carbon. a) Nanotubes; b) graphene; c) diamond; d) graphite; e) fullerene.

Differently from the other allotropic forms, it is very hard to find a univocal definition of nanotubes, because of the large variety of structures, diameters and lengths. However, the simplest possible structure of CNTs can be visualized as one graphene sheet wrapped into a cylinder-like shape. There are two main types of carbon nanotubes that can have high structural perfection.^[321] Single Wall Carbon Nanotubes (SWCNTs) consist of a single graphene sheet seamlessly wrapped into a cylindrical tube, whereas Multi Wall Carbon Nanotubes (MWCNTs) comprise an array of such nanotubes that are concentrically nested like the rings of a tree trunk. Most SWCNTs have a diameter close to 1 or 2 nm, with a tube length that can be many millions of times longer, and due to the high ratio between the two dimensions they are virtually considered mono-dimensional objects. MWCNTs instead, depending on the number of layers, have a larger diameter, up to 200 nm, with an interlayer distance close to the distance existing between graphene layers in graphite, approximately 3.3 Å.

Another important definition of the characteristic and the properties of a nanotube is the way the graphene sheet is wrapped to form the cylindrical shape.^[322] The physical quantity that describes this aspect is called Chiral Vector (C_h), or Elicity and is indicated by a pair of integers (n, m) and two versors (a_1, a_2) by the following vector equation:

$$C_h = na_1 + ma_2$$

The chiral vector is determined by the diagram in Figure 83. Herein, if we imagine that the nanotube is unraveled into a planar sheet we could individuate two lines following two different directions in the graphene sheet: the *armchair* line, which travels across each hexagon, separating them into two equal halves, and the *zigzag* line. The wrapping angle θ is formed between the chiral vector and the zigzag line. If C_h lies along the zigzag line ($\theta = 0^\circ$), it is called a zigzag nanotube; if $\theta = 30^\circ$, the tube is of the armchair type. Otherwise, if $0^\circ < \theta < 30^\circ$ then it is a *chiral* nanotube. It is possible to derive other important characteristics from these vectorial interpretations of the nanotube structure. Considering that the vector a_1 lies along the zigzag line and that the other vector a_2 is a reflection of a_1 over the armchair line, when added together, they equal the chiral vector C_h . As a consequence, from equation 1 the values of n and m may determine the chirality, or "twist" of the nanotube. This might be useful considering that the chirality affects the conductance of the nanotube, its density, its lattice structure, and other macroscopic properties. For

instance, nanotubes with $(n - m)$ multiple of three are metallic; if $(n - m)$ is not a multiple of three, they are semiconducting with a band gap that inversely depends on the nanotube diameter.^[322] Consequently, when tubes are formed with random values of n and m , we would expect that two-thirds of nanotubes would be semi-conducting, while the other third would be metallic.^[322]

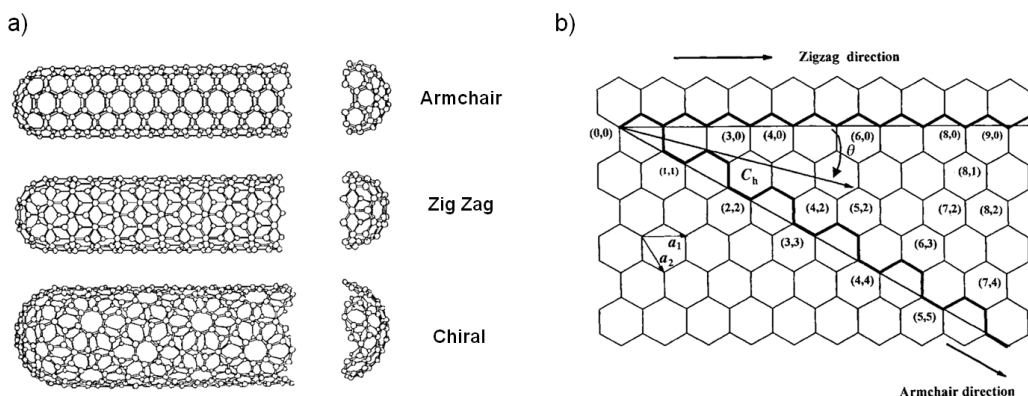


Figure 83. a) Models of armchair, zig zag and chiral types nanotubes; b) 2D graphene sheet explaining the chiral vector C_h and the parameters influencing the nanotube wrapping.^[320]

As with any material, defects can occur in the form of atomic vacancies. The possible defective structures can be classified into four main groups: *i*) topological, concerns the introduction of ring sizes other than hexagons, and one of the most known is the Stone Wales Defect,^[323] which creates pentagons and heptagons in the networks; *ii*) rehybridization (ability of carbon atom to hybridize between sp^2 and sp^3); *iii*) incomplete bonding defects (vacancies, dislocations, etc); *iv*) doping with other elements than carbon. Either they can be strategically inserted, for instance treating CNTs with very harsh acidic conditions,^[324] either defects can be present in the structure from the beginning. In any way their presence in the carbon network can lead to interesting properties and new potential nanodevices.^[325] Defects are in fact very important in the covalent chemistry of CNTs because they can serve as anchor groups for further functionalization (for more details on the chemical functionalization see section 3.3.2.2).

The synthesis of CNTs can occur in a wide range of environments. The basic prerequisites for their production are active catalysts, a source of carbon and adequate energy. The presence of the transition metal particles (*e.g.* Fe, Co, Ni) is essential for the formation of nanotubes and the diameter of the nanotube is often determined by the size of the metal particles.^[326] The fundamental methods for the preparation of CNTs include: *i*) arc discharge evaporation, *ii*) laser ablation, *iii*) solar energy, *iv*) electrolysis, *v*) chemical vapor deposition, *vi*) high pressure carbon monoxide. The focus of this dissertation it is non centered on the synthesis of CNTs, thus the interested reader is referred to some specialized reviews containing further details on their preparation and structural features.^[320]

3.3.2.2. Chemistry of Carbon Nanotubes

Because of their outstanding properties CNTs can be considered attractive candidates in many different nanotechnological and nanomedical applications. However, their major problem concerns the total lack of solubility and the difficult manipulation in common organic solvents that impose great limitations to the realistic application of pristine CNTs in materials, devices and biology. For these reasons, to be exploited into any type of devices an appropriate modification has to be undertaken in order to render them dispersible and thus processable. Along this line the chemical derivatization, either covalent either non-covalent, appears to be a powerful strategy to create homogeneous CNTs materials.^[319, 327, 328] Unluckily, the controlled functionalization of CNTs has not yet been fully

achieved: despite of the great advances solubility remains still a matter, and the field is far to be fully explored but new advances are still needed.

To introduce the reactivity of carbon nanotubes, it is essential the comparison with that of fullerenes. The reactivity of C_{60} is primarily driven by the strain produced by their spherical geometry. Important parameters to consider are the pyramidalization angle existing between conjugated carbon atoms, and the p-orbital misalignment between adjacent pairs of conjugated carbon atoms. A sp^2 -hybridized carbon atom planar implies a pyramidalization angle of 0° . Contrary, the sp^3 -hybridized carbon requires an angle of 19.5° . In the case of fullerene this angle is about 11.6° , meaning that the preferred geometry for the carbon atoms of C_{60} is trigonal rather than tetrahedral. For this reason, the chemical conversion of any trivalent to tetravalent carbon is accelerated by the strain relieved that strongly favors the addition chemistry on fullerene molecules. Beside the pyramidalization angle is the p-orbital misalignment which is very little in fullerenes as the p-orbital were found to be perfectly aligned.^[329, 330] This is not always the case, for carbon nanotubes for example. In this case, both the curvature induced pyramidalization and misalignment of the p-orbitals induce a local strain, leading to CNTs generally more reactive of a flat graphene sheet. Conceptually is useful to divide nanotubes into two regions: the end caps and the side wall. The end caps of a carbon nanotube resemble a hemispherical fullerene and its reactivity: this means that the strain relief brought by the chemical conversion of the sp^2 -hybridized carbon atoms into sp^3 -hybridized ones is such to determine a consistent reactivity of the end caps with respect of the side wall, irrespectively of the diameter of the entire tube. The side wall, instead, presents carbon atoms with a lower pyramidalization angle, but in the mean time the p-orbital misalignment is the major source of strain in that region. Furthermore, a differentiation is expected between the reactivity of carbon nanotubes of different diameters: smaller CNTs present a more consistent reactivity due to the higher strain since both the pyramidalization angles and the p-orbital misalignment of carbon nanotubes scale inversely with their diameter. This aspect explains the highest reactivity of SWCNTs and Double Wall CNTs (DWCNTs) towards addition reactions, compared to MWCNTs.

The modification of CNTs can occur in either covalent either non-covalent conditions. Specifically, the main approaches for the functionalization of carbon nanotubes can be grouped in several categories: *i*) covalent linkage of organic molecules on the CNTs skeleton; *ii*) non-covalent adsorption, wrapping and endohedral encapsulation of various molecules. The covalent functionalization may occur through amidation and esterification of oxidized SWCNTs mostly, or through addition reactions. The treatment of CNTs under strong acidic and oxidative conditions, such as sonication in a mixture of concentrated nitric and sulfuric acid, or heating in a mixture of sulfuric acid and hydrogen peroxides, results in the formation of short and opened tubes functionalized with oxidized functions as carbonyl, carboxyl and hydroxyl groups. These functionalities represent the starting point towards the further modification of nanotubes being able to react with alcohols and amines to give esters or amides. Differently, the addition chemistry involves synthetic methodologies to attach organic moieties directly onto the nanotubes sidewalls. These are mainly cycloadditions, electrophilic and nucleophilic or radical additions. Several reviews have been reported on the chemistry of SWCNTs describing exhaustive or representative examples of addition reactions as a way to modify SWCNTs.^[327, 328, 331, 332]

Two main standard procedures of amidation and esterification to be carried out on SWCNTs are reported, either using acid chlorides as intermediates or *via* carbodiimide-activated coupling. One of the first works on amidation reactions with shortened SWCNTs was reported by Haddon *et al.*^[333] They developed different types of strategies to improve the solubility of SWCNTs, functionalizing the oxidized tubes with octadecylamine and 4-tetradecylaniline (135, Scheme 29). The coupling was performed by means of oxalyl chloride passing through an acyl chloride intermediate before reacting with the desired amine. They also reported another procedure leading to the formation of zwitterions through an acid-base reaction between the oxidized CNTs and the amine. Interestingly, the long chains

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derivatives through the appearance of the characteristic photoelectron N 1s emission peak at 400.3 eV, typical of amide groups.

Other examples have been reported wherein hydrosoluble SWCNTs have been synthesized *via* the amidation protocols. Specifically, DNA-modified SWCNTs have been investigated, where the CNTs external walls have been functionalized with DNA strands.^[337] These adducts hybridized selectively with complementary sequences, with only minimal interactions with mismatched sequences. This aspect is very important as these systems may find a number of potential uses as very selective and reversible biosensors.

The alternative functionalization of CNTs by esterification of the carboxylic groups has been also extensively exploited. *Cosnier* and *Holzinger* reported the esterification reaction of a pyrrole derivative functionalized with long alkyl chains, **139**, with oxidized SWCNTs (Scheme 29).^[338] The organic derivatization on pyrrole-ester-SWCNTs derivative was found to increase the solubility of the whole system, which was easily dissolved in THF. The esterification methodology has also been largely applied to graft hydroxyl-porphyrin cores onto oxidized CNTs. Several examples are reported in literature dealing with the investigation of porphyrin-functionalized CNTs as powerful donor-acceptor complex exploitable, for instance, in photovoltaic devices. In Scheme 29 some of the porphyrin-based structures that have been functionalized to CNTs, **140-142**, are reported. However, a more detailed overview on these structures and, in general, on the covalent functionalization of porphyrin derivatives with carbon nanotubes is given in the following section 3.3.3.

3.3.3. Synthetic Approaches towards Porphyrin-CNTs Derivatives

Over the years several approaches have been developed in order to exploit the great electrical and mechanical properties of CNTs, and many have been the attempts of their derivatization for a potential employment in nanotechnology. To effectively utilize them, CNTs have been non-covalently and covalently functionalized in a number of ways to render them soluble in aqueous and organic solutions in a first instance.^[327, 331, 339-342] Subsequently, considerable research efforts have been dedicated to integrate the outstanding physicochemical properties of CNTs into practical and useful devices. In this line, the decoration of CNTs, especially SWCNTs, with chromophores has been particularly important in the development of novel structures for photovoltaic nanodevices.^[343-348] In this respect, porphyrin have received broad attention. The functionalization of CNTs with porphyrin macrocycles has been firstly used with the aim of improving the solubilization of nanotubes either in aqueous or organic solvents. In a second time, the porphyrin-CNTs composites have been widely exploited as donor-acceptor derivatives in view of their possible integration in photovoltaic devices. The intent of this section is to briefly review the non-covalent and the covalent ways of modification of CNTs with porphyrins.

3.3.3.1. Non-Covalent Approach

The supramolecular approach has been the first to be envisaged for the chemical modification of nanotubes with porphyrin cores. In principle, among the covalent and the non-covalent methods, the latter are more appealing because they do not significantly perturb the electronic and structural integrity of the nanotubes, permitting the use of both their conductivity and strength properties in eventual applications. For this reason, non-covalent strategies which involve physical adsorption of molecules capable of π -stacking or van der Waals interactions with the conjugated aromatic nanotube sidewalls are often preferred.

The first attempt to non-covalently graft a porphyrin molecule to SWCNTs was reported by the group of *Nakashima* in 2003.^[349] In this work the authors described the formation of a Zn protoporphyrin IX (**143**) SWCNTs

hybrid (**143**•SWCNTs) via one hour sonication of a solution containing **143** and SWCNTs in DMF and successive centrifugation to remove the insoluble CNTs (Figure 84a). In this way a very stable and homogeneous dispersion of **143**•SWCNTs hybrid was obtained. AFM measurements were carried out in order to reveal the structure of the modified nanotubes. Figure 84b evidences the AFM image of the DMF dispersion of **143**•SWCNTs. The top heights of the nanotubes along lines a-g were measured to be around 1.25-1.55 nm. The diameters of the nanotubes were found to range 0.9-1.5 nm, indicating the existence of individually dissolved SWCNTs in the solution since the diameter of the used SWCNTs is *ca.* 0.8-1.2 nm and the thickness of the porphyrin ring is *ca.* 0.3 nm. The porphyrin molecules were then responsible of bringing the nanotubes in solution due to the tight van der Waals and π -stacking interactions. In addition, in this work a preliminary photophysical study on the **143**•SWCNTs was reported. Specifically, UV-Vis absorption and fluorescence measurements were performed on the solution of **143**•SWCNTs (Figure 84c and d). The absorption maxima of UV-visible region for the **143**•SWCNTs DMF dispersion/solution appeared at 420 nm, characteristic of the Soret band, and 548 and 585 nm. These bands were found to be not shifted in wavelength if compared with those of the DMF solution of **143**. In parallel, fluorescence spectra were found to give evidences on the interaction between **143** and the nanotubes (Figure 84d). The peak maxima of the spectra, appearing at 588 and 643 nm, were registered at the same nanometers of those of **143** in DMF, but with a significant decrease in the fluorescence intensity for the re-solubilized **143**•SWCNTs solution. In a first instance, the fluorescence quenching has been assigned to an efficient energy transfer from the porphyrin macrocycle to the nanotubes.

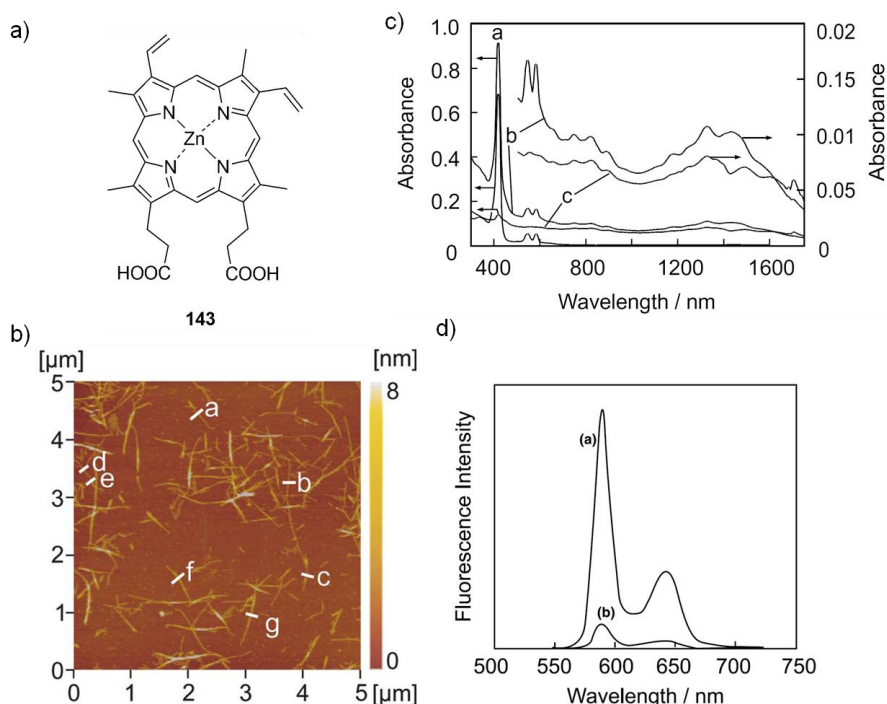


Figure 84. a) Structure of protoporphyrin IX, **143**; b) AFM image of a DMF dispersion of **143**•SWCNTs. The height profiles on the image were measured along lines a-g. c) UV-Vis-NIR spectra for DMF dispersion of solutions of **143** (a), **143**•SWCNTs (b), resolubilized **50**•SWCNTs (c); d) fluorescence spectra ($\lambda_{\text{exc}} = 420$ nm) of **143** (a) and resolubilized **143**•SWCNTs (b).^[349]

A dynamic coordinative-directed solubilization of SWCNTs in aqueous solutions has been achieved by Stoddart's group^[350] through a combination of a Zn-porphyrin complex **144** and a cis-protected Pd^{2+} complex **145**. These structures are believed to form charged acyclic and/or cyclic adducts on or around the side walls of SWCNTs (Figure 85a). The solubilization of the nanotubes in aqueous solutions only occurred when the supramolecular

complexes $[(144\cdot145)_n]^{2n+}$ were allowed to enter simultaneously into a self-assembly process with SWCNTs under mild conditions. These supramolecular complexes were prepared by adding equimolar amounts of **144** and **145** into a suspension of presonicated SWCNTs in a mixture of CH_3CN and H_2O . In order to facilitate the exfoliation of SWCNTs from bundles and to favor the intimate association with $[(144\cdot145)_n]^{2n+}$, the solution was heated under reflux. This system was characterized by high resolution TEM (Figure 85b). Specifically, upon deposition of the solution of SWCNTs and $[(144\cdot145)_n]^{2n+}$ onto the TEM grid, the formation of a thick film was observed. In particular, the film was composed of $[(144\cdot145)_n]^{2n+}$ complex, wherein the nanotubes were found to be randomly dispersed. Subsequently, due to air exposition and consequent solvent evaporation, the film of the supramolecular complex cracked. The SWCNTs, then, perpendicularly aligned with respect to the cracked part of the film and many parallel rows of nanotubes were observed.

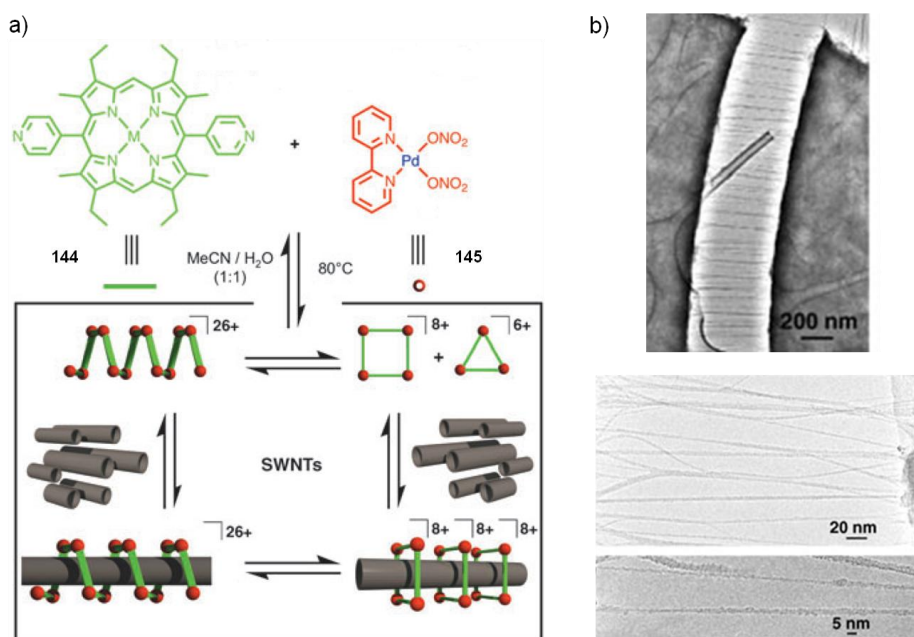


Figure 85. a) Dynamic coordination chemistry in action with SWCNTs designed by the group of Stoddart; b) HRTEM images of $[(144\cdot145)_n]^{2n+}$ complex with SWCNTs. Upper: exposed regions of a dried film along cracks that form spontaneously. Lower: magnification of precedent image showing the CNTs rows covered by $[(144\cdot145)_n]^{2n+}$.^[350]

Several other research groups have been intensively studied the behavior of porphyrin adsorbed on CNTs.^[351-355] Porphyrin-CNTs non-covalent complexes were also studied with the aim of fabricating molecular photovoltaic devices. Pioneers in this field have been the groups of Guldi and Prato.^[356] In their very first study, they described the incorporation into semitransparent ITO electrodes of non-covalent donor-acceptor system consisting of anionically functionalized porphyrin **146**, and a cationically functionalized pyrene (Py^+), stacked on SWCNTs (Figure 86a). The electrostatic interaction between the charged species of $[\text{SWCNTs}\cdot\text{Py}^+\cdot\mathbf{146}]$ was assessed through UV-Vis measurements, which exhibited the presence of the characteristic peaks of the porphyrin macrocycle at 435 nm and in the 550-600 nm region. Photocurrent measurements were performed in order to study the photo-response of the system under a luminous stimulus with monochromatic light. Specifically, upon addition of sodium ascorbate, an electron-donor that restores the oxidized porphyrin (fundamental to close the photo-electrochemical circuit), the photocurrent of the system significantly increased (Figure 86b). These results have been rationalized considering that the photoactivated porphyrin induces a charge separated state with the SWCNTs. Whereas the ITO electrode attracts the electrons from the reduced SWCNTs, the electron-donor sodium ascorbate reduces the oxidized porphyrins to close the circuit. The same measurements of photocurrent were also important to quantify the internal

photoconversion efficiency (namely the ratio of the number of charge carriers collected by the solar cell to the number of photons of a given energy that shine on the solar cell from outside and are absorbed by the cell) of the non-covalent system. The cell composed of [SWCNTs•Py⁺•**146**] reached 1.8% of efficiency. Furthermore, it is remarkably that a cell composed of a single layer of SWCNTs•Py⁺ and a single one of **146** alternated, reached 4.2% of conversion efficiency.

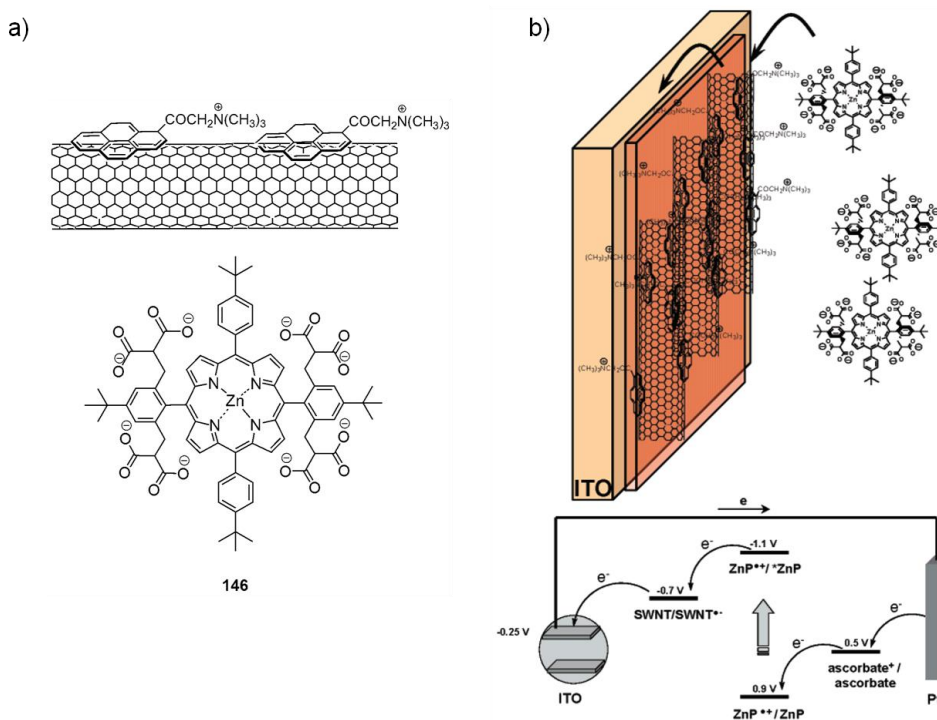


Figure 86. a) Structures forming the non-covalent assembly [SWCNTs•Py⁺•**146**] described by *Prato and Guldi*; b) schematic illustration of photocurrent generation in ITO electrodes covered with a single [SWCNTs•Py⁺•**146**] stack.^[339, 356]

Multiple units of porphyrin were also employed to form non-covalent aggregates with carbon nanotubes. The first reported example by *Adronov* and co-workers consisted in a conjugated Zn-porphyrin polymer bearing three hexadecyl branches linked via ether bonds to the aryl substituents on both the porphyrin meso positions, **147** (Figure 87a).^[357] In order to prepare complex **147**•SWCNTs, the authors described a procedure in which the porphyrin polymer and the nanotubes were solubilized in a mixture of THF and TFA. However, as confirmed by UV-Vis analysis the presence of TFA, which is often used to remove Zn²⁺ from the porphyrin core, did not affect the conjugated porphyrin **147** and no appreciable demetalation was observed (Figure 87b). The absorption of **147** in acidified THF was almost not shifted with respect to that in neat THF (Figure 40b, spectra a-b respectively). Nevertheless, significant changes were observed in the spectrum of the **147**•SWCNTs (Figure 87b, spectrum d) where marked bathochromic shifts of the Soret band from 467 to 498 nm and for the envelope of Q bands from 796 to 923 nm were detected. The origin of these shifts was ascribed to the coplanarization of the porphyrins within the polymer. In particular, the authors explained that the coplanarization of the polymer was occurring due to the template effect of the SWCNTs which restrict the torsional disorder within the polymer chain inducing the planar stacking of the polymer on the nanotube surface.

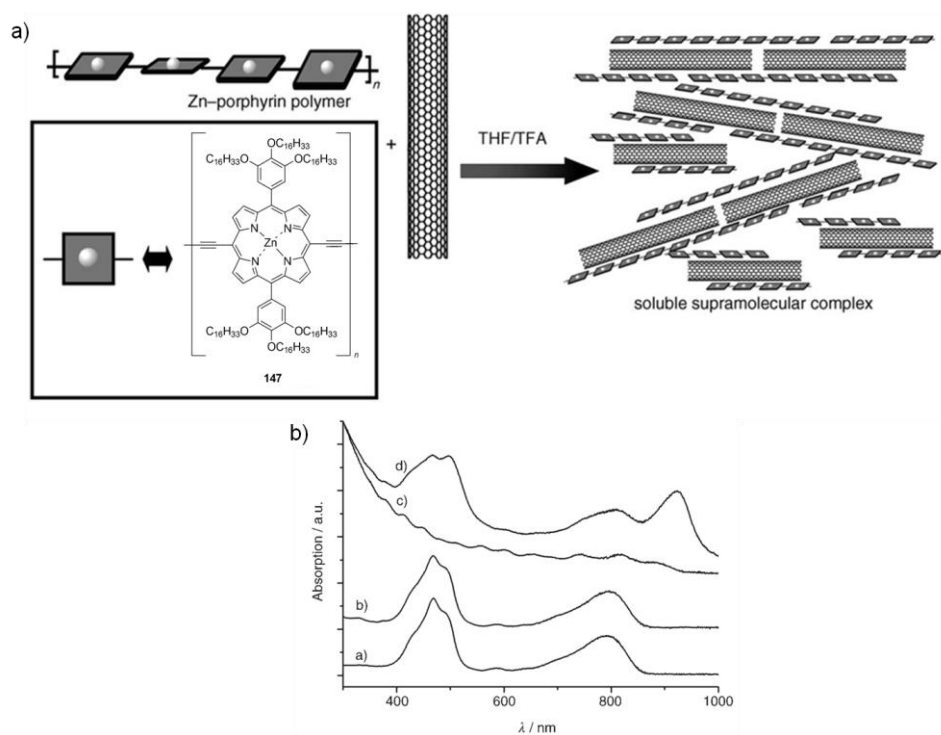
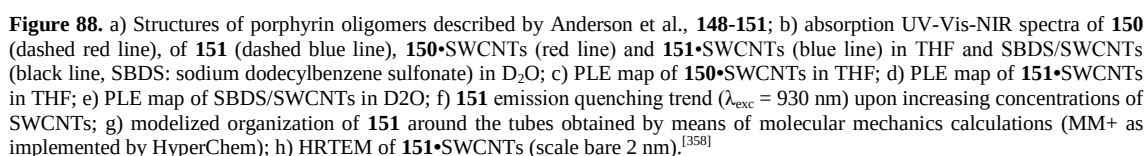


Figure 87. a) Supramolecular assembly of porphyrin polymer **147** with SWCNTs; b) absorption UV-Vis-NIR spectra of **54** in THF(a), **147** in acidified THF (b), SWCNTs in DMF (c) and **147**•SWCNTs in acidified THF (d).^[357]

A similar supramolecular assembly was recently designed by *Anderson's* group to get further information on the photophysical relationship between polymeric porphyrin chains and SWCNTs.^[358] They described the supramolecular interaction between different conjugated porphyrin oligomers, **148-151** (Figure 88a) and SWCNTs, formed in THF and successively isolated. Except monomer **148**, all the oligomers were found to completely solubilize CNTs in these conditions. However, once isolated and redissolved in THF only the tetrameric and hexameric porphyrin complexes, **150**•SWCNTs and **151**•SWCNTs, displayed good stability. As highlighted in the precedent example, same bathochromic shifts due to a coplanarization of the two porphyrin oligomers on the nanotube surface have been observed in the absorption spectrum (Figure 88b). The UV-Vis analysis evidenced also the presence of many absorption peaks in the area where $\lambda > 1000$ nm. These peaks are attributed to the numerous nanotube species present in the sample, identified by their own chiral indices (m,n). In the same way, Photoluminescence Excitation (PLE) maps also displayed the presence of numerous peaks characteristic of each type of semiconducting nanotubes (tube species are labeled with their indices in Figures 88 c-e). In general, the PLE maps of **150**•SWCNTs and **151**•SWCNTs present less emitting species compared to the same CNTs dispersed in H_2O , witnessing the different electronic environments. In order to study the electronic communication between the porphyrin oligomers and the nanotubes the supramolecular adducts were irradiated at the Q band absorption wavelength, between 850 and 900 nm. The PLE maps of **150**•SWCNTs and **151**•SWCNTs showed consequently nanotubes emission (dashed line in Figures 88c and d) while no emission was detected for CNTs alone (dashed line in Figure 88e). This is a proof of the electronic communication between the hybrids through an energy transfer process, the efficiency of which has been estimated around 10-20%. Another clue for the type of electronic communication existing in the investigated hybrids derived from the study of the porphyrin oligomers emission quenching. As depicted in Figure 88f, in fact, a marked quenching of the luminescence of **151**•SWCNTs was detected. In particular, the quenching effect presented a linear trend by increasing the concentration of CNTs into a solution of **151**. The highly efficient decrease of the hexamer luminescence in combination with the low values obtained for the energy



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presence of molecules **152** and **153** alone, meaning that the non-covalent interactions are very strong. To complete the characterization, AFM studies on mica surface were performed on **153**•SWCNTs complex upon spin coating few drops of the the complex solution in acidified THF solution (Figure 89c). The image clearly showed dispersed and almost isolated nanotubes with heights of about 2-4 nm, indicating that CNTs were debundled. The debundling was achieved *via* the organic functionalization with fused porphyrin derivatives.

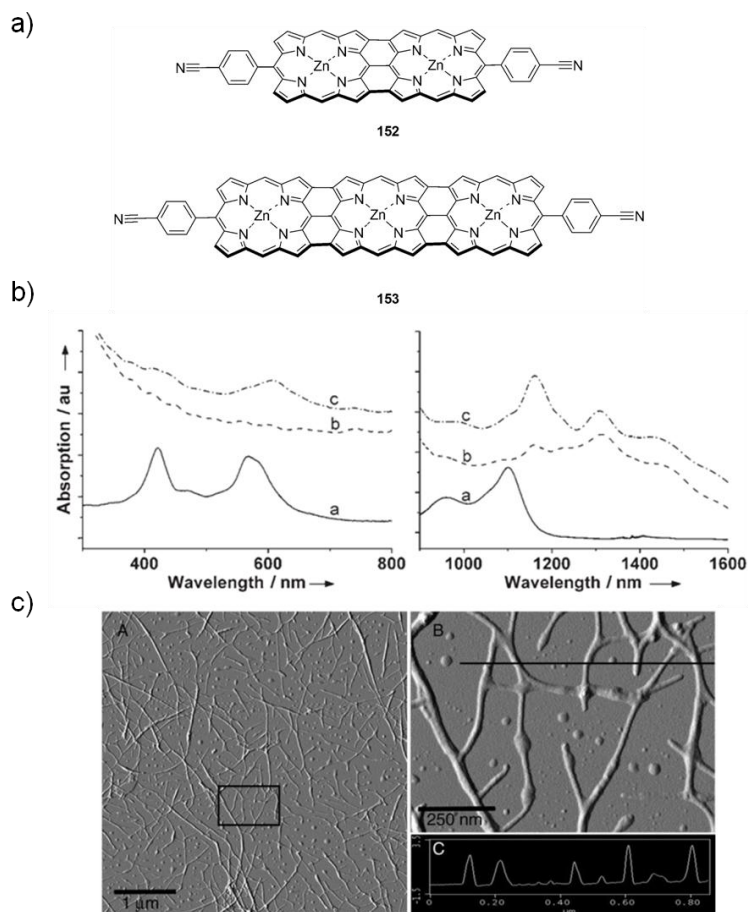


Figure 89. a) Dimeric and trimeric fused porphyrin wires, **152** and **153**; b) absorption UV-Vis-NIR spectra of **153** in acidified THF (a), SWCNTs in DMF (b) and **153**•SWCNTs in acidified THF (c); c) AFM images of **153**•SWCNTs spin-coated on mica surface. Left: $5 \times 5 \mu\text{m}$ with black box showing the region magnified in the right image. Right: magnified image and height profile of the black line is reported below.^[359]

3.3.3.2. Covalent Approach

It is generally admitted that extensive covalent functionalization of CNTs disrupts the conjugated π -system of the tube affecting the optical and electronic properties of the tube. However, two strategies have been considered in order to overcome this problem: *i*) the development of milder functionalization methodologies in order to retain the nanotube properties; *ii*) the employment of DWCNTs, wherein the covalent derivatization on the external tube can be afforded without affecting the inner tube and thus maintaining unaltered its properties.

On the other hand, when a chromophore is covalently attached to CNTs, the electronic communication, *via* electron transfer mechanisms, should be favored due to the fact that the electrons could be exchanged through space and/or through bonds. This aspect assumes a relevant importance when, for instance, covalent CNTs adducts are

considered for photovoltaic applications. As it will be reported in this section, however, this is not always occurring and often only energy transfer processes are observed.

As briefly presented in Scheme 29 of section 3.3.2.2, the very first example of covalently grafted porphyrin on SWCNTs was reported in 2004 by Sun and co-workers.^[360] In this work two porphyrin derivatives bearing a hydroxyl group were used to functionalize oxidized SWCNTs through ester functionalities. The porphyrin derivatives, reported in Figure 90a, were differentiated on the type of linker envisaged for the nanotube grafting. Specifically, porphyrin **140** features a hexyloxy chain, whilst **141** is connected to the tubes via a methylene bridge. Both **140**-SWCNTs and **141**-SWCNTs adducts were found soluble in aqueous and organic solvents. They were characterized by ¹H-NMR spectroscopy, wherein the nanotubes hybrids exhibited peaks at similar chemical shift of the corresponding porphyrin molecules, even though the peaks related to the covalent adducts appeared broader (Figure 90b). In order to investigate the electronic properties of these systems, UV-Vis absorption and steady-state fluorescence measurements were also reported (Figures 90c and d). Remarkably, the absorption spectra of **140**-SWCNTs and **141**-SWCNTs did not exhibit any significant change with respect to the spectra of **140** and **141** alone, suggesting weak contributions of the nanotubes presence. Contrary, an evident quenching of the emission of functionalized adduct **140**-SWCNTs was detected respect to the fluorescence signal of single porphyrin solution. The reduced fluorescence might be ascribed to the excited state porphyrin-to-nanotube electron transfer. Nonetheless, the authors discarded this hypothesis on the basis that any changes of the fluorescence quantum yield have been observed in solvents of different polarities. Thus, it is more probable that an intramolecular energy transfer process occurred rather than an electron transfer. The fluorescence spectrum of **141**-SWCNTs appeared, instead, exactly as the one of the solution of the single porphyrin **141**, without any observable quenching. Thus, according to the authors, there is a marked effect on type of spacer used to link the porphyrins to the tubes. Specifically, they claim that a longer spacer would drive the porphyrin core to accommodate parallel on the tube surface, easing the energy transfer between them. This conformation is not allowed with a shorter linker, which reduces the flexibility of the porphyrin.

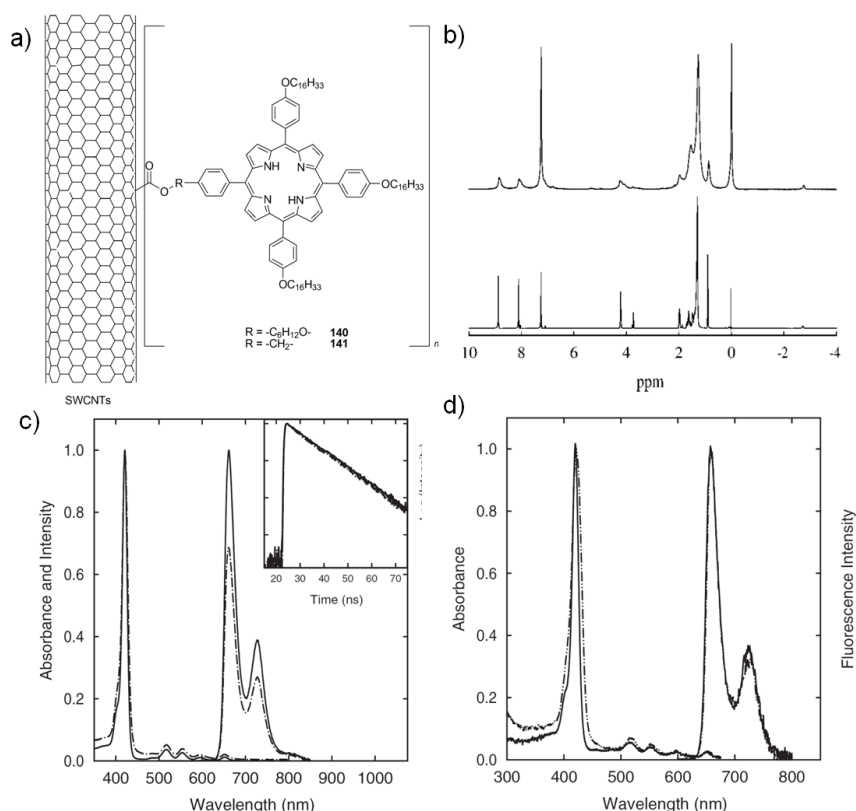


Figure 90. a) Structures of porphyrin-decorated SWCNTs with different linkers, **140**-SWCNTs and **141**-SWCNTs; b) ¹H-NMR spectra of **140**-SWCNTs (upper) and the free porphyrin **140** (bottom) in CDCl₃; c) absorption and emission spectra of **140** (solid line) and **140**-SWCNTs (dashed line) in THF at room temperature. Inset: fluorescence decays of the same solutions are compared; d) absorption and emission spectra of **141** (solid line) and **141**-SWCNTs (dashed line) in THF at room temperature.^[360]

Divergent results were, instead, described in the work of *Baskaran et al.*, wherein the photoinduced electron transfer between a monohydroxy-tetraphenyl porphyrin, **142**, and CNTs including Multi-Wall CNTs (**142**-MWCNTs) and Single-Wall CNTs (**142**-SWCNTs) were investigated (Scheme 29, section 3.3.2.1).^[361] The UV-Vis spectra of the porphyrin-CNTs hybrids showed a broad absorption in the range of 300-900 nm due to the absorption of the nanotubes (Figures 91 a-c). In the case of the MWCNTs adduct only the Soret band was clearly seen, while in the case of **142**-SWCNTs both Soret and Q bands were observed. In particular, respect to the spectrum of the single molecule **142** a bathochromic shift of about 28 nm was obtained for both the covalent derivatives. This shift was attributed to the existence in solution of the protonated form of the porphyrins, which might have been formed by an acid base reaction with the carboxylic groups of the oxidized nanotubes. Upon addition of few drops of triethylamine the Soret and Q bands came back to the original 423 nm wavelength value. These observations did not prove the presence of any energy and/or electron transfer processes. Luminescence measurements were, thus, necessary to further investigate the properties of the CNTs-conjugates. By exciting at 550 nm, a strong quenching of the fluorescence signal was detected for both the covalent hybrids (Figure 91c). This result was considered as a proof of the occurrence of an electron transfer process.

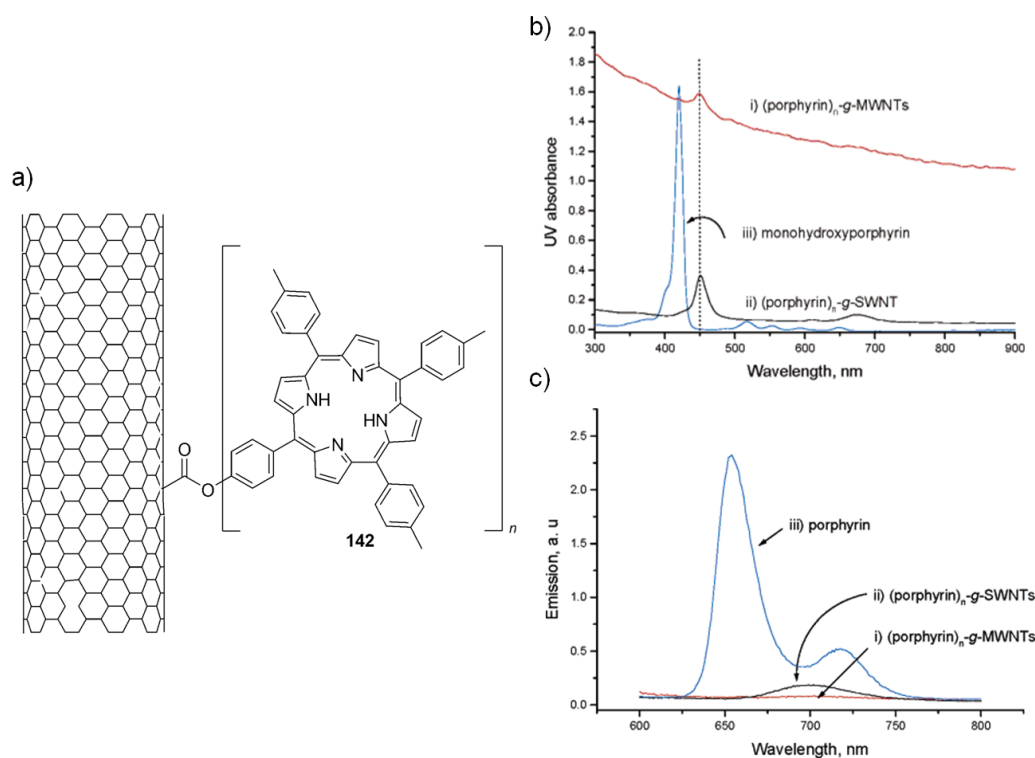
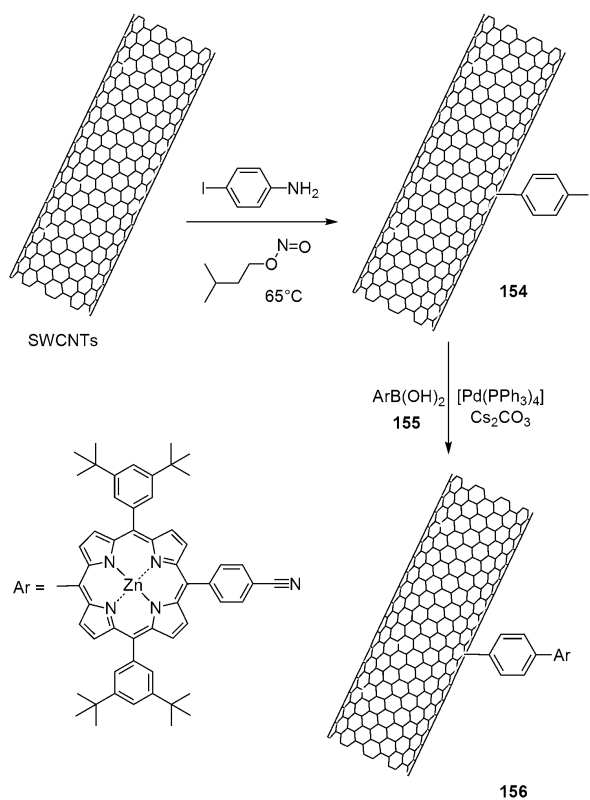


Figure 91. a) Structure of porphyrin-decorated CNTs investigated in the work of *Baskaran et al.*; b) UV-Vis spectra of **142** (blue line), **142**-SWCNTs (black line) and **142**-MWCNTs (red line); c) fluorescence spectra of **142** (blue line), **142**-SWCNTs (black line) and **142**-MWCNTs (red line).^[361]

Beside the esterification and amidation reactions as a way to graft chromophores to CNTs, *Adronov et al.* reported an alternative approach in which porphyrins were connected *via* a *Suzuki*-type cross-coupling reaction to pre-modified nanotubes.^[362] Specifically, starting from the iodophenyl-functionalized SWCNTs **154**, synthesized *via* the *Tour* reaction,^[363] porphyrin boronic ester **155** was coupled in the presence of $[\text{Pd}(\text{PPh}_3)_4]$ and Cs_2CO_3 in DMF, affording the porphyrin-functionalized SWCNTs, **156** (Scheme 30). **156** appeared soluble in several organic solvents, and was characterized *via* XPS, absorption and emission spectroscopies. XPS was employed to measure the changes in the elemental composition of **156** as a result of the cross-coupling reaction. The success of the *Suzuki* reaction was determined by analyzing the decrease in iodine content going from **154** to coupling product **156** (**154**: I $3d_{5/2}$ 2.4 at%; **156**: I $3d_{5/2}$ 0.1 at%), and by registering the appearance of nitrogen and zinc contents in the porphyrin-functionalized SWCNTs (N 1s 3.2 at%, Zn $2p_{3/2}$ 0.3 at%). In the absorption spectrum of **156** the Soret band was only 2 nm bathochromically shifted with the one of the reference porphyrin **157** (Figure 92a). Although a considerable quenching of the fluorescence signal of **156** was registered (Figure 92b), no explanation was given in the discussion of this work. Indeed, the authors just pointed out that the covalent functionalization did not substantially alter the electronic features of the hybrid.



Scheme 30. Synthesis of porphyrin functionalized CNTs, **156**, via the Suzuki cross-coupling reaction.

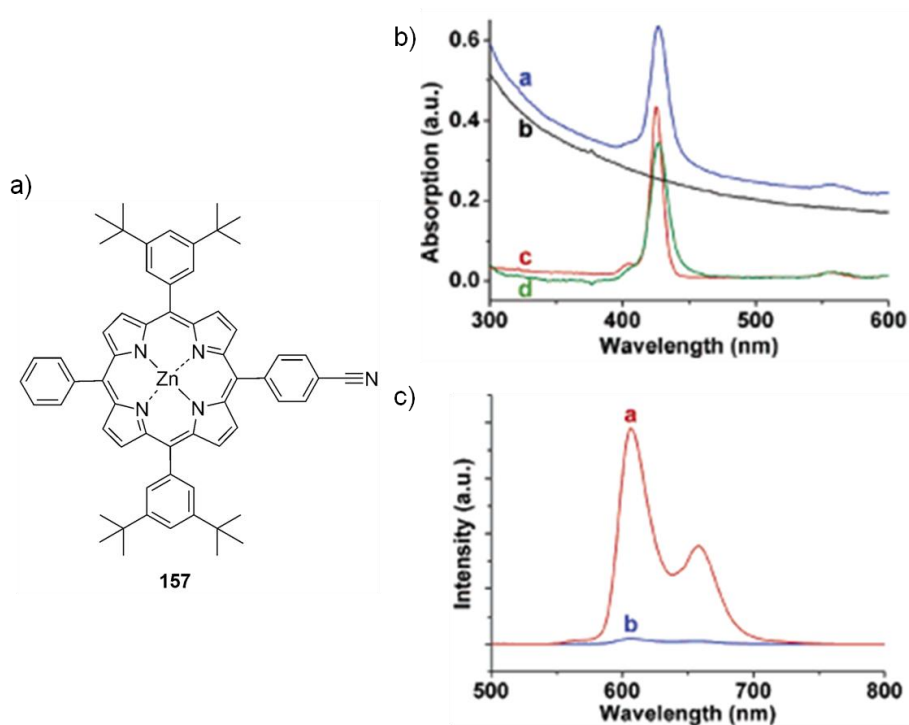
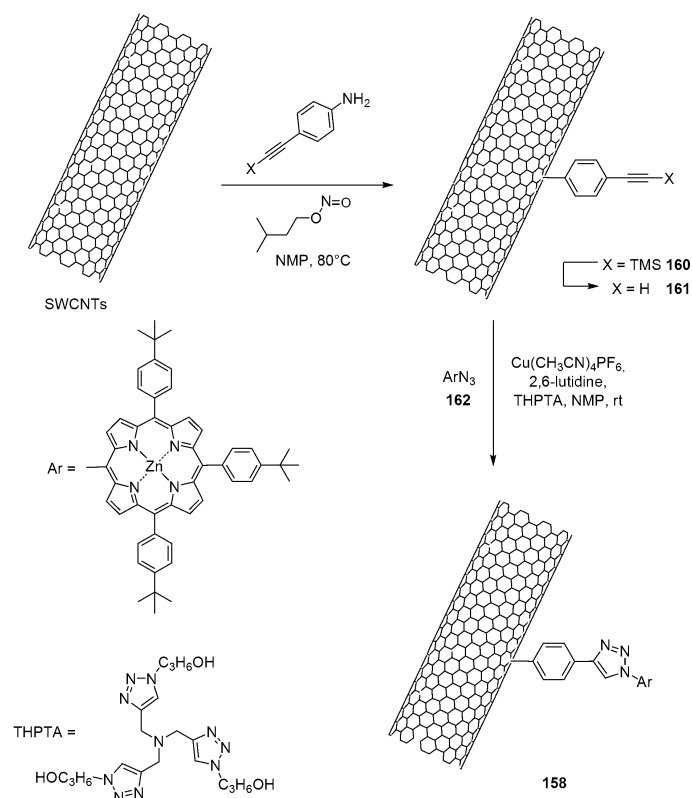


Figure 92. a) Structure of the model porphyrin **157**; b) UV-Vis spectra of **156** (blue line), **154** (black line), **157** (red line) and nanotube-bound porphyrin with nanotube absorption subtracted (green line); c) fluorescence spectra of **157** (red line), **156** (blue line).^[362]

As described for the non-covalent analogous, covalent porphyrin-CNTs hybrids were also investigated as suitable donor-acceptor conjugates for photovoltaic devices. *Guldi, Prato* and co-workers recently reported several examples of SWCNTs modified with porphyrin derivatives by means of dendronic spacers.^[339, 364-367] In one example, they designed two CNTs hybrids composed of SWCNTs linked to a porphyrin macrocycle through a triazole linker, **158**, and a second one where CNTs were modified with a second-generation triazole-based dendron bearing two porphyrin molecules, **159** (Figures 93a and b).^[366] The synthesis of adduct **158** is depicted in Scheme 31. Purified SWCNTs were functionalized applying the *Tour* reaction protocol with 4-(2-trimethylsilyl)ethynylbenzenediazonium, affording derivative **160**. The deprotected specie **161** was then coupled with azido-functionalized porphyrin **162**, via a Cu(I)-catalyzed modification of the *Huisgen* 1,3-dipolar cycloaddition.^[368] Derivative **159** was prepared with a similar pathway, through similar intermediates **160** and **161**. Hybrids **158** and **159** were characterized by XPS. In Figure 93c the survey XPS spectra of pristine SWCNTs, of intermediate **160**, and of the two porphyrin conjugates are reported; aside the corresponding high resolution spectra of the C, Zn and N peaks are displayed. All the spectra report the spectroscopic signature of carbon and oxygen, relative to the nanotube structure and to the defect sites introduced during the purification step, respectively. The spectra of the covalent conjugates, **158** and **159**, also present the signature of nitrogen and zinc, evidencing the presence of the porphyrin rings. An important information of the effective success of the triazole formation, is provided from the expanded N_{1s} region of **158**, which after deconvolution, revealed three peaks: one observed at a binding energy of 398.3 eV, characteristic of the four nitrogen atoms of the porphyrin macrocycle, one located at 401.8 eV attributed to one nitrogen of the triazole cycle, and a last peak at 400.3 eV related to the remaining two N atoms of the triazole. Clearly, the absence of the peak corresponding to the azido functional group (405 eV) witnessed the occurred linkage between the porphyrin and the modified nanotubes. A further proof for the presence of the porphyrin macrocycles on the two conjugates was adduced by the photophysical measurements (Figures 93d and e). Specifically, the absorption spectrum of the covalent adducts clearly exhibited the classical porphyrinic Soret and Q bands. The fluorescence spectra of conjugate **158** or **159** registered a considerable quenching of porphyrin **162** emission. In order to investigate the reasons of the observed luminescence quenching, transient absorption spectroscopy measurements were performed on both covalent porphyrin-nanotube systems **158** and **159** (Figures 93 f-h). From a comparison with the transition absorption experiment carried out on porphyrin **162**, the excitation at 387 nm of **158** produced two different sets of data. The first set corresponded to the single excited state of **162** attesting the successful excitation of the porphyrin (minima at 455, 580 and 630 nm in the spectrum of Figure 93f). Differently from what obtained with **162**, the singlet excited-state of the porphyrin rapidly decays in the presence of SWCNTs (Figure 93h), and a new broad peak in the region between 600 and 850 nm appeared (Figure 93f). These features led the authors to believe that a charge transfer process occurs between the linked porphyrin and the nanotubes. Similar results were shown by analyzing adduct **159**. In this case, though, the excited-state of the porphyrin was found to decay much faster (**158**: 820 ps vs **159**: 200 ps). In **159** the linker between the nanotubes and the porphyrin is the second-generation dendron that allows the porphyrin to get a closer proximity with the tube walls; this situation is not possible with the rigid spacer of derivative **158**.



Scheme 31. Synthesis of porphyrin functionalized CNTs, **158**, via the Cu(I)-catalyzed 1,3-dipolar cycloaddition described by *Prato*.

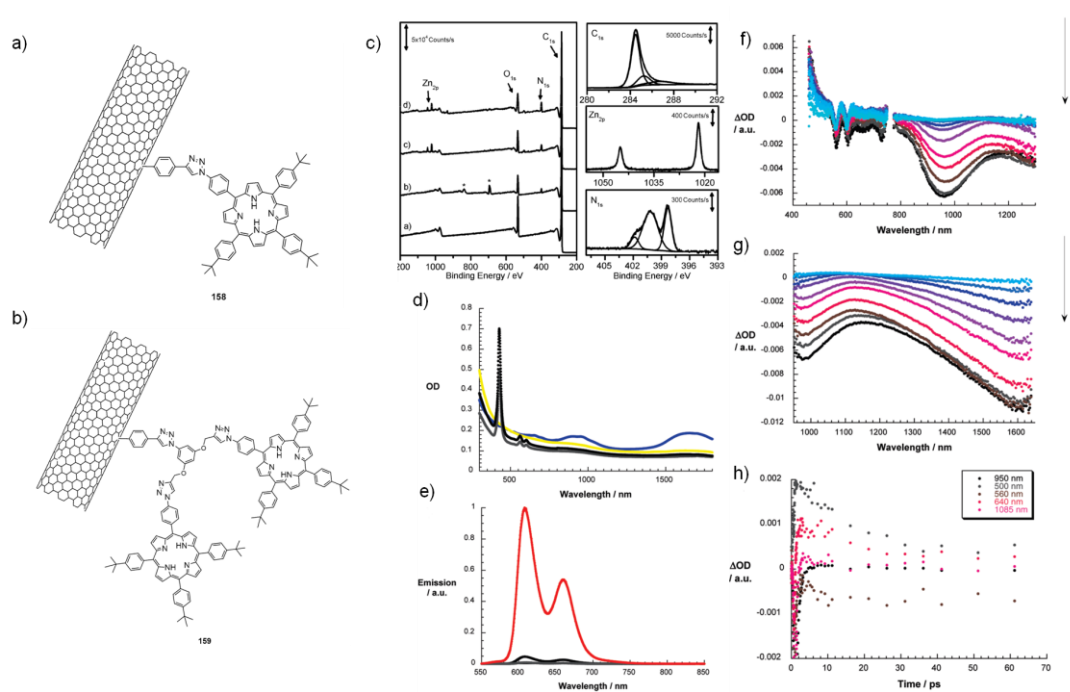


Figure 93. a-b) Structures of the porphyrin-SWCNTs systems based on triazole-type linker, **158** and **159**; c) Left: XPS spectra of purified SWCNTs (a), **160** (b), **158** (c) and **159** (d). Right: C 1s, Zn 2p and N 1s level spectra for **158**; d) absorption spectra of purified SWCNTs (blue line), **160** (yellow line), **158** (gray line) and **159** (black line) in DMF; e) room temperature fluorescence spectra of **158** (gray line), **159** (black line) and **162** (red line) in DMF; f) differential absorption spectra (visible and NIR range) obtained upon femtosecond flash photolysis ($\lambda_{\text{exc}} = 387$ nm) of **158** at room temperature; g) differential absorption spectra (extended NIR range) obtained upon femtosecond flash photolysis ($\lambda_{\text{exc}} = 387$ nm) of **158** at room temperature with time delays between 1 ps (black line) and 70 ps (blue line); h) time-absorption profiles of the spectra shown above monitoring the charge transfer.^[366]

3.3.4. “New Organic Materials for Photovoltaic Cells based on Carbon Nanotubes” (SUNTUBE) Project Objectives

The project described in these sections formed part of a collaborative network within the SOLWATT – R&D program, supported by the Walloon Region, named “*Nouveaux Matériaux Organiques pour Cellules Photovoltaïques Incorporant des Nanotubes de Carbone*” (New Organic Materials for Photovoltaic Cells based on Carbon Nanotubes, acronym: SUNTUBE). The aim of the SUNTUBE research network was to develop new organic semiconductors, with donor and acceptor abilities, and combine them with carbon nanotubes in order to be exploited within the active layer of a photovoltaic cell, gaining substantial improvements on their performances compared to those of the actual organic dispositives. To this end, the SUNTUBE project required the synthesis of novel electron-donating organic semiconductors, such as organic molecules or polymers. In view of favoring the electronic transport within the cell active layer, the SUNTUBE approach intended to incorporate CNTs, which can play the role of the acceptor and the electron transport at the same time. Though, in order to render effective the employment of CNTs, a homogeneous dispersion within the active layers is required. For this reason, the original objective of this project consisted in grafting the organic donor molecules on the external wall of nanotubes, allowing a closer contact between the two active materials and in the meantime avoiding the formation of bundles of CNTs aggregates.

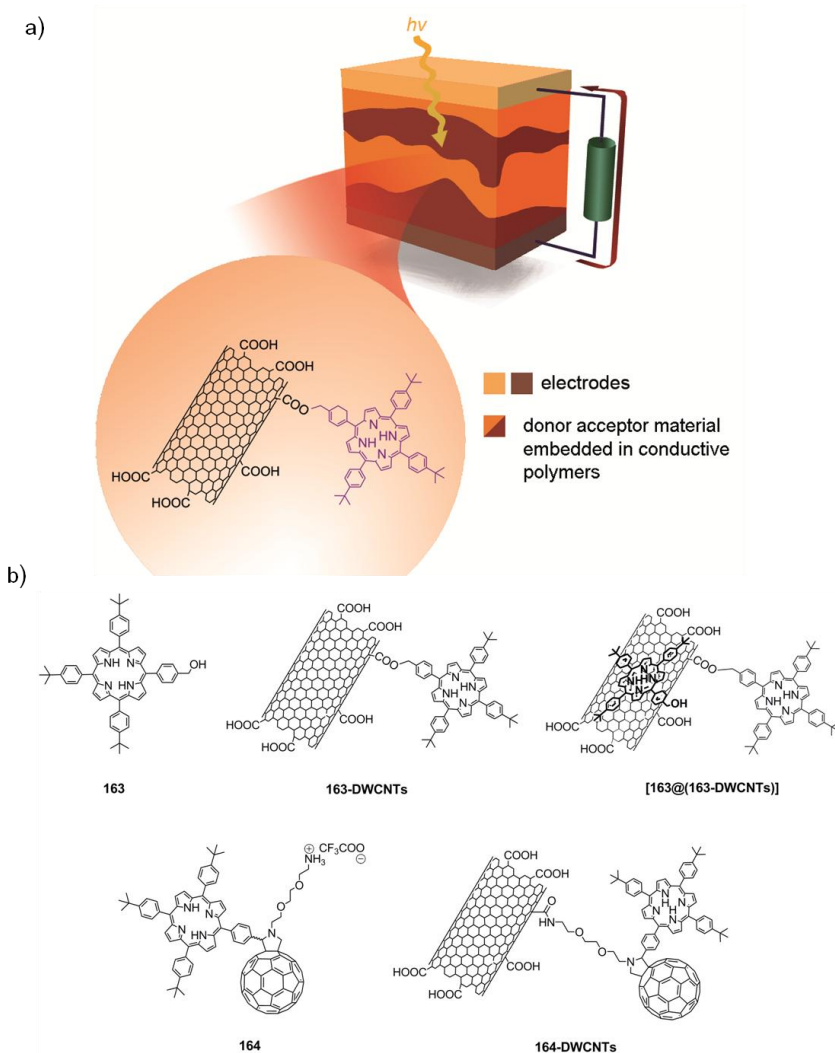


Figure 94. a) Schematic representation of a photovoltaic prototype showing the general idea of the SUNTUBE project; b) Porphyrin-based donor-acceptor systems investigated in this thesis.

The idea of this project, and thus the focus of the present part of this doctoral dissertation was to prepare porphyrin-functionalized CNTs, wherein the porphyrin molecule plays the role of the donor moiety while the nanotubes act as acceptor and/or electrons transporter (Figure 94a). As highlighted before, porphyrins due to their intrinsic electron-donor character have been proved to show electron and/or energy transfer abilities and have already been considered as important building blocks in the development of novel types of photovoltaic cells.^[301, 303] In addition, their high molar extinction coefficient, ϵ , in the visible part of the spectrum guarantees a strong absorption of the solar light.

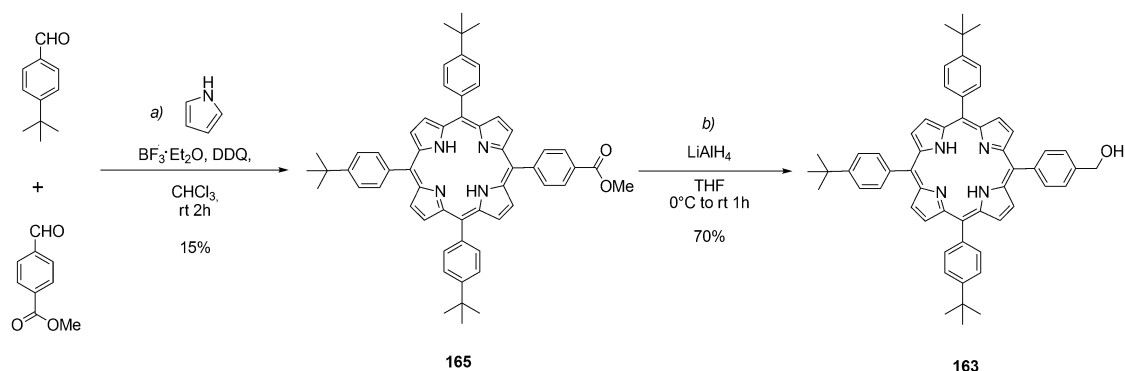
The porphyrin-CNTs conjugates envisaged in this work are depicted in Figure 94b. Pristine DWCNTs, **p-DWCNTs**, were treated in order that a covalent linkage or a physical adsorption of a monohydroxyl porphyrin derivative **163**, were both accessible. The chosen porphyrin derivative, **163**, is based on a tetrapyrrolic core differently substituted at the four *meso*-positions by three solubilizing 4-*tert*-butyl substituents and one benzyl hydroxyl function. Starting from oxidized DWCNTs, **163-DWCNTs** with the porphyrin molecule covalently linked to the external tube walls, and **163@163-DWCNTs** complex where **163** is partly covalently functionalized and partly physically adsorbed on the nanotubes, were produced by means of carbodiimide chemistry.^[369-371] Lastly, as a reference, the fully non-covalent porphyrin-CNTs hybrid **163@DWCNTs** was also prepared (see below). In parallel, porphyrin-C₆₀-DWCNTs, where the porphyrin molecule is substituted on the *N*-fulleropyrrolidine moiety (**164** in Figure 94) were also addressed in this work. Specifically, the first synthetic attempts towards conjugate **164-DWCNTs** (Figure 94b) are described in this work. This derivative was addressed due to the recognized efficiency of fullerenes in undergoing photoinduced energy/electron transfer when coupled with electron donating molecules, such as porphyrins or ferrocenes.^[303, 372]

In order to evaluate both morphological and conducting properties of the porphyrin-DWCNTs derivatives as dopants in active layers of photovoltaic cells, multilayered-type device was fabricated with the aim of investigating the interaction of the porphyrin-derived DWCNTs with a poly(3-hexylthiophene) end-capped by a pyrene unit (P3HT-Py) and containing small amounts of 1-[3-(methoxycarbonyl)propyl]-1-phenyl-[6.6]C₆₁ ([60]PCBM).

3.3.5. Synthesis of Porphyrin-Functionalized CNTs for Engineering Donor-Acceptor Components for Photovoltaic Devices

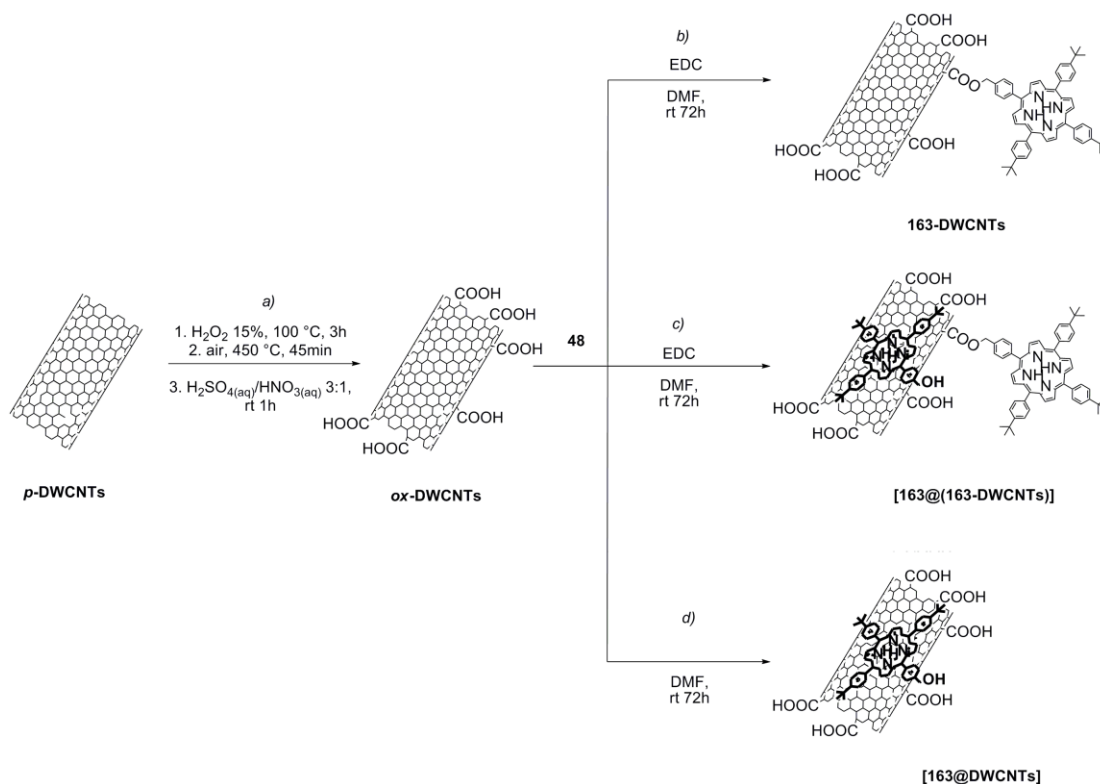
3.3.5.1. Covalently grafted Porphyrin-derivatives on CNTs

The synthesis of the starting materials and the final porphyrin-DWCNTs conjugates is outlined in Schemes 32 and 33. Due to the straightforward protocol, the mixed condensation reaction was selected as a procedure for the preparation of the porphyrin derivatives.^[373] Therefore, methyl ester porphyrin derivative **165** has been prepared following the typical Lindsay's procedure^[244, 374-376] using a 4:3:1 mixture of pyrrole, 4-*tert*-butylbenzaldehyde and methyl 4-formyl-benzoate in the presence of BF₃·OEt₂. Consecutive oxidation with DDQ (Scheme 32, path *a*) led to molecule **165** in good yield. Monosubstituted porphyrin **163** was then prepared in 70% yield from precursor **165** with LiAlH₄ (Scheme 32, path *b*).



Scheme 32. Synthesis of hydroxyl-porphyrin **163**.

In parallel, **ox-DWCNTs** were prepared following three oxidative steps (Scheme 33, path *a*). Pristine **DWCNTs**, **p-DWCNTs**, were first treated with an aq. solution of H_2O_2 (15%), following a recently reported mild procedure,^[336, 370] to open the CNTs tips and shorten their length by oxidative attacks. Subsequently, heat treatment at 450 °C for 45 min under an external air purge was carried out to remove the amorphous carbonaceous materials decreasing the carbon-coating of the metallic impurities and maximize the tip destruction. A final one-hour treatment with a 3:1 ratio mixture of aq. H_2SO_4 (95%) and HNO_3 (65%) solutions led to the final **ox-DWCNTs**. This step has been performed to enhance the number of carboxylic acid functionalities and to further remove metallic residues deriving from the catalyst. The oxidized DWCNTs were comprehensively characterized and the related results are reported in section 3.3.6.1.

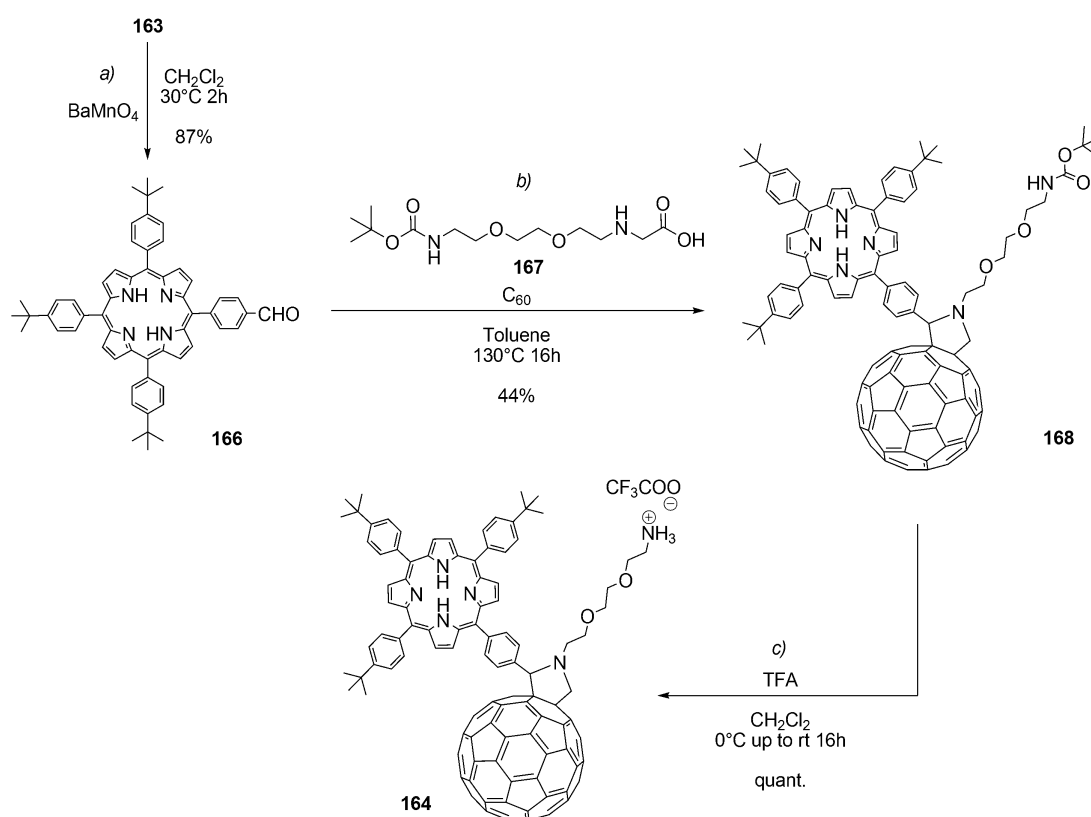


Scheme 33. Synthetic pathways towards porphyrin functionalized CNTs investigated in this thesis.

The as-prepared **ox-DWCNTs** were further used for the synthesis of the porphyrin-DWCNTs conjugates: **163-DWCNTs**, **163@163-DWCNTs** and reference **163@DWCNTs**. As depicted in Scheme 33, **163-DWCNTs** have been prepared upon sonication of a dispersion of **ox-DWCNTs** in DMF in the presence of EDC (Scheme 33, path *b*).^[336, 369-371] The final product was precipitated from DMF upon addition of H₂O to remove the excess of coupling agent and washed several times with CHCl₃ to completely discard the excess of non-reacted **163**. Meanwhile, following a slightly different protocol, conjugates **163@163-DWCNTs** were prepared (Scheme 33, path *c*). In this case, in order to preserve the adsorbed layer of **163** not covalently attached to the tube walls, the adduct was precipitated from H₂O and then directly isolated through precipitation from acetone. Finally, non-covalent derivatives **163@DWCNTs** were synthesized following the same experimental conditions as those used to prepare **163-DWCNTs** but without EDC (Scheme 33, path *d*).

3.3.5.2. Covalently grafted Porphyrin-C₆₀-derivatives on CNTs

The chosen synthetic strategy to link the porphyrin moiety to a fullerene molecule involved the 1,3-dipolar cycloaddition reaction between C₆₀, a porphyrin featuring an aldehyde function and a long chain aminoacid. In this way *N*-substituted fulleropyrrolidine derivatives can be synthesized.^[377] The long chain aminoacid was selected to improve the solubility in organic solvents of the CNTs-conjugate. The synthesis of porphyrin precursor **164** is reported in Scheme 34. Starting from porphyrin **163** the oxidation with BaMnO₄ in CH₂Cl₂ led to aldehyde **166** in 87% yield (Scheme 34, path *a*). **166** was then allowed to react through a 1,3-dipolar cycloaddition with C₆₀ and the Boc-protected aminoacid **167** that was synthesized according to a literature procedure and was already available.^[378] The Boc-protected *N*-substituted fulleropyrrolidine derivative, **168**, was then obtained with a 44% yield (Scheme 34, path *b*). In view of linking this intermediate to the **ox-DWCNTs**, the deprotection of the Boc-group was carried out. However, the deprotected compound revealed to be unstable during its chromatographic purification. Therefore, an alternative strategy was developed. Specifically, salt **164** was prepared by mixing protected derivative **168** with pure TFA overnight at 0°C, resulting in a more stable compound at room temperature (Scheme 34, path *c*). ¹H-NMR characterizations was not performed due to the poor solubility of **164** (Chapter 4). Thus, the structure of **164** was confirmed only by MALDI-HRMS spectrometry, registering the [M+1]⁺ molecular ion at 1765.5624 *m/z* of **164** (without the counteranion, Figure 95). The spectrum also reports a second peak at 955.6 *m/z* referred to a fragment of the molecule obtained after the loss of C₆₀ ([M-C₆₀]⁺).



Scheme 34. Synthesis of fullerene-porphyrin derivative **164**.

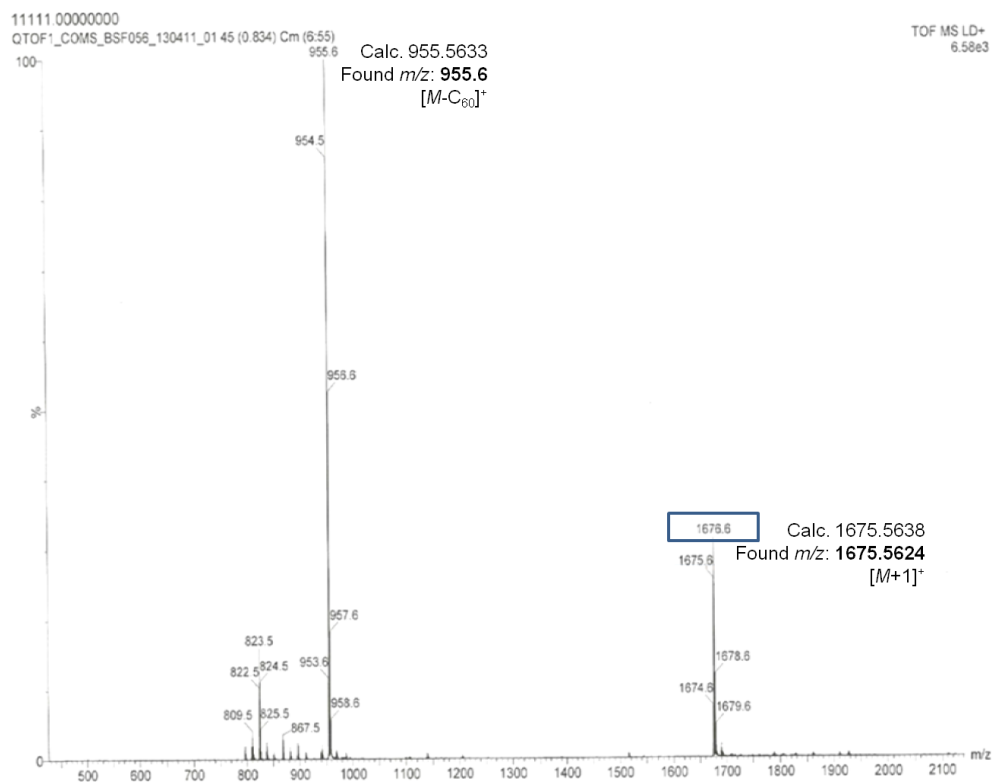
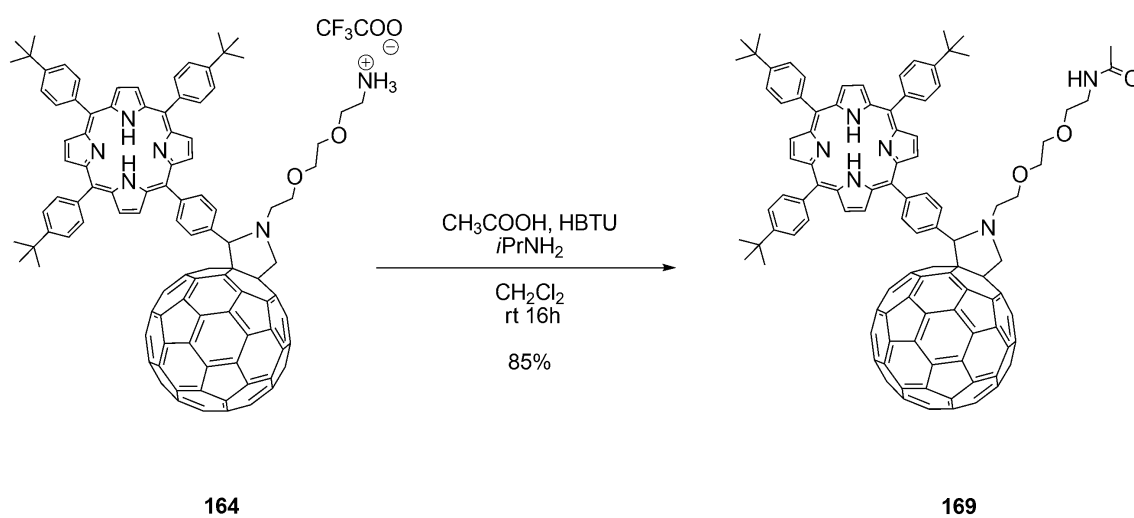


Figure 95. MALDI-HRMS spectrum of porphyrin- C_{60} trifluoroacetate salt **164** in the positive mode (matrix: DCTB MW: 250.12 g/mol).

To be involved in the preparation of the functionalized CNTs, the synthetic strategy here proposed envisages the *in situ* neutralization of **164** by the addition of a base to free the terminal NH_2 group. Before being applied on the **ox-DWCNTs**, the preparation of the corresponding acetamide **169** was performed as a proof of concept. Therefore, to a solution of acetic acid and HBTU in dried CH_2Cl_2 , **164** and $i\text{Pr}_2\text{NH}$ were added dropwise. Stirring this solution overnight at room temperature led to the formation of acetamide **169** in 85% yield (Scheme 35).

The described strategy of amidation reactions revealed to be very powerful to carry out the synthesis of CNTs-conjugates starting from unstable porphyrin-fullerene derivatives. However, the results related to the synthesis of porphyrin- C_{60} -CNTs conjugates will be reported elsewhere.



Scheme 35. Test reaction to prove the *in situ* neutralization of salt **164**.

3.3.6. Properties of Porphyrin-Functionalized CNTs Hybrids

3.3.6.1. Structural Properties of oxidized DWCNTs

As a first method to characterize the structural changes induced by the oxidative steps, X-Ray-based techniques were utilized, aiming at a qualitative and quantitative assessment of the chemical composition of the **ox-DWCNTs**. The EDX analysis of $150\ \mu\text{m}^2$ spots of both **p-DWCNTs** and **ox-DWCNTs** is reported in Figures 96 a-b. The atomic percentage (at%) compositions for C (0.277 keV), O (0.525 keV), and Fe (6.398 keV) are 94.46, 4.99 and 0.54 for **p-DWCNTs** and 87.80, 12.08 and 0.11 for **ox-DWCNTs**, respectively. These data indicate that the oxidative treatments increased the O at% content for **ox-DWCNTs** (+ 7.09 at%), decreasing at the same time the Fe at% to one fifth of the initial value (− 0.43 at%), thus indicating an enhanced purity of the sample. These results were in good agreement with those obtained by XPS investigation (Figures 96 c and d). Specifically, despite the lower beam penetration depth ($\sim 10\ \text{nm}$ and $\sim 100\ \text{nm}$ for XPS and EDX, respectively), XPS investigations assessed a clear enhancement of the O at% content in the oxidized samples (5.94 at% for O at 532.3 eV, meaning a + 3.06 at% with respect to **p-DWCNTs**). These results are in good accordance with previous findings in the literature, for which mineral acid treatments of CNTs determines high increases of the O at% content, as a consequence of the enhancement of O-bearing groups mainly ascribed to the carboxylic acid functionalities.^[324] In fact, by comparing the IR spectra (Figures 97 a and b) of the samples before and after the oxidation, a clear enhancement of the intensity of the CO-centered vibrational

transition at 1722 cm^{-1} corresponding to COOH functions is clearly distinguishable, corroborating the carboxylic acid character of the oxidized species.

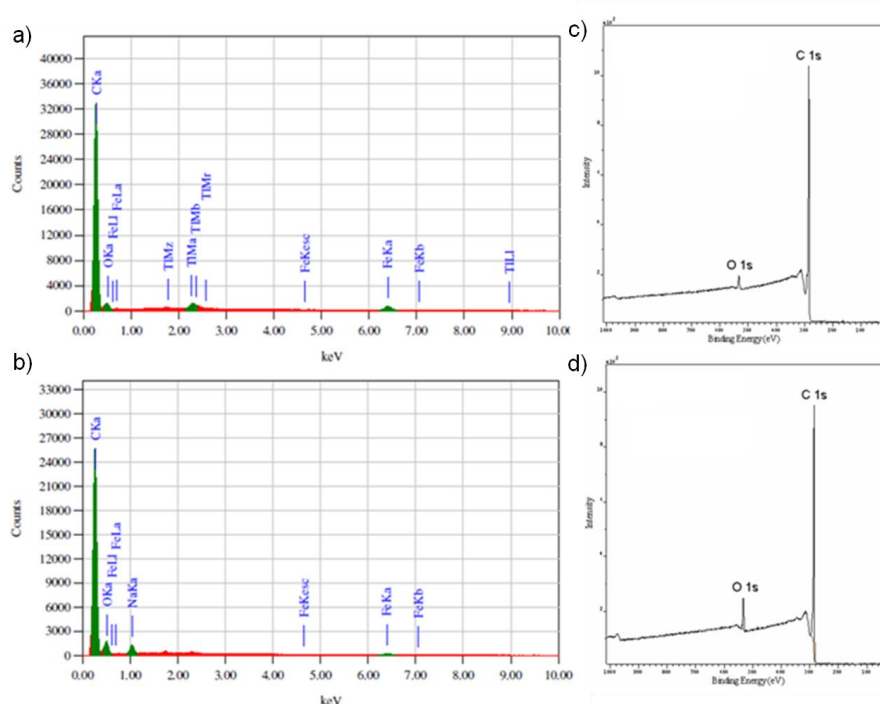


Figure 96. EDX spectra of (a) *p*-DWCNTs and (b) *ox*-DWCNTs. The compositional data as atomic percentages (at%) are C (0.277 KeV) = 94.46 at%, O (0.525 KeV) = 4.99 at% and Fe (6.398 KeV) = 0.54 at% for *p*-DWCNTs and C (0.277 KeV) = 87.80 at%, O (0.525 KeV) = 12.08 at% and Fe (6.398 KeV) = 0.11 at% for *ox*-DWCNTs respectively. XPS spectra of (c) *p*-DWCNTs and (d) *ox*-DWCNTs. The compositional data as atomic percentages (at%) are C (284.5 eV) = 97.12 at% and O (532.3 eV) = 2.88 at% for *p*-DWCNTs and C (284.5 eV) = 94.06 at% and O (532.3 eV) = 5.94 at% for *ox*-DWCNTs respectively.

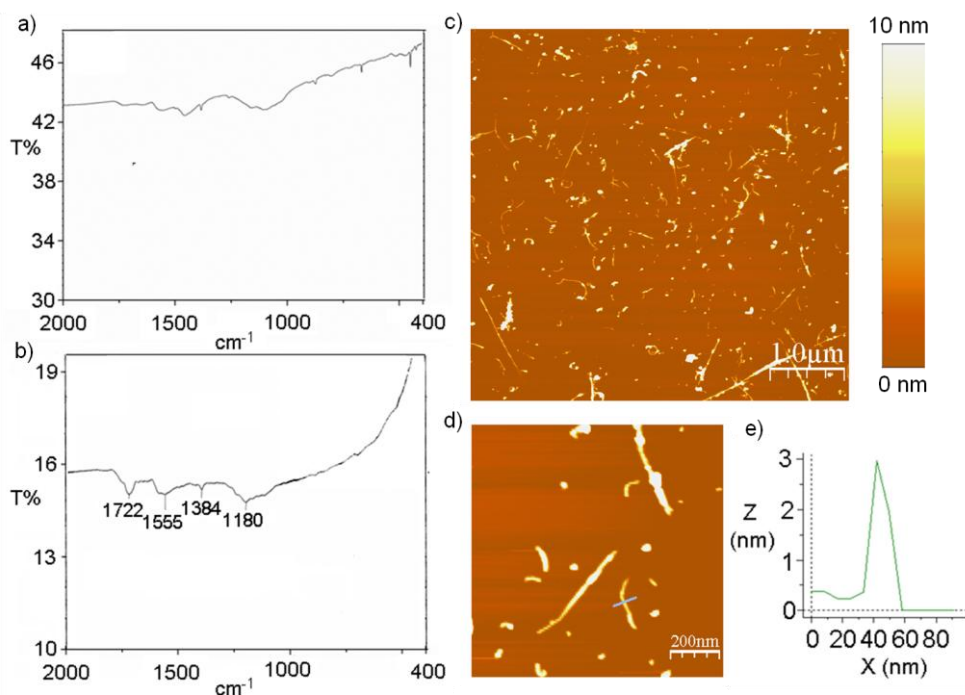


Figure 97. *ox*-DWCNTs characterization: (a) and (b) partial IR spectra of *p*-DWCNTs and *ox*-DWCNTs, respectively. A clear increment of the typical -COOH stretching signal is observed from the (a) pristine to the (b) oxidized sample, supporting the

occurred introduction of oxygenated functionalities mainly as carboxylic groups; (c) TM-AFM image (air, 298 K) of a portion of mica surface after the deposition of a **ox-DWCNTs** dispersion in DMF. Many isolated, but also bundled, short CNTs are present on the surface; (d) higher magnification TM-AFM image and (e) related height cross-section highlighting the presence of a very short, isolated DWCNTs.

A further confirmation of the presence of -COOH functionalities was provided by the TGA investigation under inert atmosphere (N₂). The weight-loss plots relative to **p-DWCNTs** (Figure 98a) and **ox-DWCNTs** (Figure 98b) display two pyrolytic events: one occurs between 100°C and 500°C, where the defunctionalization of CNTs framework takes place, and a second between 650°C and 850°C, where the CNTs undergo thermal decomposition. During the first event, the weight losses for **p-DWCNTs** and **ox-DWCNTs** are about 1% and 6% w/w, respectively. Assuming that the pyrolytic step is mainly caused by thermal decarboxylation reactions, a mass content of 1.4 $\mu\text{mol}\cdot\text{mg}^{-1}$ of -COOH functionalities is estimated.

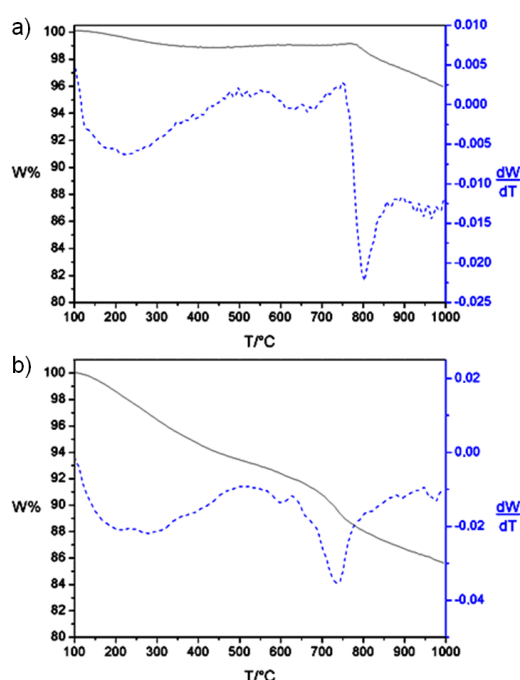


Figure 98. Temperature-modulated (—) and differential (---) gravimetric plots of (a) **p-DWCNTs** and (b) **ox-DWCNTs**, recorded under N₂ atmosphere with a thermal increase of 10 °C·min⁻¹.

In a previous report, we have described that, using dilute solutions of H₂O₂, the shortening and opening of the end caps of DWCNTs could be efficiently achieved, as shown by AFM and high-resolution TEM investigations, respectively.^[370] Since here an additional oxidative treatment with mineral acids was introduced (see above), a further microscopic analysis resulted to be necessary in order to evaluate the effectiveness of the employed oxidizing conditions on the shortening process. In fact, after the third oxidative step, shortened isolated and bundled CNTs were observed by TEM imaging (Figures 99 a and b). Nonetheless, low resolution TEM imaging techniques have a poor Z resolution, which makes problematic the differentiation between isolated and bundled CNTs and therefore difficult for the statistical evaluation of the CNTs' length. However, considering the nanoscopic resolution of the scanning probe microscopic (SPM) techniques, tapping-mode AFM (TM-AFM) imaging technique has been employed to evaluate the tube length and diameter to discriminate between isolated and bundled CNT derivatives. **ox-DWCNTs** (~0.2 mg·ml⁻¹) were imaged on mica after spin-coating of a DMF solution. A typical TM-AFM height image of such surfaces is reported in Figure 97c. By evaluating the cross-section height values for all the cylindrical objects present on different portions of the mica surfaces, it was possible to distinguish isolated and bundled CNTs as tubular

structures with height values ranging from 3 nm (isolated tubes, Figures 97d, e) to more than 10 nm (bundles, Figures 99 a-d).

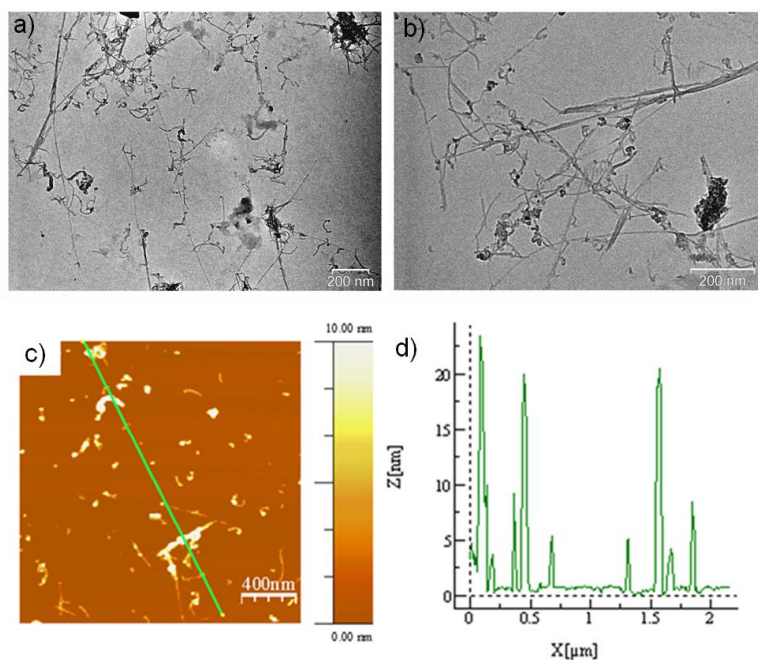


Figure 99. a-b) TEM images of different portions of a carbon-coated copper grid after the deposition of two drops of a **ox-DWCNTs** DMF dispersion ($\sim 0.2 \text{ mg}\cdot\text{ml}^{-1}$). Many isolated and bundled CNTs are present as tubular structures.; c) TM-AFM image (air, 298 K) of a portion of mica surface after the deposition of a **ox-DWCNTs** dispersion in DMF ($\sim 0.2 \text{ mg}\cdot\text{ml}^{-1}$); d) height cross-section of a surface portion where mostly bundled CNTs are present. Note that the isolated CNTs show height lower than 10 nm.

Using WSxM 2.1 (Nanotec Electronica, Spain) software, the tubes found on the surface were statistically analyzed (~ 400 objects have been analyzed) allowing to estimate the average **ox-DWCNTs** length, that resulted $234 \pm 167 \text{ nm}$ (much lower if compared to the $534 \pm 380 \text{ nm}$ value obtained in our former study^[370]). The statistical analysis became more meaningful if associated with the frequency histograms depicted in Figure S6, where the frequencies of the observed lengths have been plotted as functions of the different dimensional classes. From these histograms, it is clearly visible that the most frequent CNTs lengths are comprised in the range between 100 and 250 nm (Figure 100a), with 90% of the measured objects being shorter than 400 nm (Figure 100b).

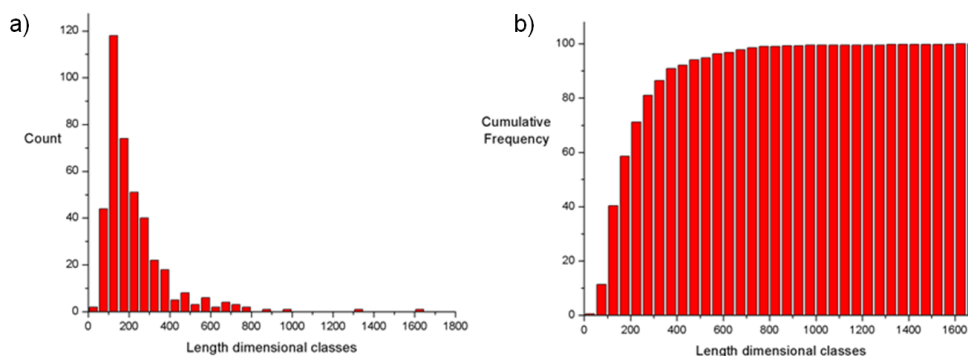


Figure 100. a) Frequency count and b) cumulative frequency plots of the length values obtained after TM-AFM characterization of **ox-DWCNTs**.

3.3.6.2. Structural Properties of Porphyrin-DWCNTs Derivatives

In order to investigate the degree of functionalization, XPS and TGA measurements were carried out. The XPS data are presented in Table 13. As expected, all samples present the signature of C and O atoms, however more important is the presence of the N signature (N 1s at 400.0 eV). Notably, going from the non-covalent **163@DWCNTs** (0.4 at%) to the covalent **163-DWCNTs** conjugate (1.1 at%), up to the complex **163@ (163-DWCNTs)** (1.8 at%) a net increase of the N atomic percentage has been observed. The maximum loading of N atoms occurs in the covalent samples as well as in the case of complex **163@ (163-DWCNTs)** due to the additional layer of physisorbed porphyrins. Similarly, the results obtained from TGA (the temperature modulated and differential thermogravimetric plots are reported in Figures 101 a-e) follow the same trend as that observed with the XPS analysis.

Table 13. Compositional data obtained after XPS analysis of the investigated CNTs derivatives.

Sample	C at%	N at%	O at%
p-DWCNTs	97.1	-	2.9
ox-DWCNTs	94.0	-	6.0
163-DWCNTs	92.5	1.1	6.4
163@ (163-DWCNTs)	89.4	1.8	8.8
163@DWCNTs	92.3	0.4	7.3

The pyrolysis of porphyrin **163** alone clearly appears with a prominent weight loss in the temperature range between 420 °C and 600 °C (Figure 101b). This weight loss step is also easily retrieved in the plot of **163@ (163-DWCNTs)** complex proving the presence of porphyrin molecules (Figure 101c, arrow c). At the same time, the differential plot of **163@ (163-DWCNTs)** reports two other pyrolytic events between 100 °C and 400 °C (Figure 101c, arrows a-b). These peaks could be rationalized as pyrolysis of both EDC-functionalities and unreacted carboxylic groups attached on the CNTs frameworks. Once that the pyrolysis of **163** occurred, after 600 °C, **163@ (163-DWCNTs)** was subjected to a 25.6% w/w loss, while **163-DWCNTs** and **163@DWCNTs** (Figures 101 d and e) presented weight losses of 9.7% w/w and 8.5% w/w, respectively. Hence, TGA observations corroborate the XPS measurements attesting the higher loading of molecule **163** on the hybrid complex **163@ (163-DWCNTs)**, therefore highlighting the effect of the diverse purification steps carried out on the covalent derivative to remove the exceeding porphyrin quantities.

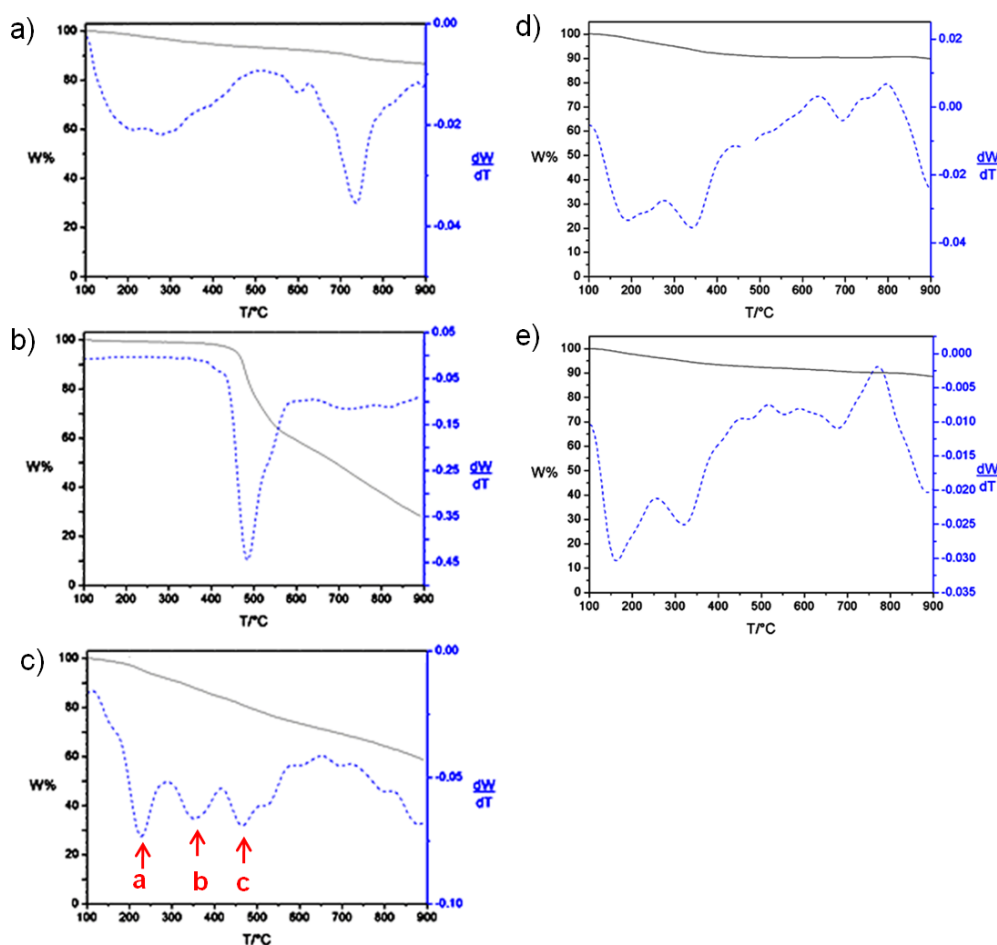


Figure 101. Temperature-modulated (—) and differential (----) gravimetric plots of (a) **ox-DWCNTs**, (b) **163**, (c) **163@(163-DWCNTs)**, (d) **163-DWCNTs** and (e) **163@DWCNTs**, recorded under N₂ atmosphere with a thermal increase of 10 °C·min⁻¹.

As a consequence of the presence of the covalently and non-covalently appended porphyrin units, the porphyrin-bearing DWCNTs show better dispersability than **ox-DWCNTs** in organic solvents such as DMF and CHCl₃. Interestingly, whereas conjugates **163-DWCNTs** and **163@DWCNTs** form stable dispersions, **ox-DWCNTs** show extensive precipitation after an initial apparent dissolution. This indirectly proves that the concentration of CNTs dispersed in solution is expected to be substantially larger for **163-DWCNTs** and **163@DWCNTs** samples, thus enabling a more thorough characterization of the DWCNTs derivatives using optical spectroscopy. Although solutions of DWCNTs derivatives are transparent in DMF and CHCl₃ and do not exhibit any floating matter by visual inspection, the DWCNTs derivatives remain dispersed in a stable colloidal-like solution. This has been further confirmed by DLS measurements that displayed the presence of two groups of nanotubes with different mean lengths (Table 14). In particular, the size distributions of the suspended carbon nanotube derivatives in clear, eyes-transparent DMF and CHCl₃ dispersions of **163-DWCNTs**, **163@DWCNTs** and **ox-DWCNTs** are shown in Figures 102 and 103, respectively; the particles size are listed in Table 14.

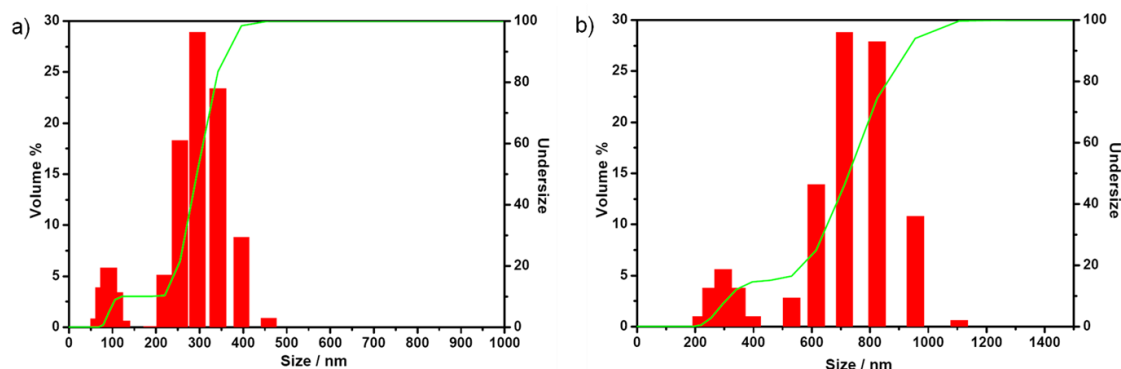


Figure 102. Size distribution of DWCNTs bundles in (a) DMF and (b) CHCl_3 dispersion of **163-DWCNTs**.

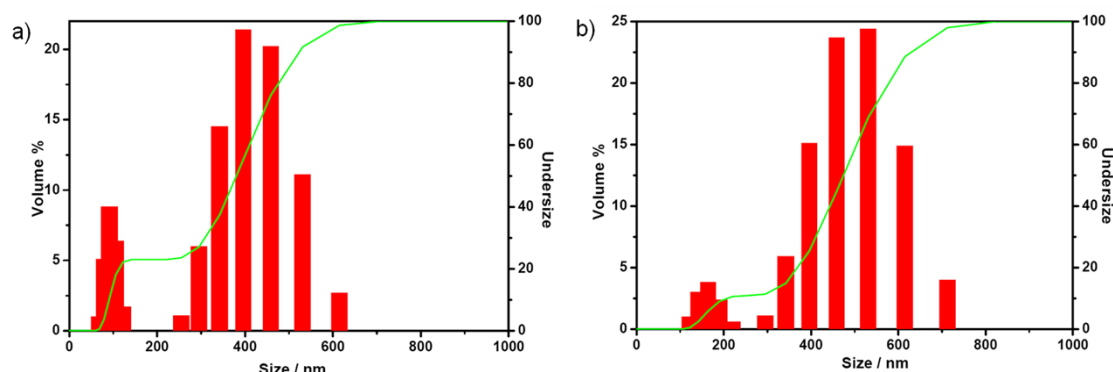


Figure 103. Size distribution of **163@DWCNTs** in (a) DMF and (b) CHCl_3 .

Table 14. Particle sizes distribution of the DWCNTs conjugates in DMF and CHCl_3 dispersions as evaluated from DLS.

Sample	Particle Size (nm)	
	DMF dispersion	CHCl_3 dispersion
ox-DWCNTs	290 ^a , 60	^b
163-DWCNTs	300, 90	730, 300
163@DWCNTs	400, 100	470 ^a , 160

^a Due to very limited dispersibility of **ox-DWCNTs**, the measurements for such materials have been carried out after removing all the floating DWCNTs, so the concentration of dispersed tubes is lower compared to the other samples; ^b impossible to be measured due to the large size of agglomerates.

From Table 14, it is clear that the particle sizes of the porphyrin-bearing DWCNTs hybrids in the dispersion are larger than that of the oxidized precursor, **ox-DWCNTs**. This is a consequence of the reduced bundling behavior of the functionalized DWCNTs caused by the presence of the porphyrin moieties, which imparts better solubility to the hybrid material. In the case of **ox-DWCNTs**, the larger nanotubes easily entangle and form large bundles that are more insoluble and quickly collected in the precipitate; accordingly, only very small and short CNTs remain in solution. However, all dispersions are not optimal for photophysical investigations because they undergo light scattering and prevent quantitative optical measurements (*vide infra*), particularly by means of transient spectroscopy upon intense laser excitation.

3.3.6.3. Theoretical Calculations on the Conformational Properties of Porphyrin-DWCNTs Derivatives

Force field-based simulations using a combined molecular mechanics and molecular dynamics approach have been carried out in order to gain insight on the interactions between the porphyrin molecule and the nanotube framework.

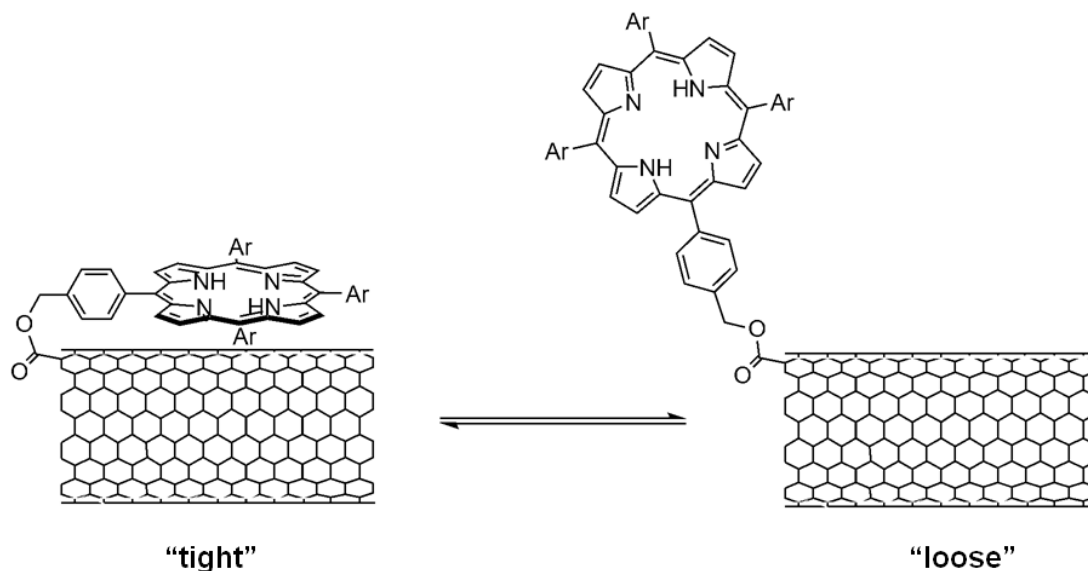


Figure 104. Schematic representations of the dynamic equilibrium existing between the “tight” and “loose” conformations of 1-DWCNTs, when **1** is linked to the tips. The same equilibrium may exist also when **163** is linked to the edge of the tube. Ar stands for 4-(*tert*-butyl)phenyl.

As reported earlier for covalently linked fullerene-porphyrin conjugates,^[379-381] several conformational equilibria can occur in solution.^[382, 383] Likewise, a dynamic equilibrium between “loose” and “tight” porphyrin-CNTs pairs, in which the carbon nanotube and the porphyrin are in the “face-to-face” conformation in the ground state, can be considered (Figure 104). The “tight” and the “loose” conformation differ in the distance between the porphyrin and the CNTs and in their solvation.^[384] The aim of this modeling is thus to determine the most probable conformation of the porphyrin unit on the CNT wall and to quantify the strength of the interactions between the two species. Two situations were modeled with the porphyrin molecule *i*) simply physisorbed on the CNT surface (*i.e.*, **163@DWCNTs**) and *ii*) chemically grafted on the CNTs framework *via* a COOCH₂ linker (*i.e.*, **163-DWCNTs**). Within the covalent conjugate, two different grafting sites were considered: along the wall or at the edge of the open tips. Figure 105 shows the top, front and side views for the three structural situations: in (a) the porphyrin is physisorbed, while in (b) and (c) the porphyrin fragment is covalently bound to the wall and at tips, respectively. In structures (a) and (b), the tetrapyrrolic ring is roughly parallel to the nanotube surface: its core is slightly bent, with a mean distance of 0.35 nm from the nanotube. This value is typical of π -stacking and the slight bending of the core allows for optimal π - π interactions. In (c), the porphyrin core is not directly interacting with the nanotube and the molecule remains flat. Note that in all three cases, CH- π interactions are present between the side groups and the nanotube surface.

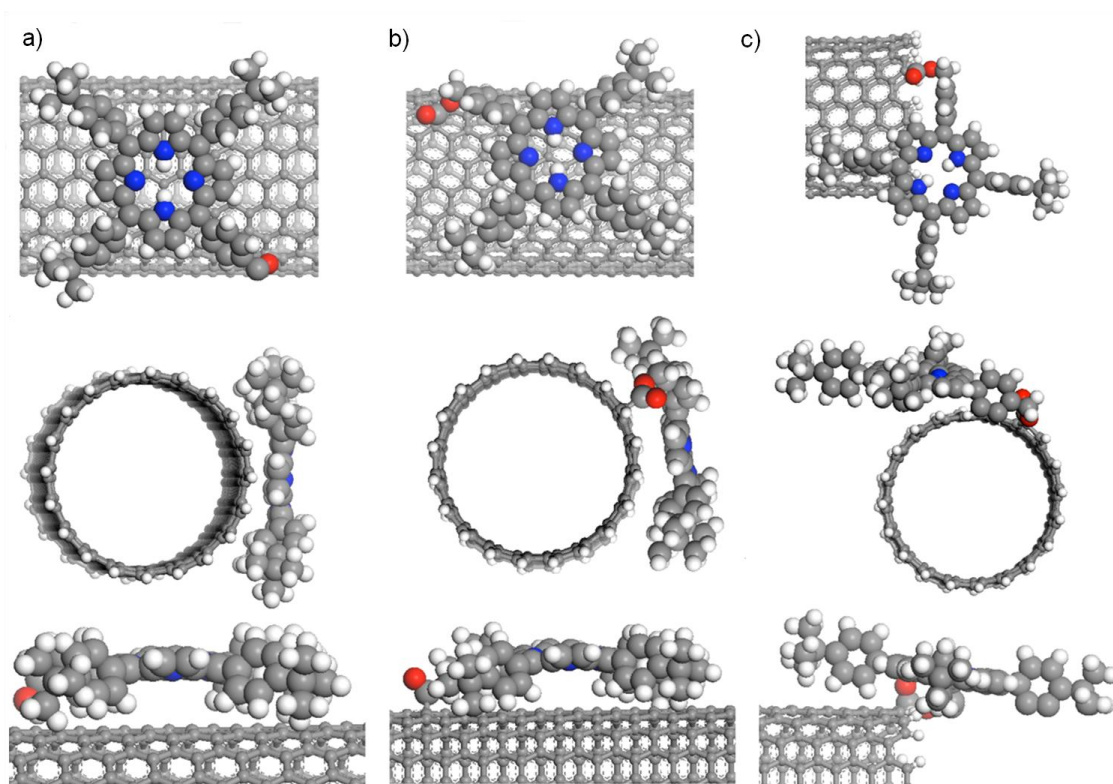


Figure 105. Top, front and side views for (a) a porphyrin molecule physisorbed and covalently-bound to the nanotube (b) wall or (c) tips in a "tight" conformation.

The potential energy for the physisorbed system cannot be strictly compared with the covalent systems, because of the different chemical composition in the two analyzed cases. Nevertheless some useful information can be obtained. The adsorption energy for a single physisorbed porphyrin molecule interacting with the SWCNTs wall is about -60 kcal/mol. Consistently, the comparison for the two grafted arrangements shows that system (b) is about 60 kcal/mol more stable than system (c), acknowledging the greater van der Waals interactions between the porphyrin and the nanotube external wall when the molecule is grafted along the side. Notably, the flexibility of the linker can allow for conformations in which the end-grafted porphyrin is partly adsorbed on the CNT wall (see below). Since the formation of carboxylic acids is expected to prominently take place at the tube ends, it is also relevant to model the presence of more than one porphyrin molecule covalently attached at the CNT edge. We have thus investigated systems having two porphyrin fragments covalently bound at the nanotube tip: the first porphyrin is attached to a fixed position and the second one is attached at an increasing distance from the first one. The various possibilities are denoted as 1-2, *i.e.*, the two molecules are attached on neighboring carbon atoms, up to 1-9, *i.e.*, where the porphyrins are on opposite sides of the nanotube edge (Figure 106). The two most stable structures have been obtained for positions 1-4 and 1-6. In the 1-4 case, one porphyrin (in red) is adsorbed on the nanotube wall, thanks to the flexibility of the $\text{COOCH}_2\text{-Ph}$ linker. The second porphyrin (in blue) is partially inside the nanotube and the two molecules only weakly interact. In contrast, the porphyrins in the 1-6 system are oriented in such a way that they can directly interact, even though the distance and orientation of the cores are such that $\pi\text{-}\pi$ interactions cannot take place (only $\text{CH}\text{-}\pi$ interactions are present). Nevertheless, the 1-4 system is almost 20 kcal/mol more stable than its 1-6 counterpart; this is likely due to the strong favorable interaction between the 'red' porphyrin molecule and the nanotube in the 1-4 model (Figure 106).

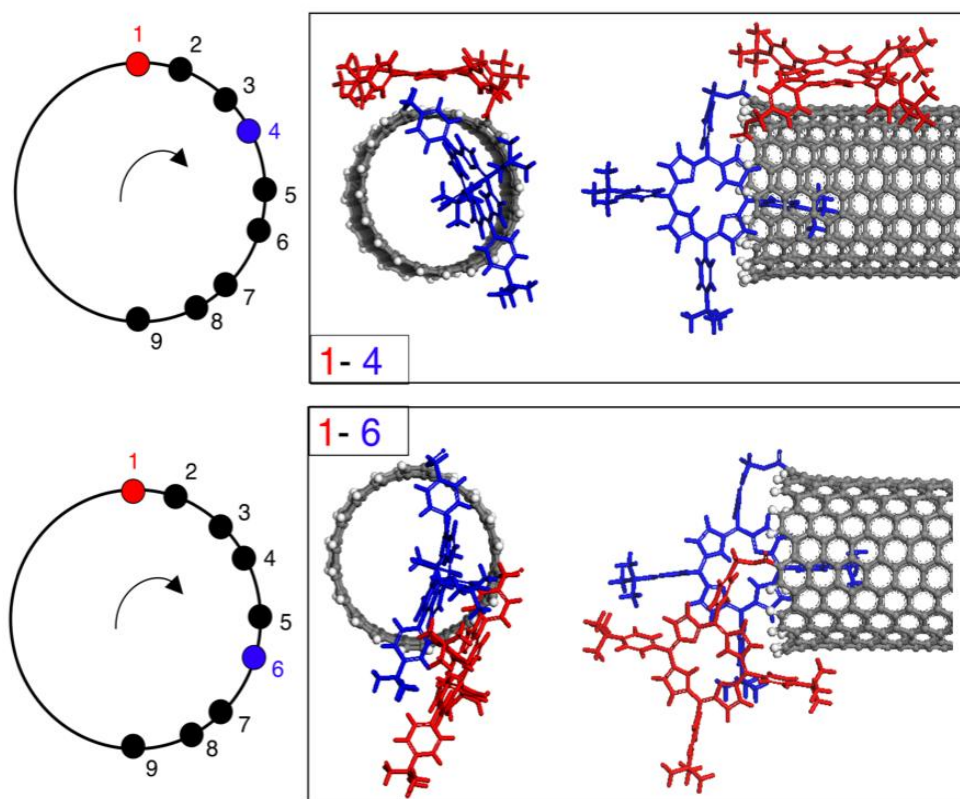


Figure 106. Front and side views for the 1-4 and 1-6 systems, in which two porphyrin molecules are attached at the nanotube tips.

3.3.6.4. Photophysical Properties of Porphyrin-DWCNTs Derivatives

The photophysical studies of hybrid materials **163-DWCNTs** and **163@DWCNTs**, and of reference samples **163** and **ox-DWCNTs** were carried out in DMF and CHCl_3 , due to their proved efficacy in dispersing the carbon nanomaterials. The electronic absorption spectra of all the materials in DMF are shown in Figure 107. Both hybrid materials **163-DWCNTs** and **163@DWCNTs** show porphyrin-centered Soret bands at 419 nm as similar to free molecules **163**, whilst the weaker Q-bands are not discernible due to the overwhelming absorption of **ox-DWCNTs** counterpart. Q-bands are barely observable in CHCl_3 dispersions along with the prominent Soret feature at 421 nm (Figure A4, *Appendix*). The different absorption intensities of the Soret band between the two hybrid materials reflect the higher porphyrin loading provided by covalent functionalization compared to the physisorbed **163@DWCNTs** sample. The broadening of the Soret band and a small shoulder around 450 nm suggests weak interporphyrin interactions, probably between those located on the same DWCNT unit (*vide supra*).^[384] In addition, as suggested by molecular modeling, several conformations between the carbon nanotube surface and the porphyrin unit in solution, may also result in broadening of the **163**-centered Soret band. Apart from the above changes, no other significant differences have been observed for the hybrid materials.^[360, 385, 386]

The luminescence spectra of **163**, **ox-DWCNTs**, **163-DWCNTs** and **163@DWCNTs** were recorded using solutions with matching absorption at the Soret band maximum (420 nm). Upon excitation, the hybrid materials show a fluorescence profile that is perfectly superimposable to that of free porphyrin **163** in DMF (Figure 108) and CHCl_3 (Figure A4, *Appendix*). The emission intensities of **163-DWCNTs** and **163@DWCNTs** are found to be lower than that of porphyrin **1** alone, but a quantitative determination cannot be made due to at least three interfering factors (see

below).^[361, 387, 388] Therefore, this observation alone cannot be ultimately indicative of photoinduced energy or electron transfer processes causing quenching of the porphyrin singlet level.^[387]

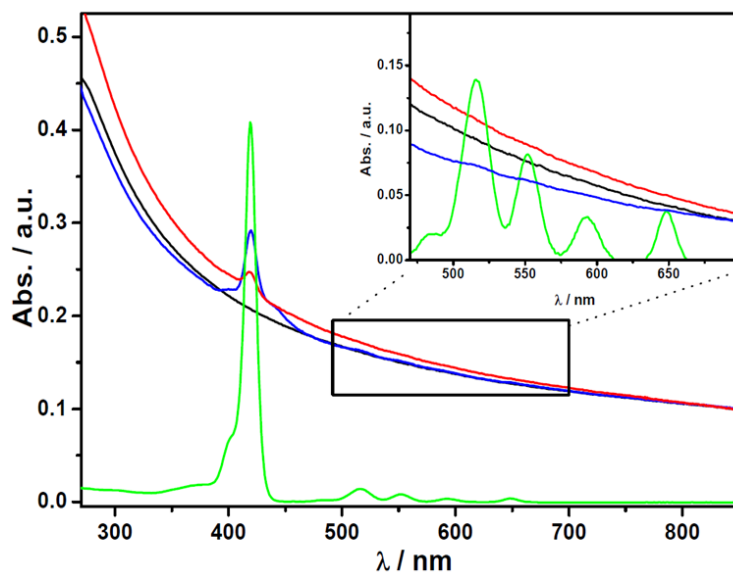


Figure 107. Electronic absorption spectra of **163** (green), **ox-DWCNTs** (black), **163-DWCNTs** (blue) and **163@DWCNTs** (red) in DMF. Inset: expanded Q-band region of all the materials. Spectra of DWCNTs materials are normalized at 850 nm.

The observed reduction of the porphyrin fluorescence intensity of **163-DWCNTs** and **163@DWCNTs** may be due to factors such as (i) light partitioning between **163** and DWCNTs, so that a considerable portion of the incoming photons causes excitation of the carbon nanotubes scaffold; (ii) excitation and emission light scattering due to the presence of particles in the hybrid dispersions, (*vide supra*); (iii) different porphyrin concentration in the hybrid dispersions due to different functionalization methodology; (iv) significant presence of quenched “tight”-type conformers in which the porphyrins-centered singlet excited state is deactivated by the DWCNTs. Notably, the singlet excited state lifetime of the porphyrin is not quenched for all samples in both solvents (Table 15). This corroborates (i)-(iv) as reasonable explanations for the observed trends in luminescence intensities of Figure 108 and underpins the lack of evidence of photoinduced phenomena between porphyrins and DWCNTs. The porphyrin fluorescence decays of **163-DWCNTs** and **163@DWCNTs** are monoexponential, suggesting a uniform physical environment for the emissive centers in the dispersions. The slightly longer porphyrin lifetime value of the hybrid materials compared to free porphyrin can be caused by the reduced vibrational relaxation of the excited states of the porphyrin moieties when anchored on the rigid CNT walls.

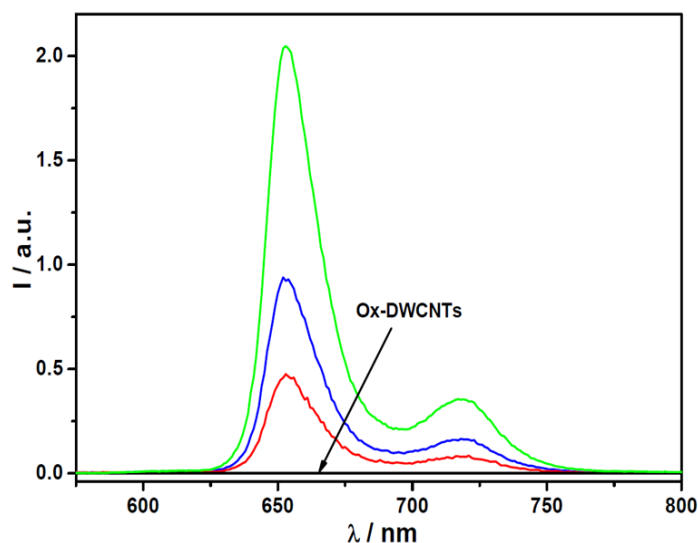


Figure 108. Emission spectra of **163** (green), **ox-DWCNTs** (black), **163-DWCNTs** (blue) and **163@DWCNTs** (red) upon excitation at 420 nm in DMF. Note: the qualitative trend of emission intensities is that observed experimentally (**163** > **163-DWCNTs** > **163@DWCNTs**) but the intensity ratios must not be taken for quantitative comparisons (see text).

To probe the triplet states of the appended porphyrins, experiments on sensitized singlet oxygen luminescence were carried out with **163**, **163-DWCNTs** and **163@DWCNTs** in CHCl_3 .⁴ Upon excitation of the porphyrin singlet bands, the lowest energy singlet state S_1 populates the lowest triplet state (T_1) through intersystem crossing. Owing to the long lifetime of porphyrin T_1 , the molecular oxygen present in the solvent deactivates it through energy transfer and forms excited singlet oxygen ($^1\text{O}_2$), which emits at 1270 nm.^[384] By monitoring the $^1\text{O}_2$ near infrared emission intensity, an indirect estimation of the triplet state generated by the porphyrins anchored on DWCNTs is obtained.^[383] The $^1\text{O}_2$ emission bands from free porphyrin **163** and hybrid materials are shown in Figure 109. Due to the same reasons indicated for fluorescence spectra, singlet oxygen emission intensities of hybrid materials are not directly comparable with that of porphyrin **163**.

Molecular modeling suggests the existence of “loose” and “tight” pairs between porphyrin and DWCNTs but, unlike the case of fullerene systems,^[383, 384] the photophysical analysis cannot provide direct evidence for such interchromophoric interactions, but anyway do not contradict such model. In fact, if the fluorophore and the quencher are approaching each other up to the shortest distance (“tight” conformation), photo-induced energy/electron transfer rates may become so fast to successfully compete with the intrinsic deactivation of the porphyrin and yield complete quenching of luminescence. In other words, this “tight” situation must lead to a virtually complete reduction of the emission intensity and a vanishingly short lifetime. On the other hand, in the case of “loose” pairs, the attached chromophores should behave as in the absence of quenching interactions and must show the characteristic luminescence properties of **163**. Hence, luminescence data are compatible with the presence of “tight” and “loose” pairs, with the latter being responsible for the residual and kinetically unquenched luminescence signals. This picture of non-interacting porphyrin/DWCNTs arrangements is supported by the observation of singlet oxygen luminescence that further signals the presence of completely unquenched porphyrin moieties in their triplet states. These findings are somewhat surprising because indicate the absence of intermediate situations, in between “tight” and “loose”, where the porphyrin-DWCNTs distance causes dynamic quenching of the porphyrin moieties with reduced singlet lifetimes.

⁴ This experiment is not possible in DMF due to insufficient dissolved oxygen content and low diffusion constant.

Table 15. Singlet lifetime values of porphyrin **1** and hybrid materials in solution and PMMA matrix

Sample	Lifetime (ns)		
	DMF	CHCl ₃	PMMA
163	10.2	7.8	4.2
163-DWCNTs	10.6	8.9	4.4 (53%) 6.5 (47%)
163@DWCNTs	11.1	9.3	1.4 (50%) 8.1 (50%)
163@(163-DWCNTs)	9.9	-	-

Finally, DMF dispersions of **163@(163-DWCNTs)** were also investigated. The absorption and emission features of **163@(163-DWCNTs)** exhibit an intensity quite similar to **163**, showing the high loading of porphyrins on DWCNTs (Figure 109 right). Also the lifetime value ($\tau = 9.9$ ns) exactly matches with that of porphyrin **163** alone.

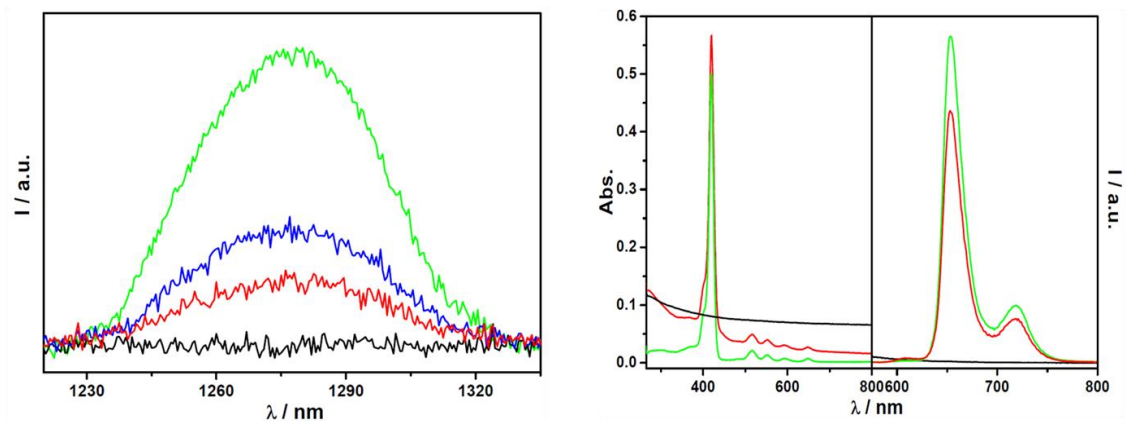


Figure 109. Left: sensitized singlet oxygen emission spectra of **163** (green), **ox-DWCNTs** (black), **163-DWCNTs** (blue) and **163@DWCNTs** (red) by exciting at 420 nm in CHCl₃. Right: Absorption (left) and emission (right, $\lambda_{\text{ex}} = 420$ nm) spectra of **163** (green), **ox-DWCNTs** (black), **163@(163-DWCNTs)** (red) in DMF.

In order to investigate the optical properties of the DWCNTs hybrids in a polymer matrix, transparent and photo-inactive PMMA polymer was chosen as a dispersive medium and related thin films were made by drop-casting CHCl₃ dispersions containing all the conjugates. In contrast to solution experiments, the spectral features of **163**, **163-DWCNTs** and **163@DWCNTs** recorded in PMMA thin films show the presence of aggregates (Figure 110). For molecule **163**, the split Soret band and the red-shifted Q-band maximum are indicative of *J*-type “head-to-tail” porphyrin aggregation. The formation of *J*-aggregates is promoted by the poor porphyrin dispersibility in aliphatic PMMA polymer and by the presence of dipoles induced by polar -OH functionality in the macrocyclic rings. According to Kasha’s theory, these large structures substantially modify the pattern of the Soret (splitting) and Q-bands (red-shifted maximum), as indeed observed here.^[389] Interestingly, the same spectral features of **163** alone are observed in the PMMA dispersion of **163-DWCNTs**, suggesting a similar ordered arrangement of the porphyrin chromophores in the rigid medium. Such *J*-type interactions are perhaps favored by steric effects induced by the presence of the highly-hindered DWCNTs framework, whereas face-to-face intramolecular interactions seem to be prevented as also confirmed by the absorption spectra obtained from solution (*vide supra*).⁵ For samples containing

⁵ π - π interactions between porphyrin and DWCNTs are insignificant due to high carboxylic acid functionalities on CNTs.

163@DWCNTs, owing to the low concentration of porphyrins, the related electronic absorption bands are masked by the strong absorption of DWCNTs. However, luminescence measurements ($\lambda_{\text{exc}} = 420 \text{ nm}$) show a weak band clearly attributable to porphyrin fluorescence, thus confirming the presence of the chromophore in the sample (Figure 110). Upon excitation of **163@DWCNTs** at 445 nm, a broader fluorescence band is detected (Figure 110), and the related excitation spectrum collected at the emission maximum shows a split Soret band, where the new feature is higher in energy (395 nm) than the characteristic band at 419 nm. Compared to **163** and **163-DWCNTs**, these findings suggest a different arrangement of the porphyrin units in **163@DWCNTs**, *i.e.* face-to-face *H*-aggregates, which are not generated in **163-DWCNTs** as discussed above.^[390] The allowed in-phase arrangement of transition dipoles in *H*-aggregates results in a higher energy electronic transition that is responsible for the Soret band peak at shorter wavelength.

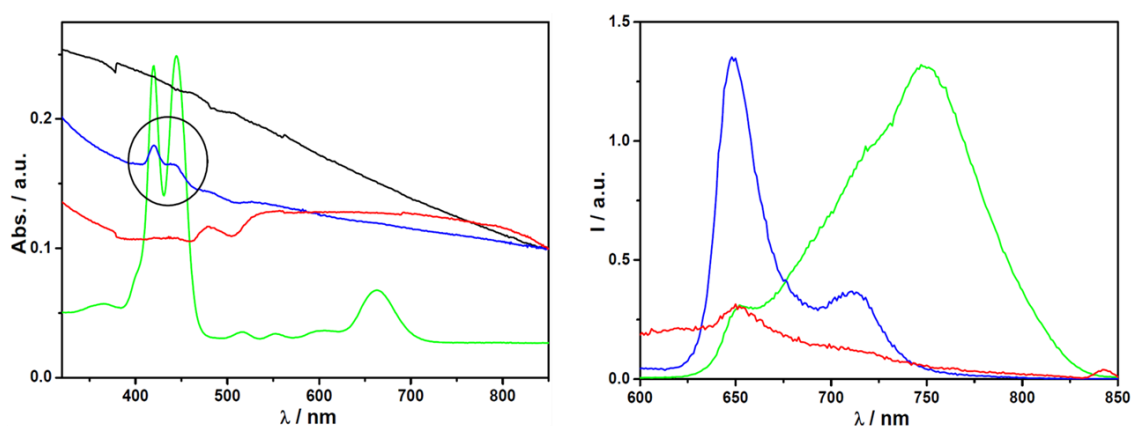


Figure 110. Left: electronic absorption spectra of **163** (green), **ox-DWCNTs** (black), **163-DWCNTs** (blue) and **163@DWCNTs** (red) in PMMA polymer matrix. Right: emission spectra of **163** (green), **163-DWCNTs** (blue) and **163@DWCNTs** (red) upon excitation at 420 nm in PMMA matrix.

On the other hand, the out-of-phase arrangement of transition dipoles generates a forbidden, low energy, transition to the S_1 state. Upon excitation of **163@DWCNTs**, the high energy S_2 level is populated, which then decays to a weakly emitting S_1 state.^[390] In *J*-aggregates, depending on the strength of interchromophoric interaction, the low energy exciton states shift the emission maxima accordingly, *i.e.* the stronger the interaction the more red-shifted the band is. The emission spectra of **163** and **163-DWCNTs** exhibit maxima at 732 and 675 nm respectively, indicating stronger interactions in the aggregates of **163** alone than in those of the more sterically congested **163-DWCNTs**.^[390] Apart from the presence of *J* and *H* aggregates, characteristic porphyrin-centered emission bands are still observed in all three materials when exciting the Soret (420 nm) and Q band (515 nm) features (Figure 110). This shows the presence of free porphyrin units, especially in the case of hybrid materials, where the porphyrin emission intensity is significantly high. The fluorescence decay profiles of **163-DWCNTs** and **163@DWCNTs**, which are fitted as biexponential, support the above rationale. Both hybrid materials possess a long and a short lifetime with a similar proportion (Table 15). Notably, the short lifetime of **163-DWCNTs** is the same as that of **163**, confirming similar aggregation processes in both materials. The long lifetime stems from non-aggregated porphyrin units as evidenced by the emission spectrum. In **163@DWCNTs**, as mentioned above, the excited S_1 state rapidly decays to the ground state ($\tau = 1.4 \text{ ns}$). Similar to the solution phase, the physisorbed porphyrins show a longer lifetime value than that of the free porphyrins. This is attributed to the reduced vibrational relaxation from the lower-lying excited state (Table 15), ultimately confirming their interaction with the DWCNTs framework.

3.3.6.5. Conductive Properties of Porphyrin-DWCNTs Derivatives

The role of the functionalized CNTs frameworks in the polymer blends for photovoltaic applications is subtle as they could behave like versatile, interpenetrating unidimensional hole-extracting materials as well as electron accepting units and conductive networks.^[316, 356, 391, 392] In addition, owing to their particular intermolecular cohesive forces (0.5 eV nm^{-1}), CNTs tend to strongly aggregate both in solution and in the solid state forming bundled structures that often cause a low reproducibility of the conducting properties and display percolation threshold of a few percent. Therefore, in order to evaluate the potential properties of the porphyrin-DWCNTs derivatives as dopants in active layers for photovoltaic systems, we have fabricated glass/ITO/PEDOT:PSS/Active Layer/Al type devices with the aim of investigating the interaction of the chemically-modified DWCNTs and of **163@163-DWCNTs** with the P3HT-Py polymer matrices addressing the reproducibility of both morphological and conducting properties of the active layers. Besides small concentrations of the DWCNTs derivative (*ca.* 1%), in order to balance the charge carrier transport to the electrodes we also added small amounts of [60]PCBM (< 5%). The realization of spin-coated thin films involved standard preparative protocols (*Chapter 4*). Specifically, a 100-nm thin film has been prepared by spin-coating a solution ($c = 15 \text{ mg/ml}$) of *p*-xylene containing the appropriate amount of derivatized DWCNTs, [60]PCBM and P3HT-Py at the desired doping levels. Samples containing **163@DWCNTs** and **163-DWCNTs** led to similar results.

Scanning Near-field Optical Microscopy AFM (AFM-SNOM) studies have been carried out to study the morphology of the thin films containing the active layers from composite dispersions of the porphyrin-based DWCNTs investigated in this work.^[393] The results are shown in Figure 111b. The typical topography of the thin films containing **163@163-DWCNTs** is presented at micro-scale in the left panel and the SNOM signal (accumulated in the transmission mode) is displayed in the right panel. Both images clearly show that the hybrids functionalized DWCNTs are debundled and are in intimate contact with the P3HT-Py polymer, as also highlighted by the uniform distribution of the tubes within the polymeric layer. At these low-doping levels, the porphyrin-DWCNTs hybrids do not protrude from the film and their UV-Vis absorbance is much smaller than that of the surrounding polymer matrix. In addition, the intrinsic UV-Vis absorption properties of the porphyrin fragments at the working wavelength (*e.g.*, 532 nm) do not seem to noticeably influence the optical contrast imaging of the functionalized DWCNTs. On the other hand, the presence of dark spots in the SNOM image is attributed to zones of the layer in which [60]PCBM molecules are aggregated.^[393]

Figure 111 presents the dark current density-voltage (*J-V*) characteristics of typical films containing the carbon nanohybrid structures at room temperature. The forward bias conditions correspond to positive voltage on the ITO electrode with respect to the Al cathode. As depicted in Figure 15a, the *J-V* dependence is asymmetric, suggesting the presence of a blocking contact (*Schottky* barrier) at the bottom of the PEDOT:PSS/active layer thin-film interface. This is responsible for the observed rectification effect as the other upper interface is supposed to behave like an Ohmic contact. At high voltages, the series resistance or the space charge build up deviates the injected current from the exponential behavior limit. Thus, the observed intensification of the forward current in the **163@163-DWCNTs**-based devices suggests a smaller hole-injection barrier compared to those reference devices containing only CNTs materials, such as *p*-DWCNTs, *ox*-DWCNTs or *p*-MWCNTs. The reported results corroborate with state-of-the-art works^[316, 391, 392] and with the standard metal-insulator-metal model, where the built-in potential across the organic thin film equals the work function difference between the Al cathode (4.3 eV) and the PEDOT:PSS anode (5.1 eV), providing a distinctive kink structure in the forward bias of the *J-V* plots. The increase in the forward current observed for films containing hybrids **163@163-DWCNTs** is accompanied by a better rectification ratio compared to the responses observed by those devices containing *p*-DWCNTs and *ox*-DWCNTs where a very similar

behavior, with minor differences in the low bias regime, has been observed. In order to evaluate the photoactive role of the porphyrin moieties within the active layer, quantum efficiency measurements (defined as the percentage of photons hitting the photoreactive surface that will produce an electron hole pair, a value used for a photosensitive device such as photographic film or a charge coupled device (CCD)) have been performed. In particular, an experimentally accessible value is the external quantum efficiency or incident photon to current efficiency (EQE) that is defined by the number of photogenerated charge carriers over the number of incident monochromatic photons. In this respect, the lineshape of the EQE profile (in arb. units), normalized at 420 nm, is displayed in the inset of Figure 111a and closely follows the absorption band of the polymer blend. No differences have been detected between active layers containing the porphyrin-doped hybrid or reference CNTs, thus displaying a negligible photochemical effect of the porphyrin moieties.

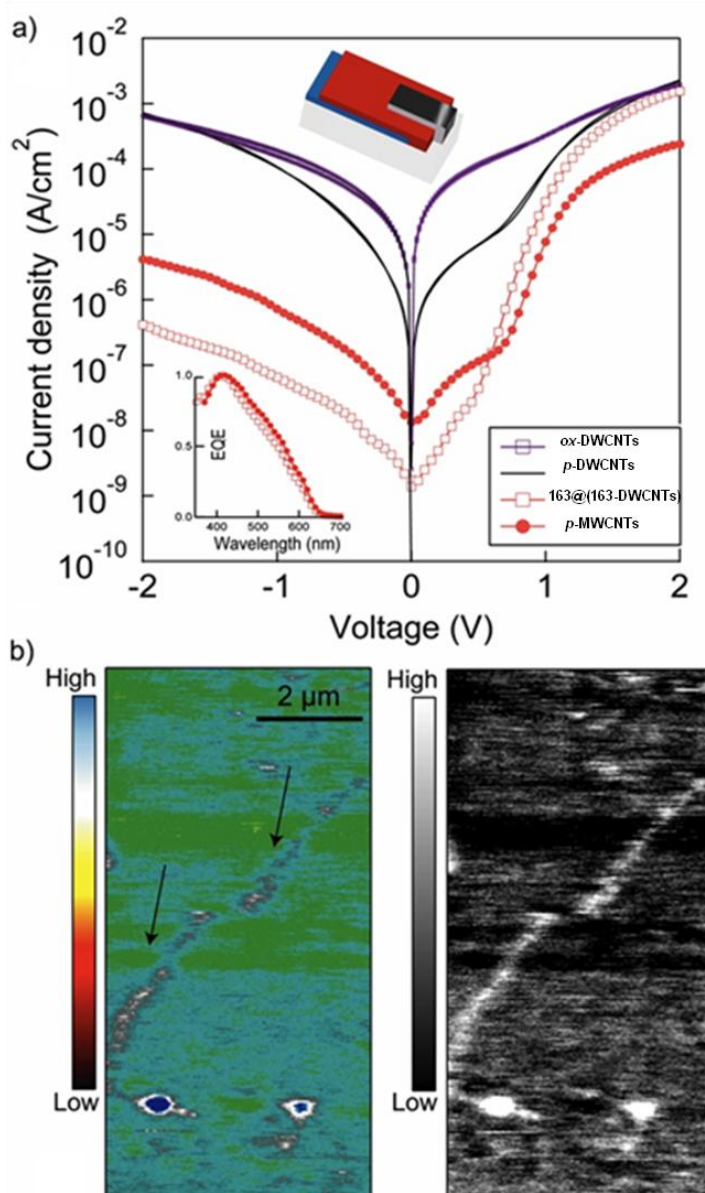


Figure 111. a) *J*-*V* curves measured in dark, at room temperature, for thin films of P3HT-Py loaded with *p*-MWCNTs and PCBM (empty squares), with *p*-DWCNTs and PCPM (black curve), with *ox*-DWCNTs and PCBM (blue curve) and doped with 163@(163-DWCNTs) and PCBM (filled circles). The device structure (glass/ITO/PEDOT:PSS/ActiveLayer/Al) is schematically shown. Inset: Normalized EQE wavelength dependencies for fabricated thin films with *p*-MWCNTs and porphyrin-functionalized DWCNTs; b) coupled AFM topography (left) and SNOM optical contrast (right) micrographs obtained under monochromatic laser radiation (532 nm) for the as-deposited active layers including 163@(163-DWCNTs).

3.4. Conclusions

This chapter described the different types of supramolecular interactions established between porphyrin molecules and hybrid surfaces. In the first sections, the self-assembly abilities of pyridyl-substituted porphyrins on metallic surfaces were studied by means of Scanning Tunneling Microscopy (STM). Subsequently, the interactions of porphyrin molecules with carbon nanotubes were investigated to engineer donor-acceptor systems for photovoltaic applications.

The self-assembly on a Cu(111) surface of novel porphyrin derivatives was firstly investigated with three porphyrin modules bearing either one, **109**, or two functional pyridyl recognition groups, **110-111**, in *cis*- and *trans*-like configurations. Unprecedented supramolecular architectures stabilized by attractive pyridyl-pyridyl interactions promoted by Cu surface atoms, were formed. The strength of the intermolecular interactions allows for conformational changes of the entire assemblies by STM manipulation. The self-assembly of both the mono-substituted and the *trans*-like porphyrins result in distinct supramolecular dimers and chains, respectively. In contrast, the molecular symmetry in combination with the molecular flexibility and surface interactions explains the multiformity of the supermolecules formed by the *cis*-specie, expressed in open three- to six-membered cyclic assemblies. Furthermore, upon combination of the different ditopic porphyrin building blocks, bicomponent cyclic supramolecules of unprecedented extended size could be engineered. In parallel, the formation of extended and highly regular homochiral nanoporous networks on Ag(111) substrate of *trans*-like porphyrin **111** was also reported in this chapter. These arrays were formed through a three-level hierarchical chiral self-assembly process, which is based on the chiral conformation adopted by derivative **111** upon surface confinement. The porosity observed in the networks might be useful for patterning and guest accommodation.

In view of organizing 2D infinite porous networks on Cu(111) surface, this chapter also addressed the synthesis and STM investigation of three tetrasubstituted pyridyl porphyrins, **117-119**. Under UHV conditions the STM analysis revealed the occurrence of degradation phenomena. Specifically, the sublimation of modules **117** and **118** afforded undefined molecular fragments on surface. The complete absence of any arranged feature resembling intact porphyrins suggested a possible decomposition of the molecules. Due to the presence of piles of π -stacked porphyrin aggregates at the solid state, the porphyrin sublimation temperature is probably higher than that of decomposition generating the molecular fragmentation. The UHV deposition of module **119**, featuring 2,5-dimethyl phenyl moieties directly linked to the porphyrin *meso*-positions, afforded the presence on Cu(111) of some isolated species that might be ascribed to single porphyrin molecules. Although single molecules of **119** were successfully deposited, a large majority of undefined fragments was also observed, suggesting similar decomposition pathways as those detected for the parent tetrapyrrolyl porphyrins. The promising result obtained with porphyrin **119** induced to believe that the π - π interaction is not the only effect that influences the sublimation of the investigated tetrasubstituted pyridyl porphyrins. While subliming, the high temperature might endorse porphyrin side reactions inducing the molecule's decomposition.

The last sections of Chapter 3 focused on the preparation and physical characterization of diverse porphyrin-derived Double-Walled Carbon Nanotubes (DWCNTs) conjugates. In particular, COOH-derived DWCNTs, produced by means of a three-step oxidative protocol, were covalently linked and physically adsorbed to a porphyrin molecule producing three derivatives, **163-DWCNTs**, **163@163-DWCNTs** and **163@DWCNTs**. The structural properties of all porphyrin-DWCNTs conjugates were fully investigated via Thermogravimetric Analysis (TGA), Energy Dispersive X-ray Spectroscopy (EDX), X-Ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Dynamic Light Scattering (DLS) experiments. The photophysical properties of the porphyrin-CNTs derivatives were investigated through absorption and emission

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spectroscopies both in solution and in the solid state. Although definitive experimental evidences could not be obtained for supporting photo-induced electron and/or energy transfer processes involving the porphyrin chromophores and the CNTs' wall, solid-state UV-vis absorption profiles unambiguously displays electronic transitions fingerprinting *J*- and *H*- type aggregates, where porphyrin molecules inter-molecularly interact “head-to-tail” and “face-to-face”, respectively. Multilayered-type devices were also engineered with the aim of investigating the interaction of the porphyrin-derived DWCNTs with polymer poly(3-hexylthiophene)-pyrene (P3HT) derivatives containing small amounts of [60]PCBM. Studies of asymmetric current density-voltage (*J*-*V*) with the investigated **163@(163-DWCNTs)** hybrid displayed a strong rectification effect corroborating state-of-the-art devices.

4. Experimental Part

4.1. Instrumentation

Thin layer chromatography (TLC) was conducted on pre-coated aluminum sheets with 0.20 mm *Machevery-Nagel* Alugram SIL G/UV254 with fluorescent indicator UV254. **Column chromatography** was carried out using *Merck Gerduran* silica gel 60 (particle size 40-63 μm). **Microwave reactions** were performed on a *Biotage AB Initiator microwave instrument* producing controlled irradiation at 2.450 GHz. **Melting points** (M.p.) were measured on a *Büchi Melting Point B-545* in open capillary tubes and have not been corrected. **Nuclear magnetic resonance** (NMR) ^1H , ^{13}C and ^{19}F spectra were obtained on a 400 MHz NMR (*Jeol JNM EX-400*) or 270 MHz (*Jeol JNM EX-270*). Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference (CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm; $\text{DMSO}-d_6$: $\delta_{\text{H}} = 2.50$ ppm, $\delta_{\text{C}} = 39.52$ ppm; $\text{Pyridine}-d_5$: $\delta_{\text{H}} = 7.19$ ppm, $\delta_{\text{C}} = 123.50$ ppm; CD_2Cl_2 : $\delta_{\text{H}} = 5.32$ ppm, $\delta_{\text{C}} = 53.80$ ppm; $\text{THF}-d_8$: $\delta_{\text{H}} = 3.58$ ppm, $\delta_{\text{C}} = 67.57$). Coupling constants (J) were given in Hz (J_1 : ortho, J_2 : meta, J_3 : para). Resonance multiplicity was described as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), q (quartet), m (multiplet) and br (broad signal). Carbon spectra were acquired with a complete decoupling for the proton. **Infrared spectra** (IR) in KBr were recorded on a *Perkin-Elmer spectrum RX 1 FT-IR System*. **UV-Vis spectra** were recorded in quartz cuvettes using a *Cary-Varian 5000*. **Liquid chromatography mass spectrometry** (LC-MS) measurements were conducted on an *Agilent 6200 series TOF mass spectrometer* equipped with ESI and APCI ionization sources and a Time Of Flight (TOF) detector, operating in positive mode. The analyte solutions were delivered to the ESI or APCI source by an *Agilent 1200 series LC system* at a flow rate of 0.25 ml/min. Typical elution gradient start from H_2O (90%) to CH_3CN (100%) for 20 minutes. ESI mode: Typical ESI conditions were capillary voltage 2.0 kV; cone voltage 65 V; source temperature 150 $^\circ\text{C}$; desolvation temperature 250 $^\circ\text{C}$; drying gas 5 L/min, nebulizer 60 psig. APCI: Typical APCI conditions were, capillary voltage 2.0 kV; cone voltage 65 V; source temperature 250 $^\circ\text{C}$; desolvation temperature 350 $^\circ\text{C}$; drying gas 5L/min; nebuliser 60 psig. Dry nitrogen was used as the ESI and APCI gas. **Mass spectrometry** was generally performed by the *Centre de spectrométrie de masse* at the *Université de Mons in Belgium* where they performed ESI-MS and MALDI-MS, on using the following instrumentation. ESI-MS measurements were performed on a *Waters QToF2 mass spectrometer* operating in positive mode. The analyte solutions were delivered to the ESI source by a *Harvard Apparatus* syringe pump at a flow rate of 5 L/min. Typical ESI conditions were, capillary voltage 3.1 kV; cone voltage 20-50 V; source temperature 80 $^\circ\text{C}$; desolvation temperature 120 $^\circ\text{C}$. Dry nitrogen was used as the ESI gas. For the recording of the single-stage ESI-MS spectra, the quadrupole (rf-only mode) was set to pass ions from 50 to 1000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. MALDI-MS were recorded using a *Waters QToF Premier mass spectrometer* equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 mW delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight analyses were performed in the reflectron mode at a resolution of about 10,000. The matrix solution (1 μl) was applied to a stainless steel target and air dried. Analyte samples were dissolved in a suitable solvent to obtain 1 mg/ml solutions. 1 μl aliquots of those solutions were applied onto the target area already bearing the matrix crystals, and air dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass ions from 100 to 1000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were analyzed with 1 s integration time. **HPLC** analyses were performed to check the purity of the compounds investigated in this thesis and were carried out on a *Varian 940-LC* liquid chromatograph system. The column used was a *Varian Pursuit C18*, 5

μm , $4.6 \times 250\text{ mm}$ column. CH_3CN was used as eluent. Examples of analyses performed for compound of Chapter 2 are reported in the Appendix, porphyrin modules were, instead, found to be poorly soluble in the HPLC eluents.

4.1.1. Specific Instrumentation and Techniques (Chapter 2)

General photophysical characterization. The photophysical characterizations together with the plastic thin films preparations were performed at the *Istituto per la Sintesi Organica e la Fotoreattività (CNR - ISOF)* of Bologna (Italy). Solvents used for photophysical determinations were spectroscopic grade (C. Erba). Acidification of the solutions was obtained by adding one drop of hydrochloric acid 37% (ACS for Analysis, C. Erba) to 3 ml of solution. The absorption spectra of dilute solutions and plastic thin films were obtained with a *Perkin-Elmer Lambda 950 UV/Vis/NIR* spectrophotometer. Molar absorptivity values (ϵ) were calculated applying the Lambert-Beer law to low absorbance spectra ($A < 1$) of compounds recorded at successive dilutions. Steady-state photoluminescence spectra were measured in right angle mode for solutions and in front face mode for solid samples, using a *Spex Fluorolog II* spectrofluorimeter, equipped with a *Hamamatsu R928* phototube. The concentration of air-equilibrated sample solutions was adjusted to obtain absorption values $A < 0.1$ at the excitation wavelength. While uncorrected luminescence band maxima are used throughout the text, corrected spectra were employed for the determination of the luminescence quantum yields (ϕ). The correction curve of the wavelength dependent phototube response between 280 and 900 nm has been obtained by using a calibrated halogen lamp source. Luminescence quantum efficiencies (ϕ_{em}) were evaluated using the method of Demas and Crosby by comparing the wavelength integrated intensities (I) with reference to a standard (ϕ_r) and by using the following equation:

$$\phi_{em} = \left(\frac{I \cdot n}{A} \right) \left(\frac{A_r}{I_r \cdot n_r} \right) \phi_r$$

where A and n are the absorbance values at the employed excitation wavelength and refractive index of the solvent, respectively. Band maxima and relative luminescence intensities are obtained with uncertainty of 2 nm and 20%, respectively. 1 cm path-length square optical *Suprasil Quartz* (QS) cuvettes were used for measurements at room temperature of dilute solutions, while capillary tubes immersed in liquid nitrogen in a cold finger quartz dewar were used for measurements of MeOH/EtOH (1:4) frozen glasses at 77 K. Luminescence lifetimes were measured with an *IBH 5000F* time-correlated single-photon counting device, by using pulsed *NanoLED* excitation sources at 278, 331 and 373 nm. Analysis of the luminescence decay profiles against time was accomplished with the *Decay Analysis Software DAS6* provided by the manufacturer. Experimental uncertainties in the lifetime determinations are estimated to be 10%. Phosphorescence spectra and lifetimes were measured at 77 K on the same *IBH 5000F TCSPC* device, by using a pulsed *SpectraLED* excitation source at 370 nm, and performing a Time-Resolved Emission Spectra (TRES) procedure. The spectrum was obtained upon selection of slices in a linearity region of the decays obtained at the different emission wavelengths. The lifetime analysis was performed on the whole series of decays with the Global Analysis Module of the *DAS6 Decay Analysis Software* provided by the manufacturer. In order to enhance the phosphorescence intensity one drop of CH_3I was added to 3 ml of MeOH/EtOH (1:4) solution. The band profiles of the corrected luminescence spectra ($I(E)$) on an energy scale (E , cm^{-1}) were analyzed according to a fitting procedure developed by Meyer and co-workers, describing the relationship between the Franck–Condon envelope and some pertinent parameters.^[394, 395] **Preparation of plastic thin film.** (section 2.4.1.2) Thin films of polymethylmethacrylate (PMMA) doped with the organic fluors were prepared from $200\text{ g}\cdot\text{l}^{-1}$ PMMA (MW = 35.000) solutions in CHCl_3

containing 1% w/w organic dyes ($2 \text{ g}\cdot\text{l}^{-1}$), spin coated on $1''\times 1''$ borosilicate glass substrates, cut from microscope slides. Before spin-coating the substrates were cleaned by first sonicating them for 10 min in H_2O with detergent (Carlo Erba AUSILAB 104, 2% deionized H_2O solution at $\text{pH} = 12.5$), then rinsing them with a slightly acidic H_2O solution, and finally washing them with acetone. Spin coating was performed by spreading from 50 to $100 \text{ }\mu\text{L}$ of the starting solution onto the spinning substrate. The spin-coating conditions (4,000 rpm for 60 s) were adjusted to give substrates fully covered with a photoactive layer of *ca.* $2.5 \text{ }\mu\text{m}$ thickness. **Determination of film thickness.** (section 2.4.1.2) When a beam of light passes through two partially reflecting surfaces (like in a thin transparent film) it generates an interference pattern which can be used to calculate the thickness of the film. Given that the film thickness is on the order of magnitude of the wavelength of the incident light, if a Vis/NIR optical absorption spectrum is recorded for such a film, the spectrum appears in the form of maxima and minima. For regions where individual cycles can be clearly resolved, the film thickness can be easily determined by using the following equations:

$$\nu = \frac{\left(\frac{n(\lambda_1)}{\lambda_1} - \frac{n(\lambda_2)}{\lambda_2} \right)}{N_{\text{cyc}}}$$

$$d = \frac{1}{2\nu}$$

where $n(\lambda_1)$ and $n(\lambda_2)$ are the refractive indices of the film at wavelengths λ_1 and λ_2 , N_{cyc} is the number of cycles in the interference fringes between λ_1 and λ_2 , and d is the thickness of the film. In our experiments, Vis-NIR absorption spectra of the films prepared in our experiments on borosilicate glass substrates have been recorded between 400 and 1.500 nm . Film thicknesses of $2.5 \pm 0.2 \text{ }\mu\text{m}$ and $2.8 \pm 0.2 \text{ }\mu\text{m}$, for samples prepared from 50 and $100 \text{ }\mu\text{L}$ of the starting solution, respectively, have been calculated using the refractive index $n_{\text{PMMA}} = 1.4896$, and assuming it to be wavelength independent. **Absolute photoluminescence quantum yield measurement.** The procedures used to determine the photoluminescence quantum yield (PLQY) are generally based on two different experimental approaches: the comparative and the absolute methods. The absolute method has been the normal approach for measurements on thin films over the last decade. In contrast to measurements of PLQY in solution, measurements on thin solid films are not straightforward. Several methods for the measurement of the absolute photoluminescence efficiency of solid state samples using an integrating sphere to collect the emitted light have been proposed.^[396] For the absolute PLQY determination of our sample we used the method proposed by *deMello* and co-workers in 1997. Three measurements are necessary to evaluate the absolute quantum yield, η : (i) the excitation source spectrum with the empty sphere; (ii) the excitation source spectrum and the emission spectrum of a sample placed in the sphere, when the excitation beam hit the sample only after diffusion by the sphere wall; (iii) the excitation source spectrum and the emission spectrum of a sample placed in the sphere, when the excitation beam hit the sample directly. The absorption coefficient, A , is defined as:

$$A = \left(1 - \frac{L_c}{L_b} \right)$$

where L_b and L_c are the spectral areas of the excitation source spectrum detected for the second and the third measurements, respectively. The number of absorbed photons is proportional to A times the spectral area, L_a , of the first measurement. Correcting for the emissions induced indirectly from the reflected excitation beam, the quantum yield can be expressed by:

$$\eta = \frac{P_c - (1 - A) \cdot P_b}{A \cdot L_a}$$

where P_b and P_c are the spectral areas of the emission profiles measured in the second and third measurements, respectively. All measurements were repeated four times. In our experimental setup, a collimated 100 W Hg arc lamp was coupled to the integrating sphere input port. Inside the sphere, a baffle is placed in front of the sphere output port in order to protect the detector from direct illumination by non-diffuse light. The sample is placed at the centre of the sphere in a home-built Teflon sample holder. The sphere output port is connected by means of a pure silica core (600 μm) solarisation-resistant optical fiber to the emission monochromator of a *SPEX Fluorolog II* fluorimeter. With this assembly, great care is taken in order to avoid perturbation by external light. The total response of the integrating sphere / detection system has been corrected by using a calibrated 45 W quartz-halogen tungsten coiled filament lamp standard of spectral irradiance by *Optronics Labs* (calibration range from 280 to 800 nm). **X-ray measurements:** were performed on a Gemini Ultra R system (4-circle kappa platform, Ruby CCD detector) using Cu K λ radiation ($\lambda = 1.54178 \text{ \AA}$) at *Université F.U.N.D.P. de Namur in Belgium*. After mounting and centering of the single crystal on the diffractometer, cell parameters were estimated from a pre-experiment run and full data sets collected at room temperature. Structures were solved by direct methods with SHELXS-86 program and then refined on F^2 using SHELXL-97 software.^[397] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms (not implicated in H-bonds) in the riding mode with isotropic temperature factors fixed at 1.2 times $U(\text{eq})$ of the parent atoms.

4.1.2. Specific Instrumentation and Techniques (Chapter 3)

Scanning Tunneling Microscopy. STM experiments were performed in a custom-designed ultrahigh vacuum (UHV) system available at the Physics Department of the *University of Munich (TUM, Germany)*, providing a base pressure below 1×10^{-10} mbar.^[398] The monocrystalline Cu(111) and Ag(111) substrates were cleaned by repeated Ar^+ sputtering cycles at an energy of 800 eV, followed by annealing at 730 K for about 10 min. Subsequently, a submonolayer coverage of porphyrin derivatives were deposited by organic molecular beam epitaxy from a thoroughly degassed quartz crucible held at 680 or 700 K. During deposition, the Cu(111) or the Ag(111) surfaces were kept at 340 or 373 K, respectively, and the pressure remained $< 5 \times 10^{-10}$ mbar. Cu atoms were evaporated from a homemade water-cooled cell by resistively heating a W filament surrounded by a Cu wire of high purity (99.9999%). All STM images were acquired by employing a low temperature *CreTec-STM*⁶ with the sample held at 6 K using electrochemically etched W tips. In the figure captions, V refers to the bias voltage applied to the sample. Regarding coverage, we define 1 monolayer (ML) as one surface fully covered by molecules. **Simulations of porphyrin derivatives** were performed in the framework of the Hyperchem 7.5 Software Package.⁷ The WSxM software was used for the analysis of STM images.^[399]

Preparation of the nanotube derivatives. Polytetrafluoroethylene (Fluorophore FH 0.45 μm) and polycarbonate (Isopore HTTP 0.2 and 0.4 μm) filters were purchased from Millipore. Muscovite (mica) sheets were obtained from Axim Enterprises and copper grids (200 square mesh) with carbon film were purchased from Electron Microscopy Sciences. **XPS characterization.** X-ray photoelectron spectroscopy analyses were performed with a *SSX-100 system* (Surface Science instrument). The photon source was a monochromatized Al K α line ($h\nu = 1486.6 \text{ eV}$) applied with a takeoff angle of 35° . In the spectrum analysis, the background signal was subtracted by Shirley's method. The C 1s

⁶ Createc D-74391 Erligheim, Germany.

⁷ HYPERCHEM; Gainesville, FL.

core level peak position of carbon atoms was taken as the reference at 284.5 eV. The spectrum analysis was carried out by fitting the peak shape obtained in the same analysing conditions and other components with mixed (Gaussian + Lorentzian) line shapes. XPS atomic ratios have been estimated from the experimentally determined area ratios of the relevant core lines, corrected for the corresponding theoretical atomic cross-sections and for a square root dependence of the photoelectrons kinetics energies. **TGA characterization.** TGA analysis were performed with a TGA Q500 instrument manufactured by TA instruments, under a N₂ flow of 40 ml min⁻¹. General method: equilibration from room temperature to 100 °C in 6 min, isothermal heating at 100 °C for 20 min, then thermal ramp from 100 °C to 1000 °C in 90 min (heating rate of 10 °C min⁻¹). **TEM characterization.** Approximately 1 mg of CNT derivatives was dispersed in 5 mL of DMF through 10 min of sonication, affording homogeneous dispersions. Two drops of the DMF dispersion were drop-casted onto the copper grid. The copper grids were then analyzed with a Tecnai-10 transmission electron microscope operating at 80 kV. **AFM characterization.** Freshly peeled mica substrates were spin-coated (3,000 rpm, 2 min) with two drops of CNTs/DMF dispersions, and then analyzed by tapping-mode AFM imaging (air, 298 K), with a Multimode 8 (*Nanoscope V*) apparatus from Veeco. Tips were phosphorous-doped silicon cantilevers ($T = 20\text{--}80$ mm, $L = 115\text{--}135$ mm, $f_0 = 200\text{--}400$ kHz, $k = 20\text{--}80$ N m⁻¹, VEECO, USA) operating at a resonant frequency of ca. 320 kHz. The statistical treatment was carried out on samples containing **ox-DWCNTs**. The data files collected with the AFM instrumentation were analyzed with WSxM 5.0 (Nanotec Electronica, Spain) software, in order to generate image files containing the sample topography. Considering as isolated DWCNTs or very thin MWCNTs only the objects with height cross-section lower than 10 nm, the length values obtained from 400 nanotubes were analyzed with the statistics tools of Origin Pro (version 7.5714). **Photophysical Studies.** Photophysical characterizations were performed at the *Istituto per la Sintesi Organica e la Fotoreattività* (CNR - ISOF) of Bologna (Italy). DMF and CHCl₃ (Carlo Erba, spectrofluorimetric grade) without further purification were used. The sonication was carried out with an Elmasonic S10, Elma Hans Schimidbauer GmbH & Co. KG, Germany, Max. potential 240 W, Frequency 37 kHz. Absorption spectra were recorded with a Perkin-Elmer Lambda 950 UV/vis/NIR spectrophotometer. Steady-state photoluminescence spectra were measured in right angle mode with an Edinburgh FLS920 spectrometer (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185 – 900 nm range). Fluorescence lifetimes were measured with an IBH 5000F time-correlated single-photon counting device, by using pulsed NanoLED excitation sources at 331, 373, 465 and 560 nm. Analysis of the luminescence decay profiles against time was accomplished with the Decay Analysis Software DAS6 provided by the manufacturer. **Device fabrication:** The implementation of the porphyrin-CNTs derivatives has been performed at the *Université Catholique de Louvain (UCL)* of Louvain-La-Neuve (Belgium). The *J-V* characteristics were measured in dark, at room temperature, with an Agilent 4156C parameter analyzer. For the measurement of the External Quantum Efficiency (EQE), light from a quartz tungsten halogen lamp was coupled into a monochromator and calibrated against a Si photodiode with known spectral response. The light incident on the device was chopped and the EQE was determined by taking the ratio of the modulated device photocurrent to that of the calibrated sensor. The surface topography of the thin films has been studied with an *alpha300S AFM-SNOM* instrument from Witec. Simultaneously with AFM-contact topography, optical transmission mapping was carried out with < 90-nm aperture cantilevers and 532 nm green laser light. We used also 635-nm laser beam light and observed no differences. For each line scan 512 data points were taken with a line scan frequency of 1 Hz.

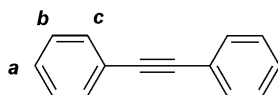
4.2. Material and General Methods

Chemicals were purchased from *Sigma Aldrich*, *Acros Organics*, *Fluorochem* and *ABCR* and were used as received. Solvents were purchased from *Sigma Aldrich*, while deuterated solvents from *Eurisotop*. Anhydrous solvents as Et₂O, THF and toluene were distilled from Na/benzophenone; CH₂Cl₂ from phosphorus pentoxide; CHCl₃ and CH₃CN from CaH₂. Anhydrous DMF was purchased from *Acros Organics*. Hydrogen peroxide (H₂O₂ 15%) was obtained from Riedel-de Haën, whereas sulfuric acid (H₂SO₄ 95%) nitric acid (HNO₃ 62%) and hydrochloric acid (HCl 32%) were purchased from Fischer Scientific. Pyridine was purchased from *Acros Organics*. MeOH, CHCl₃, acetone were purchased as reagent-grade and used without further purification. Low temperature baths were prepared using different solvent mixtures depending on the desired temperature: -78 °C with acetone/liquid N₂ or acetone/dry ice, -40 °C with CH₃CN/liquid N₂, -10 °C with ice-H₂O/NaCl, and 0 °C with ice/H₂O. Anhydrous conditions were achieved by drying *Schlenk* tubes or 2-neck flasks by flaming with a heat gun under vacuum and then purging with Argon. The inert atmosphere was maintained using Argon-filled balloons equipped with a syringe and needle that was used to penetrate the silicon stoppers used to close the flasks' necks. Additions of liquid reagents were performed using dried plastic or glass syringes.

4.3. Experimental Procedures

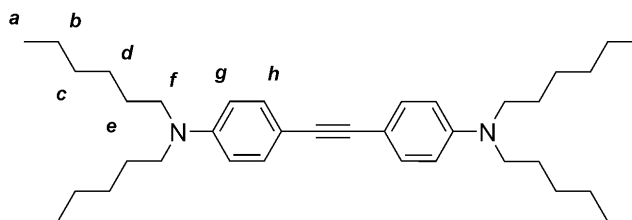
4.3.1. π -Conjugated Acetylene-Based Scaffolds

1,2-Diphenylethyne **34**



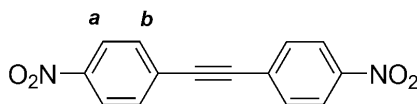
To a dried Schlenk tube, **48** (0.50 g, 2.45 mmol), dried *i*Pr₂NH (42 ml), phenylacetylene **49** (0.25 g, 2.45 mmol), [PdCl₂(PPh₃)₂] (91 mg, 0.13 mmol) and CuI (40 mg, 0.21 mmol) were added under Ar. The solution was degassed three times by “freeze-pump-thaw” cycles and stirred for 16 h at rt. Upon completion, monitored by TLC (eluent: hexane), the crude mixture was filtered through celite. The precipitate on the filter was cleaned with repeated hexane washing and the solvents evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: hexane) affording pure **34** as a white crystalline solid (0.4 g, 90%). C₁₄H₁₀, MW: 178.23 g/mol. M.p.: 53-55 °C. δ_{H} (CDCl₃, 400 MHz) 7.36-7.39 (m, 6H, *H*_a, *b*); 7.58-7.61 (m, 4H, *H*_c). δ_{C} (CDCl₃, 100 MHz) 131.77, 128.51, 128.42, 123.43, 89.56. Spectral characterization agrees with previously reported data.^[400, 401]

1,4-Bis[(*N,N*-dihexylamino)phenyl]-1,2-ethyne **35**

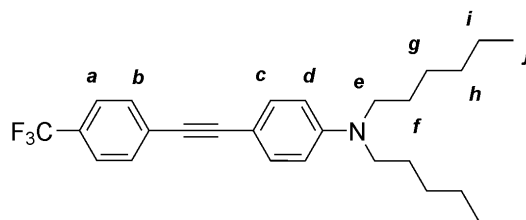


To a dried Schlenk tube, **50** (70 mg, 0.3 mmol), dried *i*Pr₂NH (7 ml), **51** (0.19 g, 0.7 mmol), [PdCl₂(PPh₃)₂] (10 mg, 0.015 mmol) and CuI (5 mg, 0.03 mmol) were added under Ar. This solution was degassed three times by “freeze-pump-thaw” cycles and stirred for 16 h at rt under Ar. The crude mixture was then filtered through celite, and the precipitate on the filter cleaned with repeated hexane washing. After the removal of the solvents *in vacuo*, the residue was purified by silica gel chromatography (eluent: hexane/CH₂Cl₂ 8:2) affording pure **35** as a dark oil (40 mg, 24%). C₃₈H₆₀N₂, MW: 544.89 g/mol. δ_{H} (CDCl₃, 400 MHz) 7.33 (d, *J* 8.5, 4H, *H_h*), 6.51 (d, *J* 8.5, 4H, *H_g*), 3.27-3.23 (m, 8H, *H_f*), 1.56 (m, 8H, *H_e*), 1.31-1.25 (m, 24H, *H_{b,c,d}*), 0.91-0.88 (m, 12H, *H_a*). δ_{C} (CDCl₃, 100 MHz) 148.21, 133.77, 111.08, 107.40, 82.53, 51.0, 31.70, 27.15, 26.76, 22.70, 14.0. Spectral characterization agrees with previously reported data.^[402]

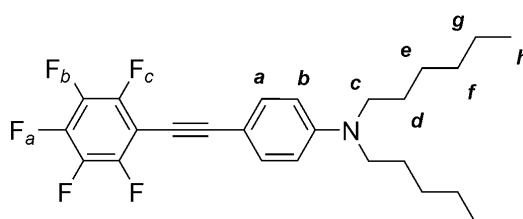
1,4-Bis(4-nitrophenyl)-1,2-ethyne **36**



To a dried Schlenk tube, 4-nitroiodobenzene **54** (75 mg, 0.3 mmol), dried DMF (2 ml), **55** (0.1 g, 0.68 mmol), [PdCl₂(PPh₃)₂] (10 mg, 0.015 mmol) and CuI (5 mg, 0.03 mmol) were added in dried *i*Pr₂NH (3 ml) under Ar. The solution was degassed three times by “freeze-pump-thaw” cycles and, subsequently, transferred into a microwave vial. It was then microwave-irradiated at 120°C for 5 min. The crude mixture was filtered through celite. The precipitate on the filter was then cleaned with repeated hexane washing and the solvent evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: hexane) affording pure **36** as a yellow powder (40 mg, 50%). C₁₄H₈N₂O₂, MW: 268.22 g/mol. M.p.: 195-198°C. δ_{H} (CDCl₃, 400 MHz) 8.25 (d, *J* 8.9, 4H, *H_a*), 7.70 (d, *J* 8.9, 4H, *H_b*). δ_{C} (CDCl₃, 100 MHz) 147.62, 132.61, 128.85, 123.80, 92.0. Spectral characterization agrees with previously reported data.^[403]

4-[(4-Trifluoromethylphenyl)ethynyl]-*N,N*-dihexylaniline **39**

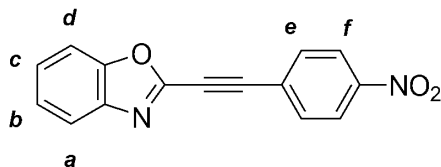
To a dried Schlenk tube, 4-iodobenzotrifluoride **60** (0.1 g, 0.36 mmol), **51** (0.24 g, 0.83 mmol), [PdCl₂(PPh₃)₂] (13 mg, 0.018 mmol) and CuI (7 mg, 0.036 mmol) were added in dried *i*Pr₂NH (10 ml) under Ar. The solution was degassed three times by “freeze-pump-thaw” cycles and stirred for 16 h at rt under Ar. Subsequently, the crude mixture was filtered through celite. The precipitate on the filter was then cleaned with repeated hexane washing and the solvents evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: hexane/CH₂Cl₂ 85:15) affording pure **39** as a yellow sticky oil (90 mg, 58%). C₂₇H₃₄NF₃, MW: 429.56 g/mol. $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2943.1, 2210.23, 2164.84, 1602.49, 1520.13, 1466.33, 1404.23, 1369.31, 1322.36, 1256.59, 1229.14, 1197.56, 1161.03, 1106.77, 1066.50, 1016.41, 840.64, 813.33, 726.79, 669.69, 596.21, 544.25. UV-Vis (MeOH, 25 °C) $\lambda_{\max}(\epsilon, \text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1})$ 245 (13100), 282 (9700), 356 (34400). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.56 (s, 4H, $H_{a,b}$), 7.37 (d, J 8.3, 2H, H_c), 6.57 (d, J 8.3, 2H, H_d), 3.30-3.26 (m, 4H, H_e), 1.58-1.56 (m, 4H, H_f), 1.32 (m, 12H, $H_{g,h,i}$), 0.89 (m, 6H, H_j). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 148.40, 133.20, 131.34, 128.33, 125.56, 125.21 (d, CF₃), 122.85, 111.26, 107.84, 93.81, 86.11, 51.05, 31.80, 27.25, 26.90, 22.80, 14.12. $\delta_{\text{F}}(\text{CDCl}_3, 376 \text{ MHz})$ -62.47. APCI-HRMS: calc. 429.2643 m/z : 430.2831 ($[M+H]^+$, C₂₇H₃₅NF₃⁺).

4-[(Pentafluorophenyl)ethynyl]-*N,N*-dihexylaniline **40**

To a dried Schlenk tube, pentafluoroiodobenzene **61** (0.22 g, 0.76 mmol), **51** (0.1 g, 0.34 mmol), [PdCl₂(PPh₃)₂] (12 mg, 0.017 mmol) and CuI (6 mg, 0.034 mmol) were added in dried *i*Pr₂NH (15 ml) under Ar. This solution was degassed three times by “freeze-pump-thaw” cycles and stirred 16 h at rt under Ar. The crude mixture was, then, filtered through celite, and the precipitate on the filter was cleaned with repeated hexane washing. After the removal of the solvents *in vacuo*, the residue was purified by silica gel chromatography (eluent: hexane/CH₂Cl₂ 9:1) affording pure **40** as a yellow sticky oil (90 mg, 60%). C₂₆H₃₀F₅N, MW: 451.51 g/mol. $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2931.37, 2207.52, 1605.63, 1526.62, 1499.28, 1452.51, 1403.55, 1369.48, 1295.65, 1256.17, 1228.71, 1190.63, 1147.89, 1109.53, 1029.21, 989.46, 966.48, 813.87, 726.91, 531.77. UV-Vis (MeOH, 25 °C) $\lambda_{\max}(\epsilon, \text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1})$ 241 (15200), 357 (42800). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.38 (d, J 8.6, 2H, H_a), 6.57 (d, J 8.6, 2H, H_b), 3.28 (m, 4H, H_c), 1.58 (m, 4H, H_d), 1.32 (m, 12H, $H_{e,f,g}$), 0.92-0.89 (m, 6H, H_h). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 148.78, 147.90 (m, C_F), 145.50 (m, C_F), 141.15 (m, C_F), 138.97 (m, C_F), 136.45 (m, C_F), 133.3, 111.07, 106.64, 103.9, 101.5 (m, C_F), 71.06, 50.95, 31.67,

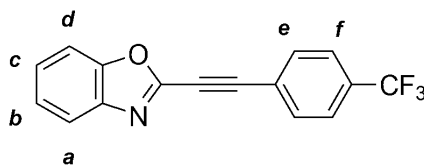
27.10, 26.75, 22.65, 14.0. δ_F (CDCl₃, 376 MHz) -137.15 (d, 2F, F_b), -155.26 (t, 1F, F_a), -162.60 (t, 2F, F_c). ESI-HRMS: calc. 451.2289 m/z : 452.2393 ($[M+H]^+$, C₂₆H₃₁F₅N⁺).

2-[2-(4-Nitrophenyl)ethynyl]-1,3-benzoxazole **41**

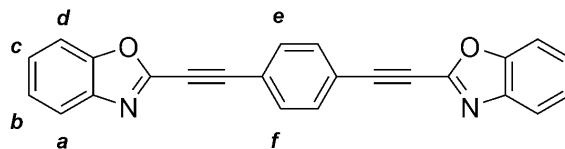


To a solution of **67** (0.1 g, 0.4 mmol) and **55** (70 mg, 0.4 mmol) in a mixture of *i*Pr₂NH (1.6 ml) and DMF (0.5 ml), [PdCl₂(PPh₃)₂] (14 mg, 0.02 mmol) and CuI (8 mg, 0.04 mmol) were added. The reaction was microwave-irradiated for 8 min at 80 °C. Upon completion, monitored by TLC (eluent: cyclohexane/CH₂Cl₂ 1:1), the solution was diluted with few drops of cyclohexane and a pale yellow precipitate obtained. The precipitate was filtered, washed with cyclohexane and recrystallized from hot cyclohexane affording pure **41** as a pale yellow powder (50 mg, 47%). C₁₅H₈N₂O₃, MW: 264.23 g/mol. M.p.: 130-132 °C. $\nu_{\max}$ (film)/cm⁻¹ 3105.72, 2360.21, 2223.65, 1591.96, 1520.15, 1343.50, 1305.53, 840.21, 765.20, 745.51. UV-Vis (CH₂Cl₂, 25 °C) $\lambda_{\max}$ (ϵ , mol⁻¹·l·cm⁻¹) 334 (25800). δ_H (CDCl₃, 400 MHz) 8.30 (d, J 6.9, 2H, H_f), 7.84 (d, J 6.9, 2H, H_e), 7.83 (d, J_1 7.4, 1H, H_d), 7.58 (d, J_1 7.4, 1H, H_a), 7.49-7.40 (dt, J_1 7.4, 2H, $H_{b,c}$). δ_C (CDCl₃, 100 MHz) 150.57, 148.28, 140.90, 133.28, 127.0, 126.85, 125.40, 123.90, 120.75, 110.81, 90.47, 81.55 (one peak is missing due to overlaps). EI-HRMS calc. 264.0535, m/z : 264.0531 ($[M]^+$ C₁₅H₈N₂O₃⁺).

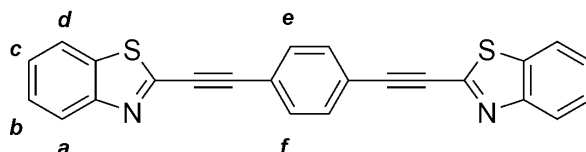
2-[2-(4-Trifluoromethylphenyl)ethynyl]-1,3-benzoxazole **42**



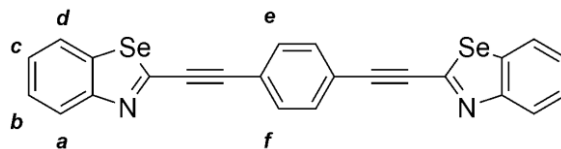
To a solution of **67** (0.2 g, 0.8 mmol) and **68** (0.2 g, 1.2 mmol) in a mixture of *i*Pr₂NH (1.8 ml) and DMF (1 ml), [PdCl₂(PPh₃)₂] (27 mg, 0.04 mmol) and CuI (14 mg, 0.078 mmol) were added. The mixture was microwave-irradiated for 4 min at 80 °C. Upon completion, monitored by TLC (eluent: cyclohexane/CH₂Cl₂ 1:1), the reaction was diluted with CH₂Cl₂, washed with an aqueous soln. of HCl (0.1M) and the organic layer dried over MgSO₄. The solvent was, then, evaporated *in vacuo* and the residue was purified by silica gel chromatography (eluent: CH₂Cl₂/cyclohexane 1:1 up to 7:3) affording pure **42** as a pale yellow powder (130 mg, 58%). C₁₆H₈F₃NO, MW: 287.23 g/mol. M.p.: 162-169 °C. $\nu_{\max}$ (film)/cm⁻¹ 3050.6, 2921.83, 2224.53, 1905.91, 1779.56, 1604.54, 1549.54, 1504.06, 1477.09, 1448.12, 1404.97, 1319.60, 1239.44, 1167.83, 1123.33, 1104.31, 1065.14, 1013.98, 942.03, 837.18, 760.82, 746.65, 651.34, 594.16, 621.46. UV-Vis (CH₂Cl₂, 25 °C) $\lambda_{\max}$ (ϵ , mol⁻¹·l·cm⁻¹) 310 (28800). δ_H (CDCl₃, 400 MHz) 7.79-7.77 (m, 3H, $H_{d,f}$), 7.69-7.67 (m, 2H, H_e), 7.57 (d, J_1 7.4, 1H, H_a), 7.47-7.41 (dt, J_1 7.4, 2H, $H_{b,c}$). δ_C (CDCl₃, 100 MHz) 150.47, 147.10, 140.94, 132.72, 126.70, 125.63, 125.60, 125.23, 124.02, 120.62, 110.72, 91.30, 79.37 (one peak is missing due to overlaps). δ_F (CDCl₃, 376 MHz) -63.0. APCI-HRMS calc. 287.0588 m/z : 288.0967 ($[M+1]^+$ C₁₉H₉F₃NO⁺).

1,4-Bis-(benzoxazol-2-ylethynyl)benzene **43**

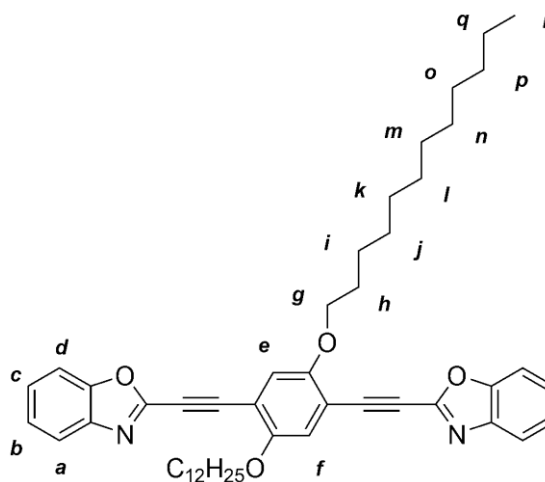
To a solution of **67** (0.1 g, 0.4 mmol) and 1,4-diethynylbenzene **70** (26 mg, 0.2 mmol) in a mixture of *i*Pr₂NH (0.9 ml) and DMF (0.5 ml), [PdCl₂(PPh₃)₂] (5.6 mg, 0.008 mmol) and CuI (8 mg, 0.04 mmol) were added. The reaction was microwave-irradiated for 5 min at 80 °C. Upon completion, monitored by TLC (eluent: cyclohexane/AcOEt 9:1), the solution was diluted with few drops of cyclohexane and a pale yellow precipitate obtained. The precipitate was filtered, washed with cyclohexane and recrystallized from hot cyclohexane affording pure **43** as a pale yellow powder (60 mg, 50%). C₂₄H₁₂N₂O₂, MW: 360.36 g/mol. M.p.: 110-112 °C. $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3040.43, 2927.22, 2218.60, 1602.15, 1551.05, 1470.43, 1446.16, 1400.53, 1338.7, 1295.69, 1236.55, 1103.73, 938.17, 831.02, 737.83, 543.99. UV-Vis (CH₂Cl₂, 25 °C) $\lambda_{\max}$ (ϵ , mol⁻¹·l·cm⁻¹) 343 (11800), 367 (7400) (low values of ϵ are due to poor solubility in the solvent). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.79 (d, *J*₁ 6.6, 2H, *H_d*), 7.71 (s, 4H, *H_{e,f}*), 7.58 (d, *J*₁ 6.6, 2H, *H_a*), 7.46-7.39 (m, 4H, *H_{b,c}*). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 157.44, 141.0, 132.56, 126.65, 125.20, 122.12, 120.58, 110.71, 101.20, 92.20, 80.0. ESI-HRMS calc. 360.0899, *m/z*: 361.0939 ([*M*+H]⁺, C₂₄H₁₃N₂O₂⁺).

1,4-Bis-(benzothiazol-2-ylethynyl)benzene **44**

To a solution of **72** (0.1 g, 0.4 mmol) and 1,4-diethynylbenzene **70** (25 mg, 0.2 mmol) in a mixture of *i*Pr₂NH (1.8 ml) and DMF (1 ml), [PdCl₂(PPh₃)₂] (5.5 mg, 0.008 mmol) and CuI (7 mg, 0.04 mmol) were added. The reaction was microwave-irradiated for 4 min at 80 °C. Upon completion, monitored by TLC (eluent: CH₂Cl₂), few drops of cyclohexane were added and a pale yellow precipitate obtained. The precipitate was filtered, washed with cyclohexane and recrystallized from hot CH₂Cl₂ affording pure **44** as a pale yellow powder (50 mg, 33%). C₂₄H₁₂N₂S₂, MW: 392.5 g/mol. M.p.: 100-102 °C. $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3051.21, 2921.83, 2223.40, 1604.02, 1549.31, 1476.81, 1447.97, 1404.9, 1319.54, 1167.5, 1122.65, 1103.77, 1013.69, 941.54, 836.17, 745.42, 760.52, 796.91, 650.7, 620.95, 593.32, 522.76. UV-Vis (CH₂Cl₂, 25 °C) $\lambda_{\max}$ (ϵ , mol⁻¹·l·cm⁻¹) 355 (51000), 378 (34000). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 8.10 (d, *J*₁ 8.0, 2H, *H_d*), 7.90 (d, *J*₁ 8.0, 2H, *H_a*), 7.68 (s, 4H, *H_{e,f}*), 7.56-7.46 (dt, *J*₁ 8.0, 4H, *H_{b,c}*). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 153.0, 141.2, 132.26, 128.20, 126.85, 126.44, 123.77, 122.50, 121.32, 95.0, 85.10. APCI-HRMS calc. 392.0442, *m/z*: 393.0482 ([*M*+H]⁺, C₂₄H₁₃N₂S₂⁺).

1,4-Bis-(benzoselenazol-2-ylethynyl)benzene **45**

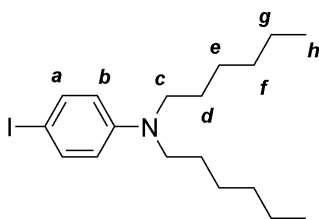
To a dried Schlenk tube, **85** (50 mg, 0.1 mmol) was dissolved in a mixture of Et₃N (0.8 ml) and DMF (3.2 ml). This solution was degassed three times by “freeze-thaw-pump” cycles. Subsequently, CsF (50 mg, 0.7 mmol) was added and the mixture was stirred for 15 min at rt under Ar. After the addition, a color change from pale yellow to dark red was observed. 1,4-diiodobenzene **87** (18 mg, 0.055 mmol), [PdCl₂(PPh₃)₂] (2 mg, 0.0026 mmol) and CuI (1 mg, 0.0055 mmol) were then added, and the reaction was further stirred for 16 h at rt under Ar. The crude mixture was then diluted with few drops of cyclohexane and a pale yellow precipitate was obtained. The precipitate was filtered, washed with cyclohexane and purified by recrystallization from hot CHCl₃ and cyclohexane, affording pure **45** as a pale yellow powder (4 mg, 15%). C₂₄H₁₂N₂Se₂, MW: 486.28 g/mol. M.p.: decomposition observed before melting point was detected. ν_{max} (film)/cm⁻¹ 2927.80, 2212.73, 1637.20, 1514.75, 1498.60, 1467.10, 1428.73, 1309.0, 1260.10, 1237.91, 1093.70, 1016.70, 879.75, 832.90, 764.33, 758.25, 718.0, 632.90, 544.80. UV-Vis (CHCl₃, 25 °C) λ_{max} (ϵ , mol⁻¹·l·cm⁻¹) 361 (-), 385 (-) (ϵ values were not measured due to poor solubility in the solvent). δ_{H} (400 MHz, CDCl₃) 8.16 (d, *J*₁ 8.2, 2H, *H_d*), 7.92 (d, *J*₁ 8.2, 2H, *H_a*), 7.67 (s, 4H, *H_{e,f}*), 7.53 (t, *J*₁ 8.2, 2H, *H_c*), 7.40 (t, *J*₁ 8.2, 2H, *H_b*). δ_{C} (100 MHz, CDCl₃) 154.60, 139.60, 132.12, 126.82, 126.38, 125.44, 124.60, 122.63, 99.80, 96.62, 87.76. ESI-HRMS calc. 486.2927, *m/z*: 487.3565 ([*M*+H]⁺, C₂₄H₁₃N₂Se₂⁺).

1,4-Bis-(benzoxazol-2-ylethynyl)-2,5-didodecyloxybenzene **47**

To a solution of **77** (50 mg, 0.1 mmol) and **67** (50 mg, 0.2 mmol) in a mixture of *i*Pr₂NH (0.5 ml) and DMF (0.5 ml), [PdCl₂(PPh₃)₂] (3 mg, 0.004 mmol) and CuI (4 mg, 0.02 mmol) were added. The reaction was microwave-irradiated for 5 min at 80 °C. When the solution was cooled down to rt, the formation of a yellow precipitate was observed. The precipitate was filtered, washed with cyclohexane and then purified by silica gel chromatography (eluent: cyclohexane/CH₂Cl₂ 2:8) affording pure **47** as a yellow powder (50 mg, 35%). C₄₈H₆₀N₂O₄, MW: 729.0 g/mol. M.p.:

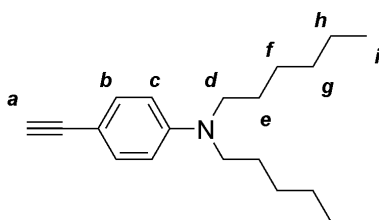
91-93 °C. $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2923.51, 2224.4, 1701.9, 1553.53, 1243.0, 1220.4, 938.17, 1131.0, 740.0. UV-Vis (CH_2Cl_2 , 25 °C) $\lambda_{\max}(\epsilon, \text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1})$ 330 (82000), 392 (78000). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.77 (d, J_1 7.1, 2H, H_d), 7.55 (d, J_1 7.1, 2H, H_a), 7.45-7.37 (dt, J 7.1, 4H, $H_{b,c}$), 7.15 (s, 2H, $H_{e,f}$), 4.04-4.06 (t, 4H, H_g), 1.89-1.85 (m, 4H, H_h), 1.55-1.53 (m, 4H, H_i), 1.29-1.23 (m, 32H, $H_{j,k,m,n,o,p,q}$), 0.85-0.87 (t, 6H, H_r). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 154.55, 150.24, 147.70, 141.17, 126.37, 125.04, 120.50, 117.37, 113.04, 110.62, 89.81, 83.10, 69.81, 31.90, 29.68, 29.61, 29.37, 29.34, 29.06, 27.87, 25.94, 22.68, 14.11 (one carbon peak of the alkylic chain is missing due to overlap). ESI-HRMS: calc. 728.4553, m/z : 729.2234 ($[M+H]^+$, $\text{C}_{48}\text{H}_{61}\text{N}_2\text{O}_4^+$).

4-(*N,N*-Dihexylamino)iodobenzene **50**



To a 100 ml round bottom two-necked flask 1-bromo-*n*-hexane (10.5 ml, 75.3 mmol), dried and degassed DMF (50 ml) and KI (12.5 g, 75.3 mmol) were added under Ar. The mixture was heated at 95 °C under vigorous stirring for 30 min. Subsequently, Na_2CO_3 (4.35 g, 41 mmol) and 4-iodoaniline **52** (5.0 g, 22.8 mmol) were added. The resulting solution was allowed to stir for further 20 h at 95 °C. After cooling to rt, the mixture was diluted with AcOEt and poured in H_2O . The organic layer was washed with brine (1 $\times$ 30 ml) and water (5 $\times$ 30 ml), dried on MgSO_4 and the solvent evaporated *in vacuo*. The residue was then purified by silica gel chromatography (eluent: cyclohexane) affording pure **50** as a pale yellow oil (5.7 g, 65%). $\text{C}_{18}\text{H}_{30}\text{IN}$, MW: 387.34 g/mol. $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.40 (d, J 9.0, 2H, H_a), 6.39 (d, J 9.0, 2H, H_b), 3.21-3.23 (m, 4H, H_c), 1.55 (m, 4H, H_d), 1.29 (m, 12H, $H_{e,f,g}$), 0.89 (m, 6H, H_h). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 147.69, 137.72, 114.07, 76.40, 51.11, 31.80, 14.14, 27.10, 26.88, 27.77. Spectral characterization agrees with previously reported data.^[404]

4-Ethynyl-*N,N*-Dihexylaniline **51**

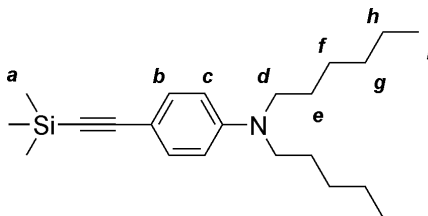


To a degassed solution of THF/MeOH (50 ml, 1:1) **50** (2.28 g, 6.4 mmol) and K_2CO_3 (1.77 g, 12.8 mmol) were added under Ar. The mixture was allowed to stir for 1 h at rt. Upon completion, monitored by TLC (eluent: CH_2Cl_2), the solution was filtered through celite. The precipitate on the filter was then washed with repeated cyclohexane washing and the solvent evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: CH_2Cl_2) affording pure **51** as a colorless oil (1.82 g, 100%). $\text{C}_{14}\text{H}_{31}\text{N}$, MW: 285.44 g/mol. $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.31 (d, J 8.9, 2H, H_b), 6.51 (d, J 8.9, 2H, H_c), 3.24 (m, 4H, H_d), 2.94 (s, 1H, H_a), 1.54 (m, 4H, H_e), 1.29 (m, 12H, $H_{f,g,h}$), 0.89 (m,

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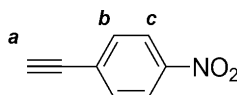
6H, H_i). δ_C (CDCl₃, 100 MHz) 148.28, 133.45, 111.09, 107.42, 85.19, 74.48, 51.03, 31.79, 27.22, 26.88, 22.77, 14.13. Spectral characterization agrees with previously reported data.^[404]

4-[(*N,N*-Dihexylamino)-2-(trimethylsilyl)ethyn-1-yl]benzene **53**



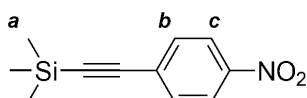
To a dried Schlenk tube, **50** (0.5 g, 1.2 mmol), dried *i*Pr₂NH (18 ml), TMSA (0.28 g, 2.9 mmol), [PdCl₂(PPh₃)₂] (42 mg, 0.06 mmol) and CuI (22 mg, 0.12 mmol) were added under Ar. The solution was degassed three times by “freeze-pump-thaw” cycles and stirred 16 h at rt under Ar. Subsequently, the crude mixture was filtered through celite. The precipitate on the filter was then cleaned with repeated hexane washing and the solvents evaporated *in vacuo*. The residue was then purified by silica gel chromatography (eluent: hexane/AcOEt 9:1) affording pure **53** as a yellow oil (0.26 g, 61%). C₂₃H₃₉NSi, MW: 357.64 g/mol. δ_H (CDCl₃, 400 MHz) 7.27 (d, *J* 13, 2H, H_b), 6.48 (d, *J* 13, 2H, H_c), 3.22 (m, 4H, H_d), 1.56-1.53 (m, 4H, H_e), 1.33-1.29 (m, 12H, $H_{f,g,h}$), 0.98-0.85 (m, 6H, H_i), 0.21 (s, 9H, H_a). δ_C (CDCl₃, 100 MHz) 148.12, 133.35, 111.10, 108.60, 106.92, 90.85, 51.0, 31.78, 27.22, 26.86, 22.76, 14.13, 0.34. Spectral characterization agrees with previously reported data.^[404]

4-Ethynylnitrobenzene **55**



To a degassed solution of THF/MeOH (30 ml, 1/1) **56** (0.75 g, 3.4 mmol) and K₂CO₃ (0.95 g, 6.8 mmol) were added under Ar. This solution was then stirred for 1 h at rt under Ar. Upon completion, monitored by TLC (eluent: hexane/CH₂Cl₂ 6:4), the crude mixture was filtered through celite. The precipitate on the filter was cleaned with repeated cyclohexane washing and the solvents evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: hexane/CH₂Cl₂ 6:4) affording pure **55** as a pale yellow powder (0.50 g, 100%). C₈H₅NO₂, MW: 147.13 g/mol. M.p.: 146-147°C. δ_H (CDCl₃, 400 MHz) 8.20 (d, *J* 8.9, 2H, H_c), 7.64 (d, *J* 8.9, 2H, H_b), 3.35 (s, 1H, H_a). δ_C (CDCl₃, 100 MHz) 147.50, 132.95, 128.91, 123.50, 82.30, 81.60. Spectral characterization agrees with previously reported data.^[405]

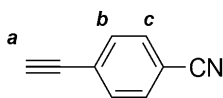
4-[(2-Trimethylsilyl)ethyn-1-yl]nitrobenzene **56**



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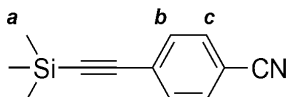
To a dried Schlenk tube, 4-iodo-nitrobenzene **54** (1.5 g, 6 mmol), TMSA (1.27 g, 13.2 mmol), [PdCl₂(PPh₃)₂] (0.21 g, 0.3 mmol) and CuI (0.11 g, 0.6 mmol) were added in dried *i*Pr₂NH (30 ml) under Ar. The solution was degassed three times by “freeze-pump-thaw” cycles and stirred 16 h at rt under Ar. The crude mixture was, then, filtered through celite. The precipitate on the filter was cleaned with repeated hexane washing and the solvent evaporated *in vacuo*. The residue was then purified by silica gel chromatography (eluent: hexane/CH₂Cl₂ 7:3) affording pure **56** as a dark yellow powder (1.0 g, 76%). C₁₁H₁₃NO₂Si, MW: 219.31 g/mol. M.p.: 90 °C. δ_{H} (CDCl₃, 400 MHz) 8.16 (d, *J* 8.9, 2H, *H_c*), 7.59 (d, *J* 8.9, 2H, *H_b*), 0.27 (s, 9H, *H_a*). δ_{C} (CDCl₃, 100 MHz) 147.13, 132.70, 130.01, 123.46, 102.70, 100.60, -0.31. Spectral characterization agrees with previously reported data.^[405]

4-Ethynylbenzonitrile **57**

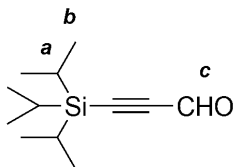


To a degassed solution of THF/MeOH (13 ml, 1:1) **56** (0.40 g, 2 mmol) and K₂CO₃ (0.55 g, 4 mmol) were added under Ar. This solution was then stirred for 1 h at rt under Ar. The crude mixture was, then, filtered through celite. The precipitate on the filter was then cleaned with repeated hexane washing and the solvents evaporated *in vacuo*. The residue was then purified by silica gel chromatography (eluent: CH₂Cl₂) affording pure **57** as a pale yellow powder (0.13 g, 50%). C₉H₅N, MW: 127.14 g/mol. M.p.: 155-157°C. δ_{H} (CDCl₃, 400 MHz) 7.62 (d, *J* 8.6, 2H, *H_b*); 7.57 (d, *J* 8.6, 2H, *H_c*), 3.29 (s, 1H, *H_a*). δ_{C} (CDCl₃, 100 MHz) 132.71, 132.0, 127.0, 118.23, 112.34, 81.85, 81.52. Spectral characterization agrees with previously reported data.^[405]

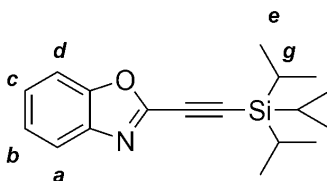
4-[(2-Trimethylsilyl)ethyn-1-yl]benzonitrile **59**



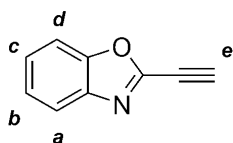
To a dried Schlenk tube, 4-iodobenzonitrile **54** (0.60 g, 2.6 mmol), dried *i*Pr₂NH (18 ml), TMSA (0.58 g, 5.9 mmol), [PdCl₂(PPh₃)₂] (91 mg, 0.13 mmol) and CuI (49 mg, 0.26 mmol) were added under Ar. The solution was degassed three times by “freeze-pump-thaw” cycles and stirred for 16 h at rt under Ar. Upon completion, monitored by TLC (eluent: hexane/AcOEt 8:2), the crude mixture was filtered through celite. The precipitate on the filter was then cleaned with repeated hexane washing and the solvents evaporated *in vacuo*. The residue was, thus, purified by silica gel chromatography (eluent: hexane/AcOEt 8:2) affording pure **59** as a dark yellow powder (0.46 g, 88%). C₁₂H₁₃NSi, MW: 199.32 g/mol. M.p.: 96-97°C. δ_{H} (CDCl₃, 400 MHz) 7.58 (d, *J* 2.0, 2H, *H_b*), 7.53 (d, *J* 2.0, 2H, *H_c*), 0.26 (s, 9H, *H_a*). δ_{C} (CDCl₃, 100 MHz) 132.41, 132.0, 128.0, 118.40, 111.75, 103.0, 99.54, -0.29. Spectral characterization agrees with previously reported data.^[405]

3-(Triisopropylsilyl)-2-propynal **62**

To a dried two-necks round bottom flask, TIPSIA (0.91 g, 5 mmol) in dried and degassed THF (10 ml) was added under Ar. This solution was cooled at -78°C and $n\text{BuLi}$ (3.4 ml, 5.5 mmol) was added drop wise. After 15 min stirring, a solution of EtOCHO (0.37 g, 5 mmol) in dried and degassed THF (5 ml) was added over a period of 1 h at -78°C . Upon completion (2 h), monitored by TLC (eluent: hexane), the mixture was warmed up, quenched with Et_2O (15 ml) and washed with H_2O (3 x 10 ml). The organic layer was then dried over MgSO_4 and the solvent evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: hexane/ Et_2O 9:1) affording pure **62** as a pale yellow oil (0.83 g, 78%). $\text{C}_{12}\text{H}_{22}\text{OSi}$, MW: 210.38 g/mol. $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 9.19 (s, 1H, H_c), 1.09 (m, 21H, $H_{a,b}$). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 176.37, 104.44, 94.7, 18.34, 11.0. Spectral characterization agrees with previously reported data.^[406]

2-(2-Triisopropylsilylethynyl)-1,3-benzoxazole **64**

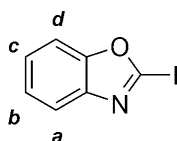
To a solution of 2-aminophenol **63** (0.11 g, 1 mmol) in MeOH (5 ml), **62** (0.25 g, 1 mmol) was added, and the so formed solution was stirred at reflux for 12 h. Subsequently, MeOH was removed under reduced pressure, CH_2Cl_2 (10 ml) and DDQ (0.6 g, 3 mmol) were added and the mixture was further stirred at rt for 30 min. Subsequently, more CH_2Cl_2 (10 ml) was added, and the organic layer was washed with saturated Na_2CO_3 (2 x 10 ml), brine (2 x 10 ml) and dried over MgSO_4 . After the removal of the solvent *in vacuo*, the residue was purified by silica gel chromatography (eluent: hexane/ Et_2O 95:5) affording pure **64** as a transparent oil (0.12 g, 41%). $\text{C}_{18}\text{H}_{25}\text{NOSi}$, MW: 299.49 g/mol. $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.73 (qd, J_1 7.2, J_2 1.5, J_3 0.7, 1H, H_d), 7.51 (qd, J_1 7.2, J_2 1.5, J_3 0.7, 1H, H_a), 7.42-7.34 (dt, J_1 7.2, J_2 1.5, 2H, $H_{b,c}$), 1.15-1.13 (m, 21H, $H_{e,g}$). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 150.1, 147.0, 140.72, 126.41, 125.0, 120.45, 110.6, 99.0, 93.4, 18.5, 11.06. Spectral characterization agrees with previously reported data.^[407]

2-Ethynyl-1,3-benzoxazole **65**

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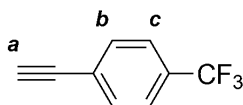
To a solution of **64** (0.1 g, 0.33 mmol) in dried and degassed THF (3 ml), TBAF (1M sol. in THF) (0.36 ml, 0.36 mmol) was added dropwise under Ar. The reaction was stirred at rt until the full deprotection was accomplished (15 min). Upon completion, monitored by TLC (eluents: toluene/CH₂Cl₂ 8:2), the mixture was diluted with H₂O (15 ml), extracted with CH₂Cl₂ (3 x 10 ml) and the organic layers dried over MgSO₄. After the removal of the solvent *in vacuo*, the residue was purified by silica gel chromatography (eluents: toluene/CH₂Cl₂ 8:2) affording pure **65** as a yellow sticky powder (20 mg, 42%). C₉H₅NO, MW: 143.14 g/mol. δ_{H} (CDCl₃, 400 MHz) 7.76 (dd, J_1 7.7, J_2 1.4, J_3 0.7, 1H, H_d), 7.54 (dd, J_1 7.7, J_2 1.2, J_3 0.7, 1H, H_a), 7.45-7.37 (dt, J_1 7.7, J_2 1.4, J_2' 1.2, 2H, $H_{b,c}$), 3.78 (s, 1H, H_e). Unstable compound, no further analysis have been performed.

2-Iodo-1,3-benzoxazole **67**

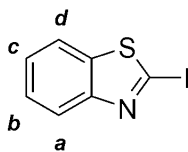


To a solution of MgBr₂·Et₂O (0.71 g, 2.7 mmol) in dried THF (6 ml), *n*BuLi (5.25 ml, 8.4 mmol) was added dropwise at -10°C under Ar. The reaction was stirred for 1 h, before the addition of 1,3-benzoxazole **66** (1.0 g, 8.4 mmol). This mixture was further stirred 2 h at rt and I₂ (2.1 g, 8.4 mmol) in dried THF (6 ml) was added. This solution was then stirred overnight at rt under Ar. Upon completion, monitored by TLC (eluents: AcOEt/cyclohexane 75:25), a saturated sol. of Na₂S₂O₃ was added until bleaching. The organic layers were then extracted with CH₂Cl₂ (3 x 20 ml), dried over MgSO₄ and the solvent evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluents: AcOEt/cyclohexane 75:25) affording pure **67** as a dark red powder (1.14 g, 54%). C₇H₄INO, MW: 245.02 g/mol. M.p.: 89-91°C. δ_{H} (CDCl₃, 400 MHz) 7.72-7.69 (m, 1H, H_d), 7.55-7.53 (m, 1H, H_a), 7.33-7.28 (m, 2H, $H_{b,c}$). δ_{C} (CDCl₃, 100 MHz) 154.1, 142.67, 125.32, 124.7, 119.31, 110.11, 108.0. Spectral characterization agrees with previously reported data.^[121]

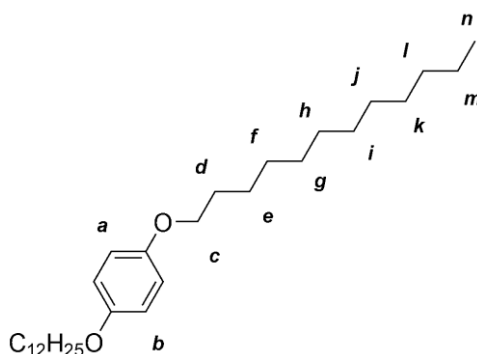
4-Ethynyltrifluoromethylbenzene **68**



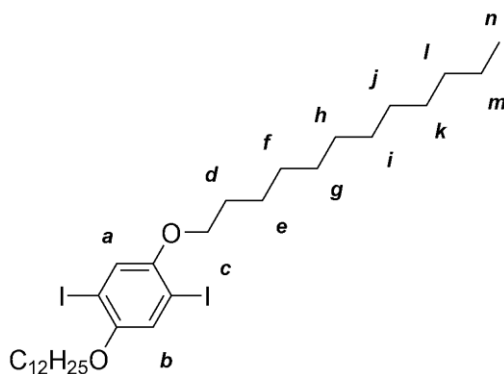
To a degassed solution of MeOH (30 ml), 4-[(2-trimethylsilyl)ethyn-1-yl]trifluoromethylbenzene **69** (1 ml, 4.2 mmol) and KOH (10 ml, 20 mmol) were added under Ar. The reaction was then allowed to stir for 30 min at rt. Upon completion, monitored by TLC (eluent: pentane), 20 ml of H₂O were added and the organic layer was extracted with CH₂Cl₂ (3 x 25 ml) and dried over MgSO₄. After the removal of the solvent *in vacuo*, the residue was purified by silica gel chromatography (eluent: pentane) affording pure **68** as a transparent oil (0.70 g, 97%). C₉H₅F₃ MW: 170.13 g/mol. δ_{H} (CDCl₃, 400 MHz) 7.58 (m, 4H, $H_{b,c}$), 3.19 (s, 1H, H_a). δ_{C} (CDCl₃, 100 MHz) 132.5, 130.60, 126.0, 125.37, 125.33, 79.7, 77.41. Spectral characterization agrees with previously reported data.^[408]

2-Iodo-1,3-benzothiazole **72**

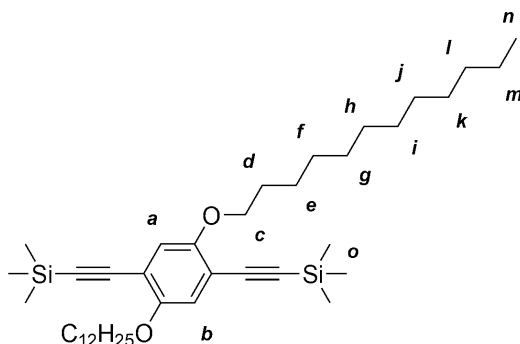
To a solution of 1,3-benzothiazole **71** (1 g, 7.4 mmol) in dried Et₂O (150 ml), *n*BuLi (1M solution in THF) (8.1 ml, 8.1 mmol) was added under Ar over a period of 15 min at -40 °C. The reaction was stirred for 10 min before the addition of I₂ (2.2 g, 8.9 mmol). This solution was further stirred overnight at rt under Ar. Upon completion, monitored by TLC (eluent: CH₂Cl₂/cyclohexane 8:2), a saturated sol. of Na₂S₂O₃ was added until bleaching. The separated organic layer was then extracted with CH₂Cl₂ (3 × 50 ml), dried over MgSO₄ and the solvents evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: CH₂Cl₂/cyclohexane 9:1) affording pure **72** as a white powder (0.7 g, 42%). C₇H₄INS, MW: 261.08 g/mol. M.p.: 90-92 °C. δ_{H} (CDCl₃, 400 MHz) 8.03 (dd, *J*₁ 8.0, *J*₂ 1.4, *J*₃ 0.7, 1H, *H*_d), 7.85 (dd, *J*₁ 8.0, *J*₂ 1.4, *J*₃ 0.7, 1H, *H*_b), 7.46-7.37 (dt, *J*₁ 8.0, *J*₂ 1.4, *J*₃ 0.7, 2H, *H*_{b,c}). δ_{C} (CDCl₃, 100 MHz) 154.24, 139.14, 126.38, 125.62, 122.56, 120.44, 105.67. Spectral characterization agrees with previously reported data.^[409]

1,4-Bis(dodecyloxy)benzene **74**

To a solution of hydroquinone **73** (4.0 g, 36 mmol) in DMF (60 ml), K₂CO₃ (50 g, 0.36 mol) was added. The reaction was stirred for 30 min at rt. Subsequently, 1-bromododecane (26 g, 0.11 mol) was added, and the mixture was stirred overnight at 60 °C. When the solution was cooled down to rt, the formation of a precipitate was observed. The suspension was then diluted with CHCl₃ (50 ml) until a clear solution was obtained. The organic phase was washed with H₂O, brine, dried over MgSO₄ and the solvent evaporated *in vacuo*. The residue was purified by recrystallization from hot MeOH affording pure **74** as a white powder (9.0 g, 55%). C₃₀H₅₄O₂, MW: 446.75 g/mol. M.p.: 71-73 °C. δ_{H} (CDCl₃, 400 MHz) 6.81 (s, 4H, *H*_{a,b}), 3.89 (t, *J* 6.4, 4H, *H*_c), 1.75 (q, *J* 6.4, 4H, *H*_d), 1.44-1.41 (m, 4H, *H*_e), 1.31-1.25 (m, 32H, *H*_{f,g,h,i,j,k,l,m}), 0.89-0.87 (t, 6H, *H*_n). δ_{C} (CDCl₃, 100 MHz) 153.14, 115.33, 68.62, 31.91, 29.7, 29.63, 29.6, 29.41, 29.38, 29.34, 26.04, 22.69, 14.13 (one carbon peak of the alkylic chain is missing due to overlap). Spectral characterization agrees with previously reported data.^[410]

1,4-Bis(dodecyloxy)-2,5-diiodobenzene **75**

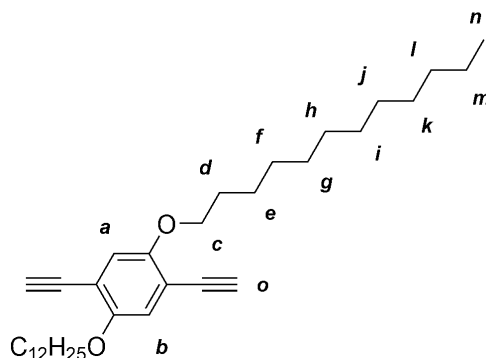
To a solution of **74** (2.0 g, 4.5 mmol) in CH_2Cl_2 (50 ml), $\text{Hg}(\text{OAc})_2$ (3.5 g, 11 mmol) and I_2 (2.8 g, 11 mmol) were added. The reaction was stirred overnight at rt. The reaction color turned pink-purple and a white precipitate was observed. The white precipitate was then filtered over celite and the purple filtrate was washed with saturated solutions of $\text{Na}_2\text{S}_2\text{O}_5$ (1×20 ml), NaHCO_3 (1×20 ml), H_2O (2×20 ml) and brine (2×20 ml). The organic layers were then dried over MgSO_4 and the solvent evaporated *in vacuo*. The residue was purified by recrystallization from hot MeOH affording pure **75** as a white powder (2.4 g, 77%). $\text{C}_{30}\text{H}_{52}\text{I}_2\text{O}_2$, MW: 698.54 g/mol. M.p.: 66-68 °C. $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.17 (s, 2H, $H_{a,b}$), 3.92 (t, J 6.6, 4H, H_c), 1.79 (q, J 6.6, 4H, H_d), 1.52-1.45 (m, 4H, H_e), 1.32-1.26 (m, 32H, $H_{f,g,h,i,j,k,l,m}$), 0.88 (t, 6H, H_n). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 152.77, 122.70, 86.25, 70.27, 31.91, 29.70, 29.60, 29.54, 29.35, 29.26, 29.10, 26.0, 22.70, 14.14 (one carbon peak of the alkylic chain is missing due to overlap). Spectral characterization agrees with previously reported data.^[410]

1,4-Bis(dodecyloxy)-2,5-(trimethylsilyl-2-ethynyl)-benzene **76**

To a solution of **75** (1.5 g, 2.1 mmol) and TMSA (0.63 g, 6.4 mmol) in a mixture of $i\text{Pr}_2\text{NH}$ (7.5 ml) and DMF (7.5 ml), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (73 mg, 0.15 mmol) and CuI (40 mg, 0.21 mmol) were added. The reaction was microwave-irradiated for 5 min at 100 °C. The solution was then allowed to reach rt and was filtered over celite. The precipitate on the filter was washed with cyclohexane and the solvent evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluents: cyclohexane/ CH_2Cl_2 7:3) affording pure **76** as a pale yellow powder (0.73 g, 55%). $\text{C}_{40}\text{H}_{70}\text{O}_2\text{Si}_2$, MW: 639.15 g/mol. M.p.: 71-73 °C. $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 6.9 (s, 2H, $H_{a,b}$), 3.93 (t, J 6.6, 4H, H_c), 1.78 (q, J 6.6, 4H, H_d), 1.49-1.47 (m, 4H, H_e), 1.29-1.25 (m, 32H, $H_{f,g,h,i,j,k,l,m}$), 0.88 (t, 6H, H_n), 0.25 (s, 18H, H_o). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 153.94, 117.0, 113.81, 101.0, 100.10, 69.35, 31.91, 29.70, 29.63, 29.43, 29.36, 29.32, 22.7,

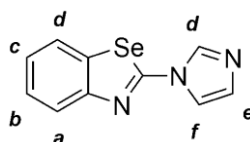
14.14, 0.15 (three carbon peaks of the alkylic chain are missing due to overlaps). Spectral characterization agrees with previously reported data.^[410]

1,4-Bis(dodecyloxy)-2,5-diethynylbenzene 77



To a degassed solution of THF/MeOH (20 ml, 1:1), **76** (0.7 g, 1.1 mmol) and K_2CO_3 (0.70 g, 5.5 mmol) were added under Ar. The reaction was stirred for 3h at rt under Ar. Subsequently, the crude mixture was filtered through celite and the solvent evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: cyclohexane/ CH_2Cl_2 6:4) affording pure **77** as white crystals (0.2 g, 40%). $C_{34}H_{54}O_2$, MW: 494.79 g/mol. M.p.: 70-73 °C. δ_H ($CDCl_3$, 400 MHz) 6.95 (s, 2H, ArH), 3.96 (t, J 6.7, 4H, H_c), 3.33 (s, 2H, H_o), 1.79 (q, J 6.7, 4H, H_d), 1.47-1.43 (m, 4H, H_e), 1.26 (s br, 32H, $H_{f,g,h,i,j,k,l,m}$), 0.88 (t, 6H, H_n). δ_C ($CDCl_3$, 100 MHz) 153.92, 117.65, 113.16, 82.38, 79.75, 69.60, 31.91, 29.65, 29.57, 29.55, 29.34, 29.31, 29.10, 25.90, 22.70, 14.12 (one carbon peak of the alkylic chain is missing due to overlap). Spectral characterization agrees with previously reported data.^[410]

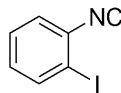
2-(1-Imidazolyl)-1,3-benzoselenazole 78



To a solution of **81** (0.40 g, 1.7 mmol) in dried THF (6 ml), selenium (0.12 g, 1.5 mmol), imidazole (0.12 g, 1.8 mmol), CuI (3 mg, 0.015 mmol) and DBU (0.22 ml, 1.5 mmol) were added under Ar. The mixture was stirred for 16 h at rt under Ar. Subsequently, the crude solution was poured into a sat. solution of $NaHCO_3$ and extracted with CH_2Cl_2 . The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (eluent: CH_2Cl_2 /AcOEt 8:2) affording pure **78** as white powder (0.14 g, 40%). $C_{10}H_7N_3Se$, MW: 248.14 g/mol. M.p.: 116-118°C. δ_H ($DMSO-d_6$, 400 MHz) 9.35 (s, 1H, H_d), 8.24 (s, 1H, H_e), 8.21 (d, J 8.1, 1H, H_d), 7.95 (d, J 8.1, 1H, H_e), 7.57 (s, 1H, H_f), 7.5 (t, J 8.1, 1H, H_c), 7.38 (t, J 8.1, 1H, H_b). δ_C ($DMSO-d_6$, 100 MHz) 158.71, 151.37, 137.42, 137.30, 127.74, 126.84, 126.50, 126.40, 124.51, 120.11. Spectral characterization agrees with previously reported data.^[125]

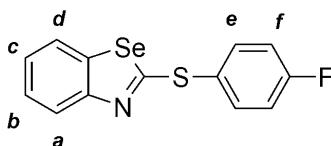
Chapter 4

1-Iodo-2-isocyanobenzene **81**



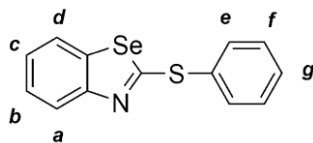
To a solution of 2-iodoaniline **79** in dried toluene (2 ml), a large excess of dried HCOOH (1.0 g, 22 mmol) was added. The reaction was stirred and refluxed for 40 h under Ar. Upon completion, monitored by TLC (eluent: CH₂Cl₂/cyclohexane 9:1), the solvent was concentrated *in vacuo*, and the crude was purified by silica gel chromatography (eluent: CH₂Cl₂/cyclohexane 9:1) affording *N*-formyl-2-iodoaniline as an inseparable mixture of two tautomers. The two compounds (0.60 g, 2.4 mmol) were then dissolved in dried CH₂Cl₂ (12 ml) and *i*Pr₂NH (1.4 ml, 14 mmol) was added under Ar. This solution was stirred for 10 min at 0 °C. Subsequently, POCl₃ (0.5 ml, 5.3 mmol) was added dropwise, and the mixture was stirred for additional 60 min at 0 °C. A solution of Na₂CO₃ 20%_p (2.4 ml) was then poured slowly and the reaction was allowed to stir for 1h at rt. Upon completion, monitored by TLC (eluent: cyclohexane/AcOEt 1:50), H₂O (8 ml) and CH₂Cl₂ (8 ml) were added. The organic layers were then washed with H₂O, dried over MgSO₄ and concentrate *in vacuo*. The residue was used in the following step without any purification due to the high instability at air.

2-(4-Fluorophenylthio)-1,3-benzoselenazole **82**



To a solution of **81** (0.55 g, 2.4 mmol) in dried THF (8 ml), selenium (0.17 g, 2.2 mmol), 4-fluorothiophenol (0.33 g, 2.6 mmol), CuI (4 mg, 0.022 mmol) and DBU (0.34 ml, 2.2 mmol) were added under Ar. The reaction was stirred for 16 h at rt under Ar. Subsequently, the formation of a precipitate was observed. The precipitate was filtered, washed with cyclohexane and purified by recrystallization from hot cyclohexane affording pure **82** as white crystals (0.4 g, 60%). C₁₃H₈FNSSe, MW: 308.23 g/mol. M.p.: 98-100 °C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1587.67, 1487.7, 1466.45, 1427.82, 1234.1, 1153.65, 979.7, 833.9, 758.5, 519.23. UV-Vis (CHCl₃, 25 °C) $\lambda_{\text{max}}(\epsilon, \text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1})$ 283 (13590). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.88 (d, J_1 7.8, 1H, H_d), 7.78-7.75 (m, 2H, H_e), 7.69 (d, J_1 7.8, 1H, H_a), 7.40 (t, J_1 7.8, 1H, H_c), 7.22-7.18 (m, 3H, $H_{b,f}$). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 173.84, 165.67, 163.15, 155.37, 138.05, 126.39, 126.44, 124.01, 123.24, 117.53, 117.31. $\delta_{\text{F}}(\text{CDCl}_3, 376 \text{ MHz})$ -108.15. EI-HRMS calc. 308.9534, m/z : 308.9527 ($[M]^+$, C₁₃H₈NSSeF⁺).

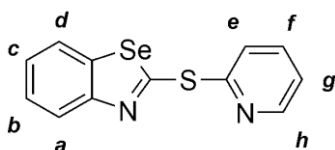
2-(Phenylthio)-1,3-benzoselenazole **83**



To a solution of **81** (0.65 g, 2.8 mmol) in dried THF (8 ml), selenium (0.2 g, 2.6 mmol), thiophenol (0.34 g, 3.1 mmol), CuI (5 mg, 0.026 mmol) and DBU (0.38 ml, 2.6 mmol) were added under Ar. The reaction was stirred for 16

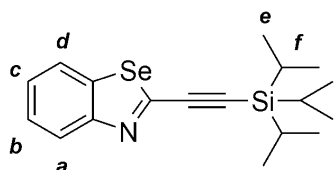
h at rt under Ar. The mixture was then poured into a sat. solution of NaHCO_3 and extracted with CH_2Cl_2 . The organic layer was dried over MgSO_4 and concentrated *in vacuo*. The residue was purified by silica gel chromatography (eluent: cyclohexane/ CH_2Cl_2 8:2) affording pure **83** as white crystals (0.08 g, 11%). $\text{C}_{13}\text{H}_9\text{NSe}$, MW: 290.24 g/mol. M.p.: 96-98 °C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3052.44, 2924.32, 1647.10, 1466.16, 1434.73, 1303.23, 976.54, 955.9, 691.45, 484.14. UV-Vis (CHCl_3 , 25 °C) $\lambda_{\text{max}}(\epsilon, \text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1})$ 286 (12392). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.89 (d, J_1 8.0, 1H, H_d), 7.79-7.77 (m, 2H, H_e), 7.68 (d, J 8.0, 1H, H_a), 7.56-7.49 (m, 3H, $H_{f,g}$), 7.4 (t, J_1 8.0, 1H, H_c), 7.2 (t, J 8.0, 1H, H_b). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 174.15, 155.33, 138.21, 135.71, 131.10, 130.10, 131.11, 126.33, 124.37, 123.96, 123.16. ESI-HRMS: calc. 290.9621, m/z : 291.9724 ($[\text{M}+\text{H}]^+$ $\text{C}_{13}\text{H}_{10}\text{NSe}^+$).

2-(2-Pyridinthio)-1,3-benzoselenazole **84**



To a solution of **81** (3.9 g, 17 mmol) in dried THF (60 ml), selenium (1.2 g, 15 mmol), 2-mercaptopyridine (2 g, 18 mmol), CuI (28 mg, 0.15 mmol) and DBU (2 ml, 15 mmol) were added under Ar. The reaction was stirred for 16 h at rt under Ar. Subsequently, the formation of a precipitate was observed. The precipitate was filtered off and the filtrate solution was concentrated and purified by silica gel chromatography (eluent: cyclohexane/AcOEt 7:3) affording pure **84** as yellow crystals (3 g, 61%). $\text{C}_{12}\text{H}_8\text{N}_2\text{SSe}$, MW: 291.23 g/mol. M.p.: 100-102 °C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1559.52, 1578.94, 1452.60, 1415.92, 1306.85, 1283.52, 1119.70, 989.50, 463.82, 755.51, 722.02, 652.60, 467.61, 429.55, 407.90. UV-Vis (CHCl_3 , 25 °C) $\lambda_{\text{max}}(\epsilon, \text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1})$ 284 (12102), 303 (12023). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 8.66-8.65 (m, 1H, H_h), 7.97 (d, J_1 8.0, 1H, H_d), 7.88 (d, J_1 8.0, 1H, H_a), 7.68 (t, J_1 8.0, 1H, H_c), 7.49-7.43 (m, 2H, H_b, H_e), 7.30-7.21 (m, 2H, $H_{f,g}$). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 163.80, 153.28, 152.75, 148.57, 137.96, 137.13, 126.03, 124.52, 123.76, 123.53, 123.37, 122.0. EI-HRMS calc. 291.9573, m/z : 291.9585 ($[\text{M}]^+$, $\text{C}_{12}\text{H}_8\text{N}_2\text{SSe}^+$).

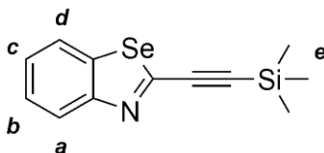
2-[(Triisopropylsilyl)ethynyl]-1,3-benzoselenazole **85**



To a solution of **82** (20 mg, 0.06 mmol) and TIPSA (17 mg, 0.09 mmol) in DMF (1 ml), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (22 mg, 0.03 mmol), CuI (12 mg, 0.06 mmol) and DIEA (0.13 ml, 0.75 mmol) were added. The reaction was microwave-irradiated for 25 min at 90 °C. The crude mixture was then filtered over celite, and the precipitate on the filter was washed with cyclohexane. The organic solvent was then evaporated *in vacuo*, and the residue was purified by silica gel chromatography (eluent: cyclohexane/ CH_2Cl_2 6:4) affording pure **85** as a pale yellow oil (23 mg, 100%). $\text{C}_{18}\text{H}_{25}\text{NSeSi}$, MW: 362.44 g/mol. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2986.73, 2867.0, 2306.0, 2061.10, 1422.25, 1265.55, 1106.70, 1084.0, 896.0, 739.90, 705.45. UV-Vis (CHCl_3 , 25 °C) $\lambda_{\text{max}}(\epsilon, \text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1})$ 237 (20893), 295 (21518). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 8.11 (d, J_1 8.0, 1H, H_d), 7.87 (d, J_1 8.0, 1H, H_a), 7.49 (t, J_1 8.0, 1H, H_c), 7.36 (t, J_1 8.0, 1H, H_b), 1.16 (m,

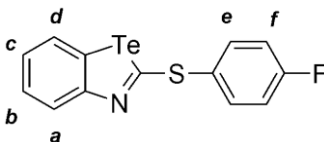
21H, $H_{e,f}$). δ_C (CDCl₃, 100 MHz) 154.23, 151.35, 139.25, 126.70, 126.30, 125.36, 124.57, 102.93, 101.13, 18.60, 11.14. APCI-HRMS: calc. 363.0921, m/z : 364.1340 ($[M+H]^+$ C₁₈H₂₆NSeSi⁺).

2-[(Trimethylsilyl)ethynyl]-1,3-benzoselenazole **86**

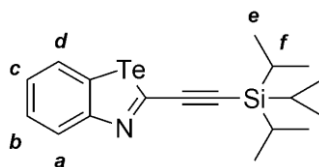


To a solution of **82** (0.5 g, 1.6 mmol) and TMSA (0.24 mg, 2.4 mmol) in DIEA (15 ml), in a sealed Schlenk tube, [PdCl₂(PPh₃)₂] (56 mg, 0.08 mmol) and CuI (30 mg, 0.16 mmol) were added under Ar. The reaction was degassed three times by “freeze-thaw-pump” cycles and stirred for 16 h at 130 °C. The reaction was then cooled down to rt and filtered on celite. The organic phase was then washed with acidic H₂O (2 × 10 ml), H₂O (2 × 10 ml), dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (eluent: cyclohexane/CH₂Cl₂ 1:1) affording pure **86** as a pale yellow oil (55 mg, 12%). C₁₂H₁₃NSeSi, MW: 278.28 g/mol. δ_H (CDCl₃, 400 MHz) 8.10 (d, J_1 8.2, 1H, H_d), 7.88 (d, J_1 8.2, 1H, H_a), 7.49 (t, J_1 8.2, 1H, H_c), 7.37 (t, J_1 8.2, 1H, H_b), 0.3 (s, 9H, H_e). The residue was not further analyzed due to the higher reactivity of the TMS-protecting groups, resulting in an unstable compound.

2-(4-Fluorophenylthio)-1,3-benzotellurazole **88**



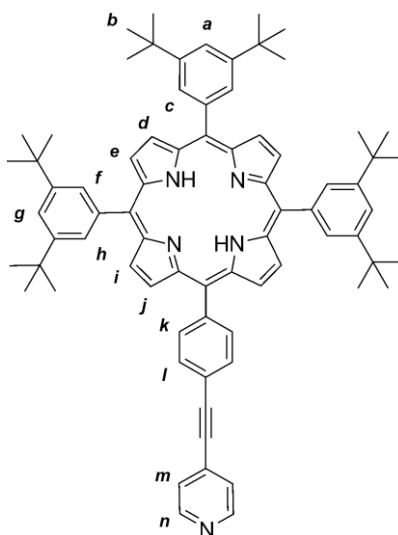
To a dried Schlenk tube, 4-fluorothiophenol (0.18 g, 1.4 mmol) and HMPA (0.63 ml, 3.6 mmol) were dissolved in dried THF (8 ml) under Ar. The reaction was stirred 5 min at −78 °C, before the addition of *n*BuLi (1M soln. in hexane) (1.4 ml, 1.4 mmol). This solution was stirred for additional 30 min at −78 °C under Ar. Subsequently, tellurium powder (0.15 g, 1.2 mmol) was added and the reaction was allowed to reach rt. At 25 °C, **81** (0.3 g, 1.3 mmol) and CuI (11 mg, 0.05 mmol) were added, and the reaction was stirred for additional 16 h at rt. The mixture was then poured into an aqueous solution of NaHCO₃ and extracted with CH₂Cl₂ (× 3). The organic layer was dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (eluent: cyclohexane/CH₂Cl₂ 2:8) affording pure **88** as a yellow powder (30 mg, 6%). C₁₃H₈FNSTe, MW: 356.87 g/mol. M.p.: 95–97 °C. $\nu_{\max}$ (film)/cm^{−1} 1584.80, 1458.21, 1417.75, 1427.82, 1225.30, 1149.45, 951.92, 830.38, 754.43, 511.43. UV-Vis (CHCl₃, 25 °C) $\lambda_{\max}$ (ε, mol^{−1}·l·cm^{−1}) 254 (10409), 293 (4803). δ_H (CDCl₃, 400 MHz) 7.93 (dd, J_1 7.9, J_2 1.1, 1H, H_d), 7.79–7.75 (m, 2H, H_e), 7.70 (dd, J_1 7.9, J_2 1.1, 1H, H_a), 7.39 (t, J_1 7.9, J_2 1.4, 1H, H_c), 7.23–7.18 (m, 2H, H_f), 7.09 (t, J_1 7.9, J_2 1.1, J_2 1.4, 1H, H_b). δ_C (CDCl₃, 100 MHz) 165.91, 165.40, 162.13, 138.35, 138.27, 130.90, 127.10, 124.90, 124.16, 117.74, 117.52. δ_F (CDCl₃, 376 MHz) −107.18. EI-HRMS calc. 358.9424, m/z : 359.9478 ($[M+1]^+$, C₁₃H₉NSTeF⁺).

2-[(Triisopropylsilyl)ethynyl]-1,3-benzotellurazole **89**

To a solution of **88** (0.1 g, 0.25 mmol) and TIPSA (0.06 ml, 0.37 mmol) in DMF (1.5 ml), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (90 mg, 0.12 mmol), CuI (47 mg, 0.025 mmol) and DIEA (0.5 ml, 2.5 mmol) were added. The reaction was microwave-irradiated for 20 min at 90 °C. The crude mixture was then filtered over celite, diluted with CH_2Cl_2 , washed with H_2O and concentrated *in vacuo*. The residue was purified by silica gel chromatography (eluent: cyclohexane/ CH_2Cl_2 1:1) affording pure **89** as a pale yellow oil (0.13 g, 97%). $\text{C}_{18}\text{H}_{25}\text{NTeSi}$, MW: 411.08 g/mol. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2955.40, 2836.95, 2497.60, 2190.10, 1910.71, 1590.12, 1504.52, 1354.25, 1249.55, 1148.74, 1090.80, 893.91, 810.40, 746.81, 708.35. UV-Vis (CHCl_3 , 25 °C) λ_{max} (ϵ , $\text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$) 252 (13508), 307 (9694). $\delta_{\text{H}}(\text{CDCl}_3$, 400 MHz) 8.23 (dd, J_1 7.9, J_2 1.1, 1H, H_d), 7.87 (dd, J_1 7.9, J_2 1.1, 1H, H_a), 7.47 (t, J_1 7.9, J_2 1.1, 1H, H_c), 7.24 (t, J_1 7.9, J_2 1.1, 1H, H_b), 1.15 (m, 21H, $H_{e,f}$). $\delta_{\text{C}}(\text{CDCl}_3$, 100 MHz) 160.36, 149.70, 136.30, 131.46, 127.32, 127.21, 125.94, 107.14, 105.16, 18.64, 11.20. APCI-HRMS: calc. 413.0818, m/z : 414.0895 ($[\text{M}+\text{H}]^+$ $\text{C}_{18}\text{H}_{26}\text{NTeSi}^+$).

4.3.2. Porphyrin Scaffolds

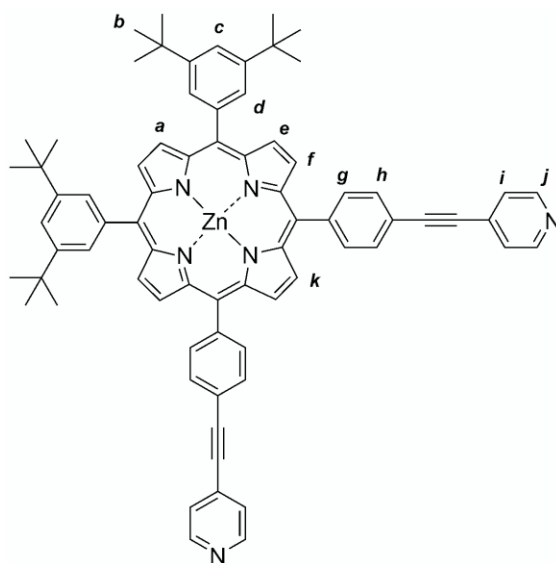
4.3.2.1. Porphyrin Scaffolds for Engineering Nanostructured Surfaces

5,10,15-Tris-(3,5-bis-*tert*-butylphenyl)-20-[4-(pyrid-4-yl-ethynyl)phenyl]porphyrin **109**

To a solution of porphyrin **114** (0.2 g, 0.2 mmol) in a mixture of THF/MeOH (4 ml, 1:1), K_2CO_3 (54 mg, 0.4 mmol) was added under Ar and the solution was stirred for 2 h at rt. Subsequently, the crude mixture was filtered through celite, and the precipitate on the filter cleaned with repeated CH_2Cl_2 washing. The solvent was evaporated *in*

vacuo, affording the free alkyne porphyrin (60 mg, 30%) as a purple solid. The latter (30 mg, 0.03 mmol) was then dissolved in dried *i*Pr₂NH (1 ml), and 4-iodopyridine (6 mg, 0.03 mmol), [PdCl₂(PPh₃)₂] (1 mg, 0.001 mmol) and CuI (1 mg, 0.004 mmol) were added under Ar. The solution was degassed three times by “freeze-pump-thaw” cycles and stirred for 16 h at rt under Ar. The crude mixture was diluted with CH₂Cl₂ (5 ml), washed with acidic H₂O, dried on MgSO₄. After the evaporation of the solvents, the residue was purified by silica gel chromatography (eluent: from cyclohexane/CH₂Cl₂ 4:6 to pure CH₂Cl₂), and by several precipitations from CH₂Cl₂/MeOH, affording pure **109** as a purple powder (17 mg, 50%). C₇₅H₈₁N₅, MW: 1052.48 g/mol. M.p. > 250 °C. $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2961.40, 2904.14, 2219.81, 1588.80, 1474.76, 1362.87, 1260.85, 1247.15, 1096.49, 803.48. UV-Vis (CH₂Cl₂, 25 °C) $\lambda_{\max}$ (ϵ , mol⁻¹·l·cm⁻¹) 422 (800000), 518 (272721), 554 (163915), 648 (79965). $\delta_{\text{H}}(\text{CDCl}_3/\text{TFA}-d$ 400 MHz) 8.97 (d, *J* 6.7, 2H, *H_n*), 8.77-8.76 (m, 2H, *H_j*), 8.72-8.67 (m, 8H, *H_{d,e,i,j}*), 8.40-8.38 (m, 6H, *H_{c,f,h}*), 8.31-8.29 (m, 2H, *H_k*), 8.18 (d, *J* 6.7, 2H, *H_m*), 8.1-8.08 (m, 3H, *H_{a,g}*), 1.67 (s, 54H, *H_b*), (Pyrrole-NH not visible). $\delta_{\text{C}}(\text{CDCl}_3/\text{TFA}-d$ 100 MHz) 151.54, 151.47, 146.47, 145.75, 145.55, 144.63, 143.0, 141.59, 141.28, 138.70, 138.0, 133.97, 133.85, 132.75, 129.76, 129.22, 128.85, 128.78, 128.40, 126.20, 125.14, 124.91, 121.82, 119.45, 104.90, 87.10, 35.32, 31.50 (four aromatic peaks are missing due to overlap). ESI-HRMS: calc. 1052.6570, *m/z*: 1052.6532 ([*M*+H]⁺, C₇₅H₈₂N₅⁺).

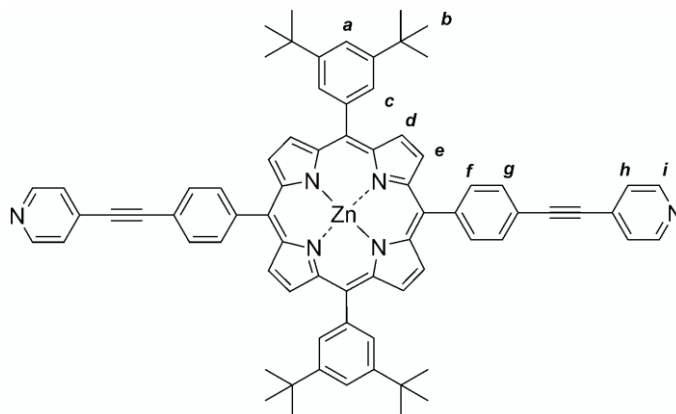
{5,10-Bis-(3,5-bis-*tert*-butylphenyl)-15,20-[4-(pyrid-4-yl-ethynyl)phenyl]porphyrinato}-N²¹,N²²,N²³,N²⁴zinc(II)
110



To a solution of **115** (12 mg, 0.01 mmol) in a mixture of dried *i*Pr₂NH and THF (1 ml, 1/1), 4-iodopyridine (5.5 mg, 0.02 mmol), [PdCl₂(PPh₃)₂] (1 mg, 0.002 mmol) and CuI (1 mg, 0.004 mmol) were added. The solution was degassed three times by “freeze-pump-thaw” cycles and stirred for 16 h at rt under Ar. The reaction was, then, diluted with CH₂Cl₂ (5 ml), filtered on celite, dried on Na₂SO₄ and the solvents evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: CH₂Cl₂/pyridine 98:2) and by several precipitations from CH₂Cl₂/MeOH, affording pure **110** as dark purple powder (6 mg, 36%). C₇₄H₆₆N₆Zn, MW: 1104.76 g/mol. M.p. > 250°C. $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2959.81, 2866.03, 2220.16, 1590.32, 997.09, 796.29, 715.55. UV-Vis (CH₂Cl₂, 25°C) $\lambda_{\max}$ (ϵ , mol⁻¹·l·cm⁻¹) 426 (636902), 553 (38537), 595 (31024). $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2/\text{Pyridine}-d_5$ 400 MHz) 9.01 (m, 4H, *H_{f,k}*), 8.92 (m, 4H, *H_{a,e}*), 8.64 (d, *J* 4.0, 4H, *H_j*), 8.24 (d, *J* 8.3, 4H, *H_h*), 8.14 (m, 4H, *H_d*), 7.93 (d, *J* 8.3, 4H, *H_g*), 7.85 (s broad, 2H, *H_c*), 7.49 (d, *J* 4.0, 4H, *H_i*), 1.49 (s, 36H, *H_b*). $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2/\text{pyridine}-d_5$ 100 MHz) 150.60, 150.43, 149.68, 144.81,

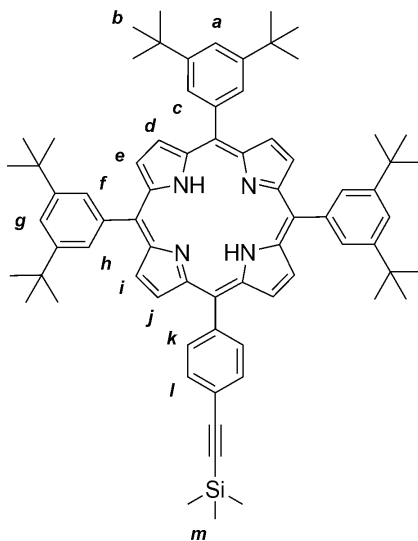
142.41, 132.50, 132.22, 131.53, 131.30, 130.70, 129.98, 129.95, 121.10, 120.88, 119.30, 94.37, 87.60, 34.98, 31.55, (four peaks are missing due to overlaps with the pyridine- d_5 peaks). MALDI-HRMS: calc. 1102.4640, m/z : 1102.4680 ($[M]^+$, $C_{74}H_{66}N_6Zn^+$).

{5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-[4-(pyrid-4-yl-ethynyl)phenyl]porphyrinato}- $N^{21},N^{22},N^{23},N^{24}$ zinc(II)
111



To a solution of **116** (18 mg, 0.02 mmol) in a mixture of dried iPr_2NH and THF (1 ml, 1/1), iodopyridine (8.2 mg, 0.04 mmol), $[PdCl_2(PPh_3)_2]$ (1 mg, 0.002 mmol) and CuI (1 mg, 0.004 mmol) were added. The solution was degassed three times by “freeze-pump-thaw” cycles and stirred for 16 h at rt under Ar. Subsequently, the formation of a purple precipitate was observed. The precipitate was filtered, washed with CH_2Cl_2 , purified by silica gel chromatography (eluent: CH_2Cl_2 /pyridine 8:2) and purified by precipitation from pyridine and MeOH, affording pure **111** as a dark purple powder (9 mg, 48%). $C_{74}H_{66}N_6Zn$, MW: 1104.76 g/mol. M.p. > 250 °C. $\nu_{max}(\text{film})/\text{cm}^{-1}$ 2962.80, 2220.16, 1560.32, 1110.37, 999.73, 794.62, 669.30. UV-Vis (CH_2Cl_2 , 25 °C) λ_{max} (ϵ , $\text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$) 426 (202684), 553 (8182), 596 (3440). $\delta_H(\text{CD}_2\text{Cl}_2/\text{Pyridine-}d_5$ 400 MHz) 8.95 (d, J 4.6, 4H, H_e), 8.9 (d, J 4.6, 4H, H_d), 8.64 (d, J 5.7, 4H, H_i), 8.24 (d, J 8.0, 4H, H_g), 8.07 (m, 4H, H_c), 7.94 (d, J 8.0, 4H, H_f), 7.82 (s br, 2H, H_a), 7.51 (d, J 5.7, 4H, H_h), 1.52 (s, 36H, H_b). $\delta_C(\text{CD}_2\text{Cl}_2/\text{pyridine-}d_5$ 100 MHz) 150.53, 150.02, 148.59, 144.83, 142.36, 134.80, 132.35, 131.34, 130.03, 129.96, 125.60, 122.47, 121.08, 120.86, 119.51, 94.01, 87.53, 34.97, 31.53, (two peaks are missing due to overlaps with the pyridine- d_5 peaks). MALDI-HRMS: calc. 1102.4640, m/z : 1102.4648 ($[M]^+$, $C_{74}H_{66}N_6Zn^+$).

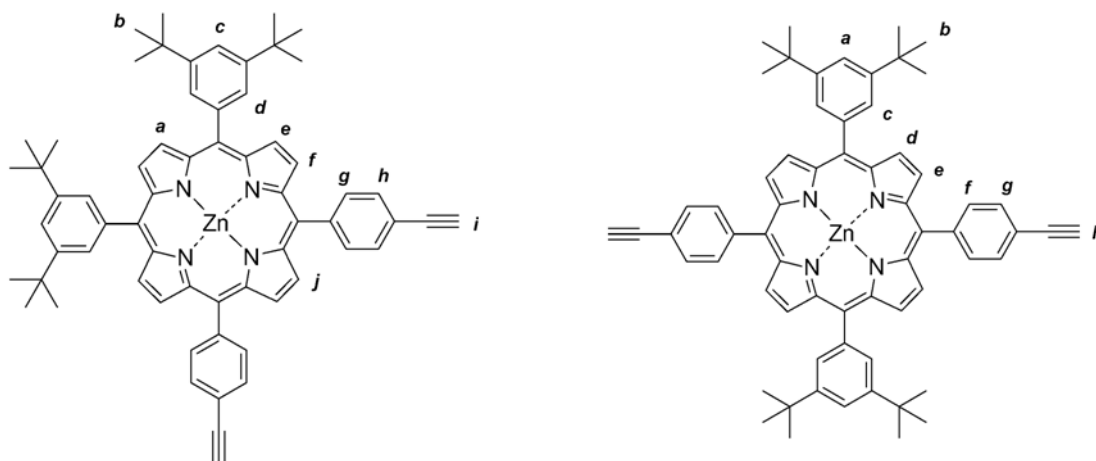
5,10,15-Tris-(3,5-bis-*tert*-butylphenyl)-20-[4-(trimethylsilylethynyl)phenyl]porphyrin **114**



To a stirred solution of 3,5-bis-*tert*-butylbenzaldehyde **112** (1.5 g, 6.9 mmol) in dried and distilled CH_2Cl_2 (900 ml), 4-(trimethylsilyl)ethynylbenzaldehyde **113** (0.46 g, 2.3 mmol), freshly distilled pyrrole (0.61 g, 9.2 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.45 g, 3.2 mmol) were added. After stirring the reaction for 1 h at rt, DDQ (1.5 g, 7 mmol) was added. The resulting dark solution was stirred for additional 1 h at rt under Ar. The mixture was filtered on SiO_2 (eluent: CH_2Cl_2) and the solvent evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: cyclohexane/ CH_2Cl_2 3:7) affording pure **114** as a purple powder (0.7 g, 20%). $\text{C}_{73}\text{H}_{86}\text{N}_4\text{Si}$, MW: 1047.57 g/mol. M.p. > 250 °C. δ_{H} (CDCl_3 200 MHz) 8.98 (m, 6H, $H_{d,e,i}$), 8.89 (s, 2H, H_j), 8.26 (d, J 8, 2H, H_l), 8.2 (s, 6H, $H_{c,f,h}$), 7.94 (d, J 8, 2H, H_k), 7.86 (s, 3H, $H_{a,g}$), 1.6 (s, 54H, H_b), 0.44 (s, 9H, H_m) (Pyrrole-NH not visible). δ_{C} (CDCl_3 75 MHz) 153.76, 152.36, 148.78, 148.75, 142.93, 141.34, 141.30, 134.43, 131.50, 130.40, 129.84, 129.80, 124.63, 124.41, 123.30, 123.05, 122.50, 121.80, 121.60, 121.12, 118.70, 105.30, 95.50, 35.23, 31.94, 29.90, 25.85, 0.32 (two peaks are missing due to overlaps). Spectral characterization agrees with previously reported data.^[411]

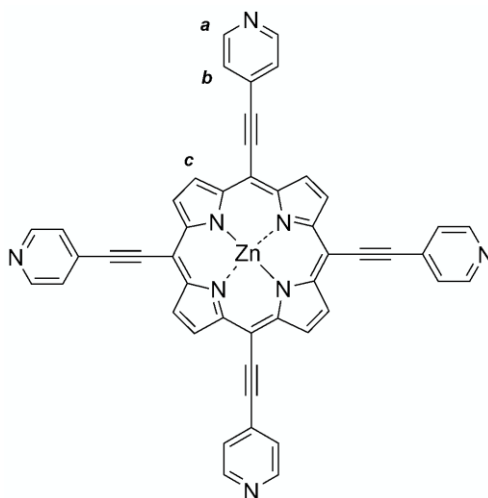
{5,10-Bis-(3,5-bis-*tert*-butylphenyl)-15,20-[4-(ethynyl)phenyl]porphyrinato}- $N^{21},N^{22},N^{23},N^{24}$ zinc(II) **115**

and {5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-[4-(ethynyl)phenyl]porphyrinato}- $N^{21},N^{22},N^{23},N^{24}$ zinc(II) **116**



To a stirred solution of 3,5-bis-*t*-butylbenzaldehyde **112** (0.5 g, 2.3 mmol) in dried and distilled CH_2Cl_2 (500 ml), 4-(trimethylsilyl)ethynylbenzaldehyde **113** (0.46 g, 2.3 mmol), freshly distilled pyrrole (0.31 g, 4.6 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (44 mg, 0.3 mmol) were added. The reaction was stirred for 1 h at rt under Ar, and DDQ (1.5 g, 7 mmol) was added. This resulting dark solution was further stirred for 10 min at rt. The crude mixture was, then, filtered on SiO_2 (eluent: CH_2Cl_2) and concentrated *in vacuo*. The residue was purified by silica gel chromatography (eluents: cyclohexane/ CH_2Cl_2 2:8) affording a mixture of the two TMS-protected porphyrin isomers (*cis*-like, *trans*-like) (tot: 100 mg, 0.09 mmol) as purple powder. The two compounds were then dissolved in dried and degassed THF/MeOH solution (3 ml, 1:1), and K_2CO_3 (54 mg, 0.4 mmol) was added under Ar. The reaction was stirred for 4 h at rt. Subsequently, the crude mixture was filtered through celite, and the precipitate on the filter cleaned with repeated CH_2Cl_2 washing. The solvents were evaporated *in vacuo*, affording the isomeric mixture of ethynyl porphyrins **115** and **116** (50 mg, 0.06 mmol) as purple powder. The two isomers were dissolved in CHCl_3 (3.5 ml) and a solution of $\text{Zn}(\text{OAc})_2$ (0.1 g, 0.6 mmol) in MeOH (3.5 ml) was added. The reaction was stirred in the dark for 2 h at rt, and then refluxed for additional 2 h. The crude mixture was washed with H_2O (10 ml), dried on Na_2SO_4 and concentrated *in vacuo*. The residue was, then, purified by repeated silica gel chromatography columns (eluents: cyclohexane/ CH_2Cl_2 4:6) and by precipitations from THF/MeOH, affording the two separated isomers as purple crystals. **115** (12 mg, 23% yield). $\text{C}_{64}\text{H}_{60}\text{N}_4\text{Zn}$, MW: 950.6 g/mol. M.p. > 250°C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2960.59, 2902.90, 2866.24, 2101.54, 1592.02, 1000.76, 795.77, 715.97. UV-Vis (CH_2Cl_2 , 25 °C) λ_{max} (ϵ , $\text{mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$) 424 (169116), 552 (7767), 593 (3203). $\delta_{\text{H}}(\text{THF}-d_8$, 400 MHz) 8.83 (m, 8H, $H_{a,e,f,j}$), 8.16 (m, 4H, H_h), 8.07 (m, 4H, H_g), 7.84 (m, 6H, $H_{c,d}$), 3.75 (s, 2H, H_i), 1.52 (s, 36H, H_b). $\delta_{\text{C}}(\text{THF}-d_8$, 100 MHz) 150.42, 150.27, 149.73, 149.59, 148.31, 144.15, 142.62, 134.33, 131.88, 131.70, 131.10, 130.90, 129.95, 129.58, 122.14, 121.71, 120.62, 119.28, 83.50, 78.77, 34.73, 31.10. MALDI-HRMS: calc. 948.4109, m/z : 948.4113 ($[M]^+$, $\text{C}_{64}\text{H}_{60}\text{N}_4\text{Zn}^+$). **116** (18 mg, 34%). $\text{C}_{64}\text{H}_{60}\text{N}_4\text{Zn}$, MW: 950.6 g/mol. M.p. > 250 °C. $\delta_{\text{H}}(\text{THF}-d_8$, 400 MHz) 8.86 (d, J 4.6, 4H, H_d), 8.8 (d, J 4.6, 4H, H_e), 8.16 (m, 4H, H_g), 8.08 (m, 4H, H_f), 7.84 (m, 4H, H_c), 7.82 (m, 2H, H_a), 3.75 (s, 2H, H_h), 1.52 (s, 36H, H_b). $\delta_{\text{C}}(\text{THF}-d_8$, 100 MHz) 150.4, 149.63, 148.34, 144.17, 142.6, 134.31, 131.82, 130.96, 129.91, 129.75, 122.0, 121.7, 120.6, 119.45, 83.5, 78.73, 34.73, 31.1. Spectral characterization agrees with previously reported data.^[412]

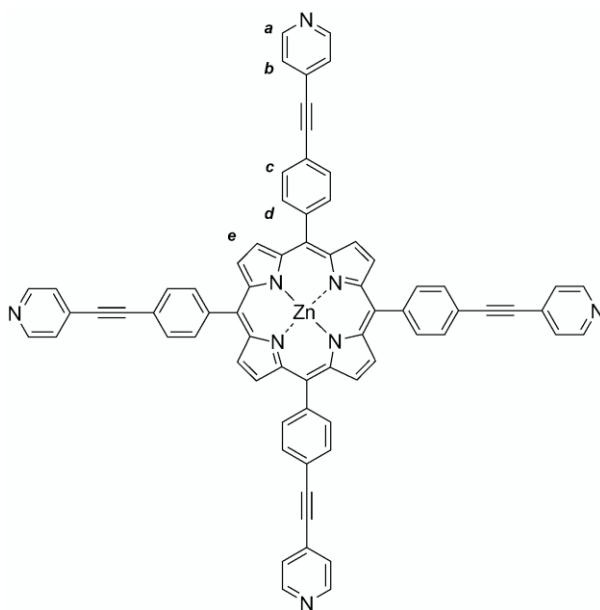
5,10,15,20-tetrakis-Pyridylethynylporphyrinato- $N^{21},N^{22},N^{23},N^{24}$ -zinc(II) **117**



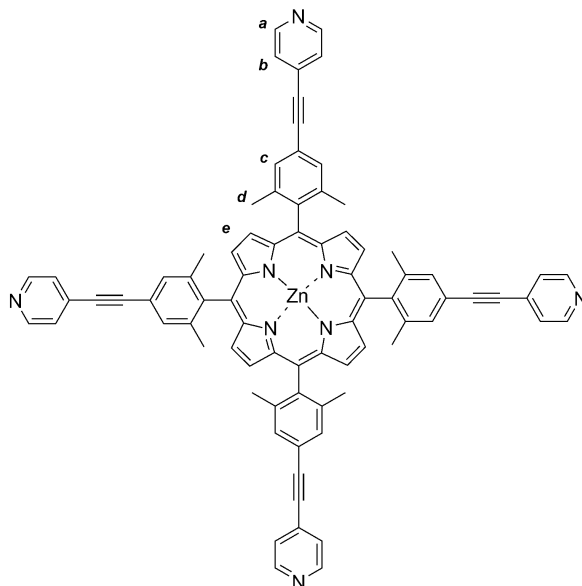
To a solution of **122** (15 mg, 0.043 mmol) in dried $i\text{Pr}_2\text{NH}$ and pyridine (2 ml, 1/1), 4-iodopyridine (37 mg, 0.18 mmol), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (1.5 mg, 0.002 mmol) and CuI (1 mg, 0.004 mmol) were added. The solution was degassed

three times by “freeze-pump-thaw” cycles and stirred for 16 h at rt under Ar. After this time, the formation of a dark precipitate was observed. The precipitate was filtered, washed with MeOH and purified by precipitation from pyridine and MeOH, affording **117** as dark green crystals (17 mg, 50%). $C_{48}H_{24}N_8Zn$, MW: 778.17 g/mol. Due to the low solubility of the product it has not been possible to perform the ^{13}C -NMR characterization. Mp.: 197-199 °C. $\nu_{max}(\text{film})/\text{cm}^{-1}$ 2190.90, 1590.54, 1212.41, 1060.0, 787.71, 464.92. UV-Vis (CH_2Cl_2 /Pyridine 25 °C) λ_{max} (ϵ , $\text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$) 482 (51089), 626 (2568), 678 (6147). $\delta_H(\text{Pyridine-}d_5$ 400 MHz) 9.92 (s, 8H, H_c), 8.95 (d, J 4.5, 8H, H_a), 7.97 (d, J 4.5, 8H, H_b). MALDI-HRMS: calc. 776.1415, m/z : 776.1402 ($[M]^+ C_{48}H_{24}N_8Zn^+$).

5,10,15,20-tetrakis-[4-(pyrid-4-yl)ethynyl]phenyl]porphyrinato- $N^{21},N^{22},N^{23},N^{24}$ zinc(II) **118**

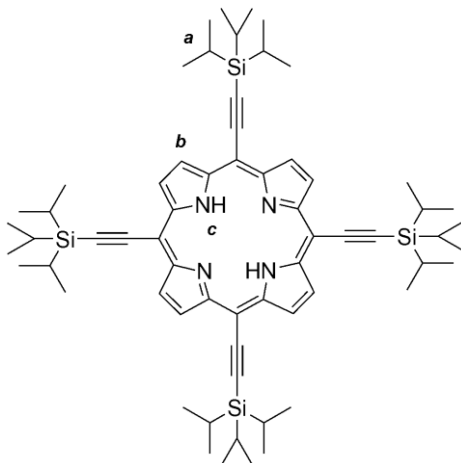


To a solution of **124** (20 mg, 0.026 mmol) in dried iPr_2NH (1 ml), 4-iodopyridine (22 mg, 0.1 mmol), $[PdCl_2(PPh_3)_2]$ (1 mg, 0.002 mmol) and CuI (1 mg, 0.004 mmol) were added. The solution was degassed three times by “freeze-pump-thaw” cycles and stirred for 16 h at rt under Ar. After this time, the formation of a dark-green precipitate was observed. The precipitate was filtered, washed with MeOH, purified by silica gel chromatography (eluent: CH_2Cl_2 /pyridine 9:1). The resulting powder was then precipitated from pyridine and MeOH, affording pure **118** as dark green crystals (10 mg, 40%). $C_{72}H_{40}N_8Zn$, MW: 1082.55 g/mol. M.p. > 250 °C. $\nu_{max}(\text{film})/\text{cm}^{-1}$ 2218.10, 1590.11, 994.11, 809.41, 716.0. UV-Vis (CH_2Cl_2 , 25 °C) λ_{max} (ϵ , $\text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$) 429 (187105), 556 (11228), 599 (5789). $\delta_H(CD_2Cl_2/\text{Pyridine-}d_5$ 400 MHz) 8.90 (s, 8H, H_e), 8.60 (d, J 4.5, 8H, H_a), 8.20 (d, J 8.0, 8H, H_c), 7.90 (d, J 8.0, 8H, H_d), 7.47 (d, J 4.5, 8H, H_b). $\delta_C(CD_2Cl_2/\text{Pyridine-}d_5$ 100 MHz) 150.25, 150.14, 144.71, 135.07, 132.07, 131.51, 130.26, 125.8, 121.47, 120.34, 94.11, 87.87. MALDI-HRMS: calc. 1080.2667, m/z : 1080.2068 ($[M]^+ C_{72}H_{40}N_8Zn^+$).

5,10,15,20-*tetrakis*-[2,5-dimethyl-4-(pyrid-4-yl-ethynyl)phenyl]porphyrinato- $N^{21},N^{22},N^{23},N^{24}$ zinc(II) **119**

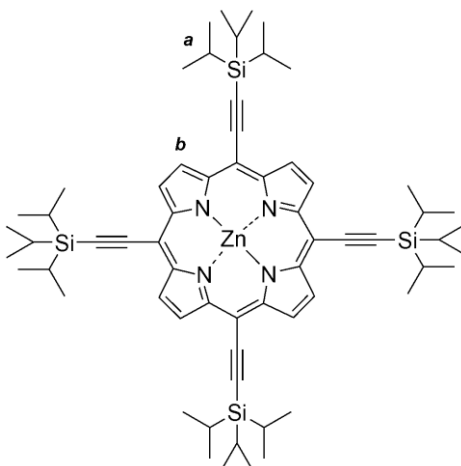
To a solution of **129** (0.15 g, 0.14 mmol) in CHCl_3 (8 ml), $\text{Zn}(\text{OAc})_2$ (0.25 g, 1.4 mmol) dissolved in MeOH (8 ml) was added. The reaction was stirred in the dark at rt for 2h and then refluxed for additional 4h. The crude mixture was then washed with H_2O (20 ml), dried on Na_2SO_4 and concentrated *in vacuo*. The residue was purified by precipitation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$, affording **130** (0.08 g, 48%) as a purple solid. $\text{C}_{72}\text{H}_{76}\text{N}_4\text{Si}_4\text{Zn}$, MW: 1175.15 g/mol. MALDI-HRMS: calc. 1172.4439, m/z : 1172.4484 ($[\text{M}]^+ \text{C}_{72}\text{H}_{76}\text{N}_4\text{Si}_4\text{Zn}^+$). Due to high insolubility in organic solvents only HRMS characterization has been performed. Hence, porphyrin **130** (0.08 g, 0.076 mmol) was dissolved in a mixture of dried THF/MeOH (4 ml, 1:1) and K_2CO_3 (0.1 g, 0.7 mmol) was added. The reaction was stirred at rt for 3h. Subsequently, the crude solution was diluted with THF, washed with H_2O , dried on Na_2SO_4 and concentrated *in vacuo*. The resulting product was purified by precipitation in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ affording **131** (25 mg, 37%) as a purple powder. $\text{C}_{60}\text{H}_{44}\text{N}_4\text{Zn}$, MW: 886.42 g/mol. MALDI-HRMS: calc. 884.2857, m/z : 884.2848 ($[\text{M}]^+ \text{C}_{60}\text{H}_{44}\text{N}_4\text{Zn}^+$). Even in this case the residue was found to be highly insoluble and only HRMS characterization was performed. Thus, to a solution of ethynyl porphyrin **131** (25 mg, 0.033 mmol) in dried THF (1 ml) and $i\text{Pr}_2\text{NH}$ (2 ml), 4-iodopyridine (29 mg, 0.14 mmol), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (1 mg, 0.0016 mmol) and CuI (1 mg, 0.003 mmol) were added. The reaction was degassed by three “freeze-pump-thaw” cycles and stirred for 16h at rt. The mixture was, then, diluted with CH_2Cl_2 (5 ml), filtered on celite, dried on Na_2SO_4 and concentrated *in vacuo*. The residue was thus purified by silica gel chromatography (eluent: $\text{CH}_2\text{Cl}_2/\text{pyridine}$ 9:1) and by precipitation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$, affording pure **119** as a purple powder (5 mg, 12%). $\text{C}_{80}\text{H}_{56}\text{N}_8\text{Zn}$, MW: 1194.76 g/mol. M.p. > 250°C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2964.0, 2212.76, 1590.49, 1489.05, 1261.34, 993.71, 818.52, 796.99, 568.39. UV-Vis ($\text{CH}_2\text{Cl}_2/\text{Pyridine}$, 25 °C) λ_{max} (ϵ , $\text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$) 432 (385000), 564 (42000), 602 (15000). $\delta_{\text{H}}(\text{CDCl}_3/\text{pyridine-}d_5$, 400 MHz) 8.57 (d, J 4.2, 8H, H_a), 8.55 (s, 8H, H_e), 7.60 (s, 8H, H_c), 7.41 (d, J 4.2, 8H, H_b), 1.78 (s, 24H, H_d). $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2/\text{pyridine-}d_5$ 100 MHz). 149.93, 144.13, 140.11, 131.50, 130.72, 130.24, 125.58, 121.47, 117.10, 94.44, 86.61, 21.47 (one peak is missing due to an overlap with the pyridine- d_5 peaks). MALDI-HRMS: calc. 1192.3919, m/z : 1192.3931 ($[\text{M}]^+ \text{C}_{80}\text{H}_{56}\text{N}_8\text{Zn}^+$).

5,10,15,20-*tetrakis*-Triisopropylsilylethynylporphyrin **120**



To a stirred solution of **62** (0.5 g, 2.4 mmol) and freshly distilled pyrrole (0.16 g, 2.4 mmol) in dried and distilled CH_2Cl_2 (250 ml), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (44 mg, 0.3 mmol) was added under Ar. The mixture was stirred for 1 h at rt under Ar and DDQ (0.50 g, 2.4 mmol) was added. The resulting brown solution was stirred for 10 min at rt. The crude mixture was, then, filtered on SiO_2 (eluent: CH_2Cl_2) and the solvent evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluents: $\text{CH}_2\text{Cl}_2/\text{cyclohexane}$ 8:2) affording pure **120** as dark green crystals (35 mg, 6%). $\text{C}_{64}\text{H}_{94}\text{N}_4\text{Si}_4$, MW: 1031.8 g/mol. M.p.: 173–175 °C. δ_{H} (CDCl_3 , 400 MHz) 9.57 (s br, 8H, H_b), 1.54–1.45 (m, 84H, H_a), -1.70 (s, 2H, H_c). δ_{C} (CDCl_3 , 100 MHz) 107.68, 102.55, 100.23, 19.11, 11.82 (two peaks are missing due to overlaps). Spectral characterization agrees with previously reported data.^[413]

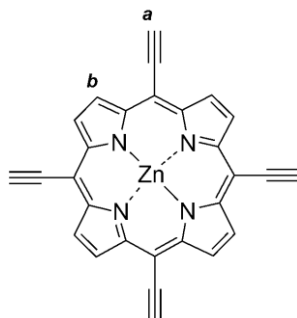
5,10,15,20-*tetrakis*-Triisopropylsilylethynylporphyrinato- $N^{21}, N^{22}, N^{23}, N^{24}$ zinc(II) **121**



To a solution of **120** (0.12 g, 0.12 mmol) in CHCl_3 (7 ml), a solution of $\text{Zn}(\text{OAc})_2$ (0.22 g, 1.2 mmol) in MeOH (7 ml) was added. The mixture was stirred in the dark at rt for 2 h and then refluxed for additional 2 h. Upon completion, monitored by TLC (eluents: cyclohexane/ CH_2Cl_2 1:9), the mixture was washed with H_2O (25 ml), dried on MgSO_4 and the solvent evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluents: cyclohexane/ CH_2Cl_2 1:9) and by precipitation in $\text{CH}_2\text{Cl}_2/\text{MeOH}$, affording pure **121** as dark green crystals (0.11 g,

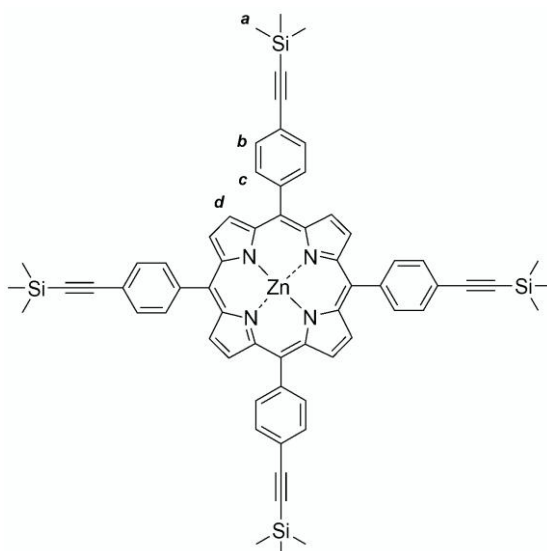
85%). $C_{64}H_{92}N_4Si_4Zn$, MW: 1095.19 g/mol. M.p.: 160-162 °C δ_H (CDCl₃, 400 MHz) 9.70 (s, 8H, H_b), 1.47 (m, 84H, H_a). δ_C (CDCl₃, 100 MHz) 152.23, 131.75, 108.63, 102.70, 98.60, 19.14, 11.90. Spectral characterization agrees with previously reported data.^[413]

5,10,15,20-*tetrakis*-Ethynylporphyrinato- $N^{21},N^{22},N^{23},N^{24}$ zinc(II) **122**



To a solution of **121** (50 mg, 0.04 mmol) in a mixture of CH₂Cl₂/THF (8 ml, 1:1), TBAF (1M soln. in THF) (0.3 ml, 0.27 mmol) was added under Ar. The reaction was stirred at rt until the full deprotection was accomplished (1 h). Upon completion, monitored by TLC (eluent: CH₂Cl₂), the mixture was diluted with a mixture of water and MeOH (10 ml, 1:1) and a precipitate was observed. The precipitate was filtered, washed with MeOH and H₂O and purified by precipitation from CH₂Cl₂ and MeOH, affording **122** as dark green crystals (15 mg, 78%). $C_{28}H_{12}N_4Zn$, MW: 469.83 g/mol. M.p.: 154-156 °C. δ_H (THF-*d*₈, 400 MHz) 9.62 (s, 8H, H_b), 4.70 (s, 4H, H_a). δ_C (THF-*d*₈, 100 MHz) 152.22, 131.51, 101.29, 85.44, 85.11. Spectral characterization agrees with previously reported data.^[414]

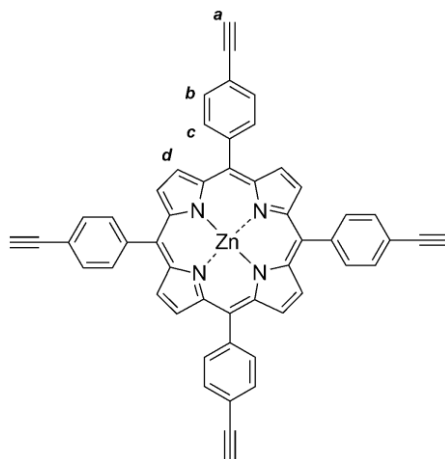
5,10,15,20-*tetrakis*-[4-(Trimethylsilyl)ethynyl]phenylporphyrinato- $N^{21},N^{22},N^{23},N^{24}$ zinc(II) **123**



To a stirred solution of 4-(trimethylsilyl)ethynylbenzaldehyde **113** (1.6 g, 8 mmol) and freshly distilled pyrrole (0.54 g, 8 mmol) in dried and distilled CHCl₃ (800 ml), BF₃·Et₂O (0.83 ml, 2.6 mmol) was added under Ar. The mixture was stirred for 1h at rt under Ar, and *p*-chloranil (1.5 g, 6 mmol) was added. The resulting brown solution was stirred for 1h at reflux. The mixture was, then, filtered on SiO₂ (eluent: CH₂Cl₂) and the solvent evaporated in

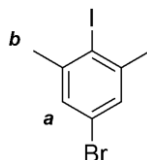
vacuo. The crude (0.89 g, 0.89 mmol, 45% yield), which was relatively pure after the filtration through silica, was then dissolved in CHCl_3 (45 ml). A solution of $\text{Zn}(\text{OAc})_2$ (1.63 g, 8.9 mmol) in MeOH (45 ml) was added and the mixture was refluxed for 2h. After cooling the mixture to rt, the solvent was removed *in vacuo*, and the crude product was purified by silica gel chromatography (eluents: $\text{CH}_2\text{Cl}_2/\text{cyclohexane}$ 3:7) affording pure **123** as a purple solid (0.88 mg, 42%). $\text{C}_{64}\text{H}_{60}\text{N}_4\text{Si}_4\text{Zn}$, MW: 1062.9 g/mol. M.p.: > 250 °C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3292.1, 3268.4, 3031.7, 2959.1, 2159.3, 1809.8, 1603.6, 1490.5, 1395.2, 1338.5, 1249.6, 997.1, 866.0, 855.8, 846.6, 808.6, 796.8, 658.4. UV-Vis (CH_2Cl_2 , 25 °C) λ_{max} (ϵ , $\text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$) 423 (582190), 552 (22480), 593 (7107). $\delta_{\text{H}}(\text{THF}-d_8$, 400 MHz) 8.76 (s, 8H, H_d), 7.93 (d, J 8.1, 8H, H_b), 7.73 (d, J 8.1, 8H, H_c), 0.38 (s, 36H, H_a). $\delta_{\text{C}}(\text{THF}-d_8$, 100 MHz) 147.42, 143.20, 134.87, 131.50, 130.81, 123.80, 120.22, 106.32, 95.85, 0.26. MALDI-HRMS: calc. 1060.3187, m/z : 1060.3184 ($[\text{M}]^+$ $\text{C}_{64}\text{H}_{60}\text{Si}_4\text{N}_4\text{Zn}^+$).

5,10,15,20-tetrakis-Ethynylphenylporphyrinato- $N^{21},N^{22},N^{23},N^{24}$ zinc(II) 124



To a solution of **123** (0.15 g, 0.14 mmol) in dried THF (8 ml), TBAF (1M sol. in THF) (0.9 ml, 0.9 mmol) was added under Ar. The reaction was stirred 3 h at rt. The crude mixture was, then, diluted with CH_2Cl_2 , washed with H_2O , dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel chromatography (eluents: $\text{CHCl}_3/\text{cyclohexane}$ 1:1) and by precipitation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$, affording pure **124** as a purple powder (40 mg, 40%). $\text{C}_{52}\text{H}_{28}\text{N}_4\text{Zn}$, MW: 774.21 g/mol. M.p. > 250 °C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3414.32, 3293.35, 2959.0, 2925.10, 2849.40, 2107.25, 1723.42, 1603.70, 1488.80, 1338.45, 1205.33, 1104.35, 1066.27, 995.90, 807.30, 796.0, 655.80, 608.55. UV-Vis (CH_2Cl_2 , 25 °C) λ_{max} (ϵ , $\text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$) 424 (573824), 553 (22480), 593 (7107). $\delta_{\text{H}}(\text{DMSO}-d_6$, 400 MHz) 8.79 (s, 8H, H_d), 8.18 (d, J 8.0, 8H, H_b), 7.84 (d, J 8.0, 8H, H_c), 3.77 (s, 4H, H_a). $\delta_{\text{C}}(\text{DMSO}-d_6$, 100 MHz) 149.14, 143.30, 134.42, 131.83, 130.0, 121.12, 119.70, 83.60, 81.90. ESI-HRMS: calc. 772.1605, m/z : 772.1603 ($[\text{M}]^+$ $\text{C}_{52}\text{H}_{28}\text{N}_4\text{Zn}^+$).

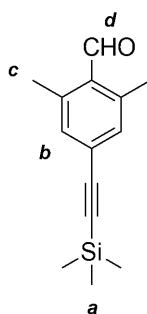
3,5-Dimethyl-4-iodobromobenzene 125



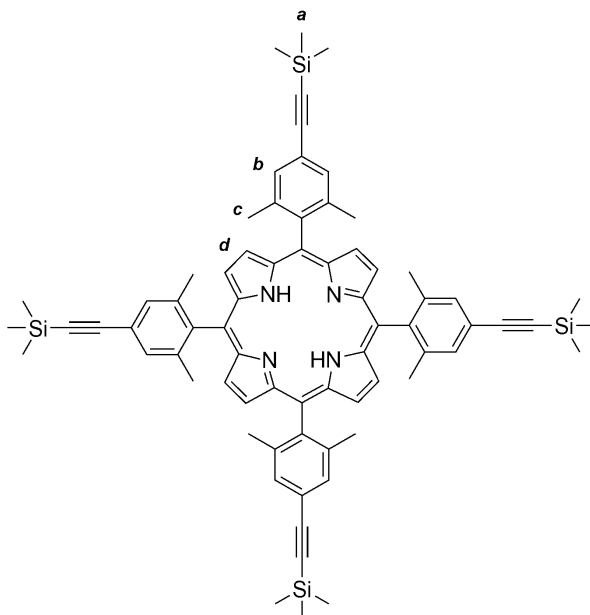
To a solution of 2,6-dimethyl-4-bromoaniline (1 g, 5 mmol) in THF (8 ml), a mixture of concentrated HCl and H_2O (4.4 ml, 1/1) was added and the solution was stirred for 75 min at rt and then cooled to 0-5°C. A chilled solution

of NaNO₂ (0.79 g, 11 mmol) in H₂O (8 ml) was added while maintaining the reaction temperature below 5°C. Subsequently, additional H₂O (3 ml) and a solution of KI (1.82 g, 8.5 mmol) in H₂O (1.6 ml) were added at 0°C. After the addition the mixture was diluted with H₂O (2.4 ml) and THF (15 ml), and it was warmed up to rt. This solution was then stirred for 16 h at rt. Upon completion, monitored by TLC (eluent: cyclohexane/AcOEt 7:3), the crude mixture was neutralized with Na₂CO₃, filtered and the filtrate washed with saturated Na₂S₂O₃ solution, H₂O, dried over MgSO₄ and evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluent: cyclohexane/AcOEt 7:3) affording pure **125** as white powder (1.16 g, 74%). C₈H₈BrI, MW: 310.95 g/mol. M.p.: 36–38°C. δ_{H} (CDCl₃, 400 MHz) 7.20 (s, 2H, *H_d*), 2.44 (s, 6H, *H_b*). δ_{C} (CDCl₃, 100 MHz) 143.91, 129.55, 121.62, 106.42, 29.37. Spectral characterization agrees with previously reported data.^[415]

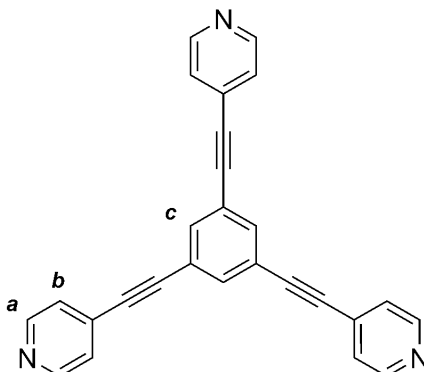
2,6-Dimethyl-4-trimethylsilylbenzaldehyde **128**



To a solution of **125** (0.5 g, 1.6 mmol) in DMF (2.5 ml), CuCN (0.14 g, 1.6 mmol) was added and the reaction was stirred for 12 h at reflux. Subsequently, the mixture was cooled to rt and a solution of FeCl₃ (50 mg, 0.3 mmol) in concentrated HCl (0.025 ml) and H₂O (0.1 ml) was added. The resulting solution was then heated up to 75 °C and stirred for additional 20 min. After cooling to rt, the mixture was extracted with CH₂Cl₂ (3 × 10 ml), washed with brine (10 ml), dried over MgSO₄ and concentrated *in vacuo*. The residual crude **126** (1.5 g, 7.1 mmol) was then dissolved in dried CH₂Cl₂ (20 ml) and DIBALH (1M soln. in hexane) (7.8 ml, 7.8 mmol) was added dropwise under Ar at 0°C. The reaction was stirred at 0 °C for 10 min and then it was allowed to reach rt and stirred for additional 4h. After this time, the crude solution was diluted with CH₂Cl₂, washed with acidic H₂O (2 × 10 ml), H₂O (10 ml), dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (eluent: cyclohexane/AcOEt 10:1) affording **127** as a brown oil. The compound was used for the next step without being fully characterized due to difficulties on its purification by column chromatography. Thus, compound **127** (1.3 g, 6 mmol) was then dissolved in dried *i*Pr₂NH (40 ml) and TMSA (0.9 g, 9.1 mmol), [PdCl₂(PPh₃)₂] (0.21 g, 0.3 mmol) and CuI (0.11 g, 0.6 mmol) were added. The reaction was degassed three times by “freeze-pump-thaw” cycles and stirred for 16h at 80 °C under Ar. After cooling the mixture to rt, it was filtered through celite and the filter cleaned with repeated hexane washing. After the evaporation of the solvent *in vacuo*, the residue was purified by silica gel chromatography (eluent: cyclohexane/CH₂Cl₂ 1:1) affording pure **128** as brown oil (1.0 g, 72%). C₁₄H₁₈OSi, MW: 230.37 g/mol. δ_{H} (CDCl₃, 400 MHz) 10.57 (s, 1H, *H_d*), 7.19 (s, 2H, *H_b*), 2.57 (s, 6H, *H_c*), 0.25 (s, 9H, *H_a*). δ_{C} (CDCl₃, 100 MHz) 192.82, 141.05, 132.84, 131.98, 127.56, 104.05, 97.69, 20.28, -0.17. Spectral characterization agrees with previously reported data.^[416]

5,10,15,20-tetrakis-(2,5-Dimethyl-4-trimethylsilylethynyl)porphyrin 129

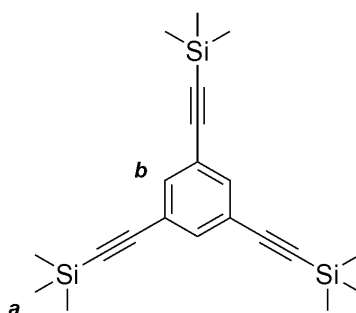
To a stirred solution of **128** (0.5 g, 2.2 mmol) and freshly distilled pyrrole (0.15 g, 2.2 mmol) in dried and distilled CHCl_3 (400 ml), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (84 mg, 0.3 mmol) was added dropwise. The reaction was stirred for 16h at rt under Ar, and DDQ (0.65 g, 2.8 mmol) was added. The resulting brown solution was stirred for 2h at rt. Subsequently, the mixture was filtered on SiO_2 (eluent: CH_2Cl_2) and the solvent evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluents: CH_2Cl_2 /cyclohexane 7:3) affording pure **129** as a purple powder (80 mg, 13%). $\text{C}_{72}\text{H}_{78}\text{N}_4\text{Si}_4$, MW: 1111.75 g/mol. M.p.: > 250 °C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2959.04, 2152.77, 1686.81, 1469.57, 1249.11, 868.32, 845.30, 687.09. UV-Vis (CH_2Cl_2 , 25 °C) $\lambda_{\text{max}}(\epsilon, \text{mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1})$ 419 (844843), 514 (50822), 546 (20926), 590 (20926). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 8.60 (s, 8H, H_d), 7.62 (s, 8H, H_b), 1.85 (s, 24H, H_c), 0.37 (s, 36H, H_a) (Pyrrole-NH not visible). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 141.60, 139.81, 130.54, 122.89, 117.02, 105.36, 94.40, 21.60, 0.09 (two peaks are missing due to overlaps). MALDI-HRMS: calc. 1110.5304, m/z : 1110.5326 ($[M]^+$ $\text{C}_{72}\text{H}_{78}\text{N}_4\text{Si}_4^+$).

1,3,5-Tris(pyridin-4-ylethynyl)benzene 132

To a solution of **134** (85 mg, 0.55 mmol) in dried $i\text{Pr}_2\text{NH}$ (4 ml), 4-iodopyridine (0.37 g, 1.8 mmol), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (19 mg, 0.03 mmol) and CuI (10 mg, 0.05 mmol) were added under Ar. The mixture was degassed by

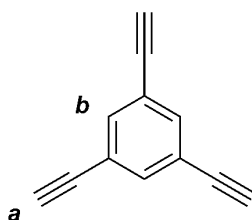
three “freeze-pump-thaw” cycles and stirred for 16h at rt. The crude solution was filtered through celite and the precipitate was cleaned with repeated cyclohexane washing. After the removal of the solvent *in vacuo*, the residue was purified by silica gel chromatography (eluents: AcOEt/cyclohexane 7:3) affording pure **132** as a white crystalline solid (0.15 g, 22%). $C_{27}H_{15}N_3$, MW: 381.43 g/mol. M.p.: 233-235 °C. δ_H (CDCl₃, 400 MHz) 8.64 (d, *J* 6.0, 6H, *H_a*); 7.74 (s, 3H, *H_c*), 7.38 (d, *J* 6.0, 6H, *H_b*). δ_C (CDCl₃, 100 MHz) 149.94, 135.18, 130.58, 125.50, 123.37, 91.40, 88.22. Spectral characterization agrees with previously reported data.^[285]

1,3,5-Tris-trimethylsilylethynylbenzene **133**



To a solution of 1,3,5-tribromobenzene (1 g, 3.2 mmol) in dried Et₃N (20 ml), TMSA (1.4 g, 14 mmol), [PdCl₂(PPh₃)₂] (0.11 g, 0.16 mmol) and CuI (61 mg, 0.32 mmol) were added. The solution was degassed by three “freeze-pump-thaw” cycles and stirred for 16h at rt. The crude mixture was filtered through celite and the precipitate was cleaned with repeated cyclohexane washing. After the removal of the solvent *in vacuo*, the residue was purified by silica gel chromatography (eluents: CH₂Cl₂/cyclohexane 4:96) affording pure **133** as a white crystalline solid (0.28 g, 24%). $C_{27}H_{15}N_3$, MW: 381.43 g/mol. M.p.: 71-73°C. δ_H (CDCl₃, 400 MHz) 7.49 (s, 3H, *H_b*); 0.22 (s, 27H, *H_a*). δ_C (CDCl₃, 100 MHz) 134.91, 123.60, 103.11, 95.57, -0.18. Spectral characterization agrees with previously reported data.^[405]

1,3,5-Triethynylbenzene **134**

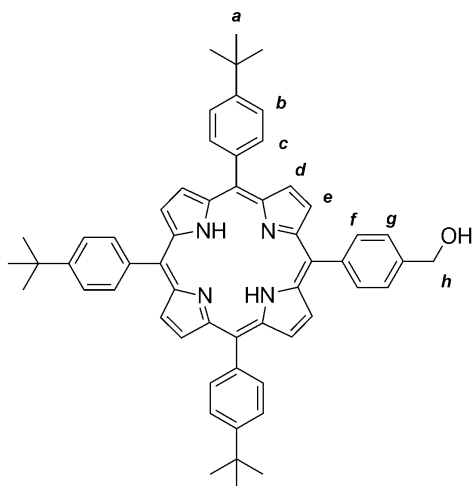


To a solution of **133** (0.25 g, 0.67 mmol) in a mixture of dried THF (2.5 ml) and MeOH (2.5 ml), K₂CO₃ (0.58 g, 4.2 mmol) was added under Ar. The reaction was stirred for 2h at rt. The mixture was then diluted with CH₂Cl₂, washed with H₂O, dried over MgSO₄ and the solvents evaporated *in vacuo*. The residue was purified by silica gel chromatography (eluents: CH₂Cl₂/cyclohexane 1:1) affording pure **134** as a pale yellow solid (90 mg, 88%). $C_{12}H_6$, MW: 105.17 g/mol. M.p.: 103-104°C. δ_H (CDCl₃, 400 MHz) 7.57 (s, 3H, *H_b*), 3.10 (s, 3H, *H_a*). δ_C (CDCl₃, 100 MHz) 135.67, 122.91, 81.70, 78.71. Spectral characterization agrees with previously reported data.^[405]

Chapter 4

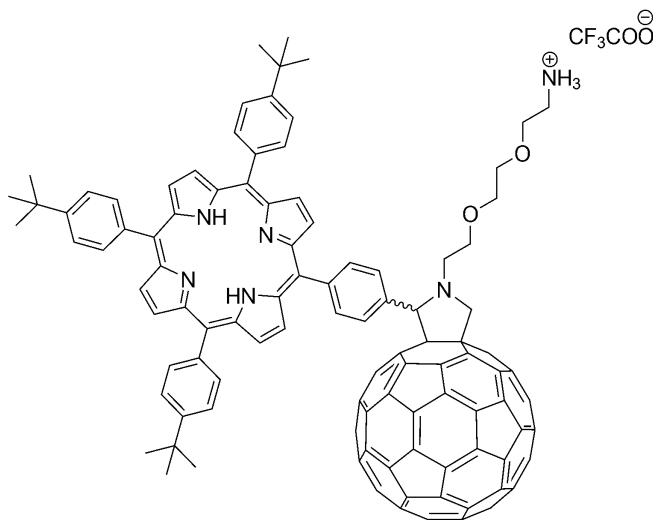
4.3.2.2. Porphyrin Scaffolds for Engineering Donor-Acceptor Components Photovoltaic Devices

5-(4-Hydroxybenzyl)-10,15,20-tris-(4-*tert*-butylphenyl)porphyrin **163**



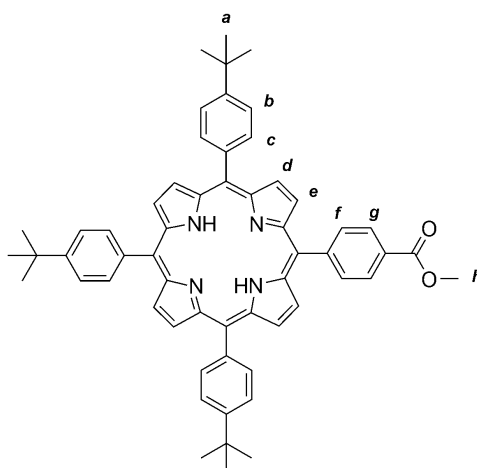
To a solution of **154** (0.7 g, 1.02 mmol) in dried THF (74 ml), LiAlH₄ (77 mg, 2.04 mmol) was added at 0 °C and the solution was stirred for 1h under Ar. The reaction was then allowed to warm to rt and quenched with H₂O. The organic layers were then dried on Na₂SO₄ and concentrated *in vacuo*. The residue was purified by a silica gel chromatography (eluent: CH₂Cl₂) and by precipitation from CH₂Cl₂/MeOH affording **163** as a purple solid (500 mg, 70%). C₅₇H₅₆N₄O, MW: 813.08 g/mol. M.p. > 250 °C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3027.25, 2956.45, 2864.20, 2359.91, 1556.20, 1501.95, 1473.55, 1397.35, 1348.92, 1266.41, 1221.70, 1185.90, 1107.55, 1020.61, 981.90, 966.85, 879.90, 848.41, 732.75, 577.55, 456.25, 426.70, 413.90. UV-Vis (CH₂Cl₂, 25 °C) λ_{max} (ϵ , mol⁻¹·l·cm⁻¹) 419 (630808), 517 (15342), 552 (5926), 592 (848). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 8.87 (m, 6H, *H_d*), 8.82-8.81 (m, 2H, *H_e*), 8.22 (d, *J* 7.8, 2H, *H_g*), 8.15-8.13 (m, 6H, *H_b*), 7.76 (d, *J* 7.8, 8H, *H_f*), 5.07 (d, 2H, *H_h*), 1.97 (s br, 1H, OH), 1.61 (s, 27H, *H_a*) (Pyrrole-NH not visible). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 150.47, 141.71, 140.09, 139.14, 134.79, 134.45, 125.27, 123.59, 120.34, 120.22, 119.35, 65.44, 34.88, 31.68 (three peaks are missing due to overlaps). MALDI-HRMS: calc. 812.4454, *m/z*: 812.4451 ([*M*]⁺, C₅₇H₅₆N₄O⁺).

2-{4-[5-10,15-tris-(4-*tert*-butylphenyl)porphyrin-20-yl]phenyl}-N-[2-[2-(2-ammoniumtrifluoroacetate-ethoxy)-ethoxy]-ethyl]-3,4-[1,9-(C₆₀-I_h)-fullero]pyrrolidine **164**



To a solution of **168** (0.05 g, 0.028 mmol) in dried CH₂Cl₂ (20 ml), TFA (1.53 g, 13 mmol) was added dropwise at 0 °C. The mixture was stirred for 16h at rt under Ar. After the removal of the solvent *in vacuo*, the residue was then dissolved in toluene and a precipitate was observed. The precipitate was filtered and washed with toluene and Et₂O affording pure **164** as a dark green powder (0.05 g, 100%). [C₁₂₄H₇₁N₆O₂⁺], MW: 1676.30 g/mol. M.p. > 250 °C. MALDI-HRMS: calc. 1675.5639, *m/z*: 1675.5624 ([*M*]⁺, C₁₂₄H₇₁N₆O₂⁺).

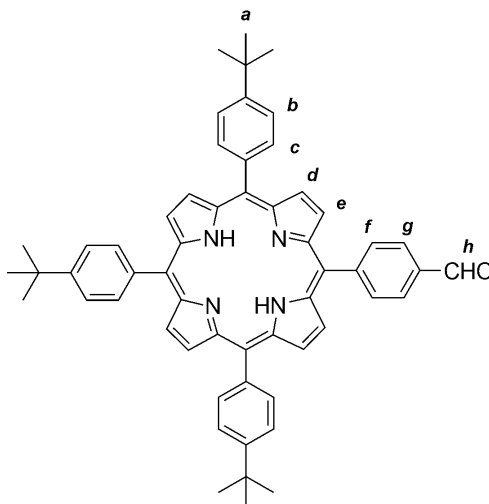
5-(4-Methoxycarbonylphenyl)-10,15,20-tris-(4-*tert*-butylphenyl)porphyrin **165**



To a stirred solution of methyl-4-formylbenzoate (0.83 g, 5.1 mmol) in dried and distilled CHCl₃ (1 l), 4-*tert*-butylbenzaldehyde (2.50 g, 15 mmol), freshly distilled pyrrole (1.34 g, 20 mmol) and BF₃·Et₂O (0.95 g, 7.0 mmol) were added. This solution was stirred for 1h at rt under Ar, and DDQ (3.4 g, 15 mmol) was added. The resulting dark solution was stirred for 10 min at rt. The crude mixture was filtered on SiO₂ (eluent: CH₂Cl₂) and concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography (eluent: CH₂Cl₂/cyclohexane 8:2) affording pure **165** as purple powder (0.65 g, 16%). C₅₈H₅₆N₄O₂, MW: 841.09 g/mol. M.p.: decomposition observed before

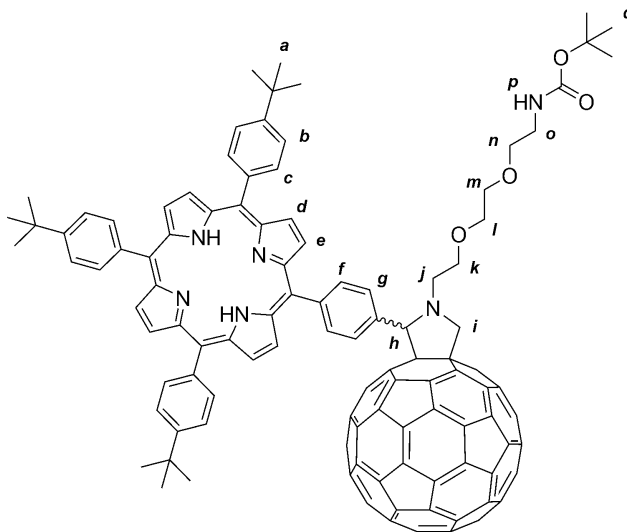
melting point was detected. $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 8.90-8.88 (m, 6H, H_d), 8.72 (s br, 2H, H_e), 8.44 (d, J 8.0, 2H, H_g), 8.32 (d, J 8.0, 2H, H_f), 8.16-8.13 (m, 6H, H_c), 7.77-7.75 (m, 6H, H_b), 4.12 (s, 3H, H_h), 1.62 (s, 27H, H_a). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 167.40, 150.55, 147.22, 140.0, 139.08, 139.03, 134.63, 134.45, 129.42, 127.85, 123.63, 120.73, 120.45, 118.13, 52.41, 34.90, 31.68 (one peak is missing due to overlaps). Spectral characterization agrees with previously reported data.^[376]

5-(4-Formylphenyl)-10,15,20-tris-(4-*tert*-butylphenyl)porphyrin **166**



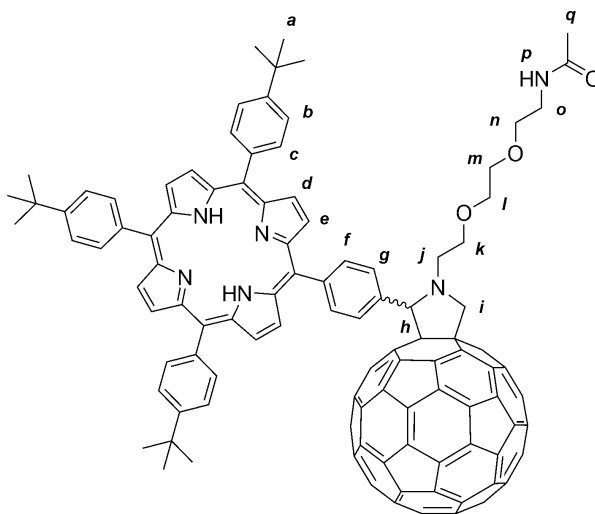
163 (0.28 g, 0.34 mmol) was dissolved in dried CH_2Cl_2 (50 ml) and stirred at 30 °C for 1h. Subsequently, BaMnO_4 (0.52 g, 2.0 mmol) was added and the solution was stirred for additional 1h at 30 °C. Upon completion, monitored by TLC (eluent: CH_2Cl_2), the mixture was diluted with CH_2Cl_2 and filtered on celite. The precipitate on the filter was then washed with CH_2Cl_2 , and the resulting solution dried over MgSO_4 and concentrated *in vacuo*. The residue was purified by precipitation from $\text{CHCl}_3/\text{MeOH}$ affording pure **166** as a purple powder (0.24 g, 87%). $\text{C}_{57}\text{H}_{54}\text{N}_4\text{O}$, MW: 811.06 g/mol. M.p. > 250 °C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3441.60, 2961.41, 1702.65, 2359.90, 1600.73, 1546.0, 1501.50, 1471.81, 1397.75, 1361.70, 1266.72, 1203.65, 1107.31, 1020.70, 981.55, 966.31, 847.20, 734.10, 577.55, 411.71. UV-Vis (CH_2Cl_2 , 25 °C) λ_{max} (ϵ , $\text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$) 419 (371321), 517 (8785), 552 (5926), 592 (1692). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 10.39 (s, 1H, H_h), 8.91-8.88 (m, 6H, H_d), 8.76 (m, 2H, H_e), 8.40 (d, J 8.0, 2H, H_g), 8.29 (d, J 8.0, 2H, H_f), 8.15-8.13 (m, 6H, H_c), 7.77-7.75 (m, 6H, H_b), 1.61 (s, 27H, H_a) (Pyrrole-NH not visible). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 192.49, 150.59, 148.89, 138.97, 135.48, 135.24, 134.46, 127.99, 123.65, 120.93, 120.57, 34.90, 31.68 (four peaks are missing due to overlaps). MALDI-HRMS: calc. 810.4298, m/z : 810.4313 ($[M]^+$, $\text{C}_{57}\text{H}_{54}\text{N}_4\text{O}^+$).

2-{4-[5,10,15-tris-(4-*tert*-butylphenyl)porphyrin-20-yl]phenyl}-*N*-{2-[2-(2-*tert*-butoxycarbonylamino-ethoxy)-ethoxy]-ethyl}-3,4-[1,9-(C₆₀-I_h)-fullero]pyrrolidine **168**



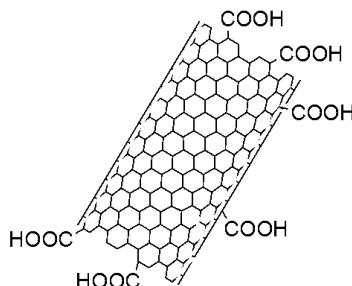
To a dried and degassed solution of C₆₀ (0.21 g, 0.3 mmol) in toluene (250 ml), **166** (0.24 g, 0.3 mmol) and the **167** aminoacid (0.23 g, 0.74 mmol) were added. The mixture was stirred for 16h at 130 °C under Ar. After cooling the reaction to rt, the solvent was evaporated *in vacuo*. The residue was then purified by silica gel chromatography (eluent: toluene) and by precipitation from CHCl₃/Et₂O affording pure **168** as a brown solid (0.24 g, 44%). C₁₂₉H₇₈N₆O₄, MW: 1775.41 g/mol. M.p. > 250 °C. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2959.56, 2329.51, 1707.07, 1504.39, 1363.06, 1266.88, 1108.05, 967.02, 800.03, 729.26, 526.94. UV-Vis (CH₂Cl₂, 25 °C) $\lambda_{\text{max}}(\epsilon, \text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1})$ 256 (107000), 329 (46000), 420 (446000), 517 (16000), 553 (9000), 591 (4000). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 8.87 (s, 8H, $H_{d,e}$), 8.13-8.11 (m, 10H, $H_{c,f,g}$), 7.76-7.74 (m, 6H, H_b), 5.16-5.09 (m, 2H, H_i), 4.99 (m, 1H, H_p), 4.12-4.10 (m, 4H, $H_{n,o}$), 3.85-3.76 (m, 4H, $H_{j,k}$), 3.63-3.61 (m, 2H, H_m), 3.35 (m, 2H, H_l), 2.98 (m, 1H, H_h), 1.60 (s, 27H, H_a), 1.42 (s, 9H, H_q). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 156.14, 155.92, 153.58, 153.36, 152.72, 150.47, 146.87, 146.40, 146.05, 145.85, 145.81, 145.73, 145.67, 145.54, 145.50, 145.45, 145.39, 145.33, 145.16, 145.10, 145.01, 144.95, 144.91, 144.80, 144.71, 144.28, 143.95, 143.63, 142.75, 142.52, 142.46, 142.31, 142.21, 142.18, 142.05, 142.0, 141.80, 141.75, 141.70, 141.62, 141.57, 141.53, 141.50, 141.35, 141.31, 141.20, 139.82, 139.80, 139.40, 139.21, 139.14, 139.0, 82.10, 79.24, 70.66, 70.60, 70.43, 68.93, 67.63, 52.34, 40.42, 34.90, 31.70, 28.44 (peaks are missing due to overlaps). MALDI-HRMS: calc. 1774.6085, m/z : 1774.6028 ($[M]^+$, C₁₂₉H₇₈N₆O₄⁺).

2-[4-[5-10,15-tris-(4-*tert*-butylphenyl)porphyrin-20-yl]phenyl]-*N*-{2-[2-(2-acetamidyl-ethoxy)-ethoxy]-ethyl}-3,4-[1,9-(C₆₀-I_h)-fullero]pyrrolidine **169**



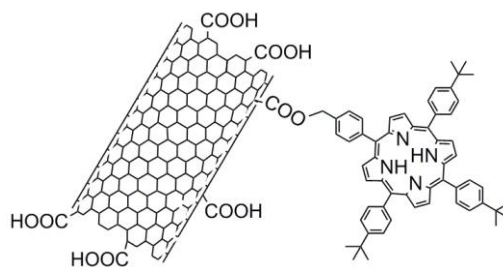
A solution of AcOH (0.84 mg, 0.014 mmol) and HBTU (11 mg, 0.028 mmol) in dried CH₂Cl₂ (1 ml) was stirred for 30 min at rt under Ar. Subsequently, a solution of **164** (25 mg, 0.028 mmol) and *i*Pr₂NH (0.012 ml, 0.084 mmol) in dried CH₂Cl₂ (4 ml) was added dropwise at rt under Ar. The reaction was stirred in the dark for 16h at rt. Upon completion, monitored by TLC (eluents: toluene/EtOH 95:5), the solvent was evaporated *in vacuo*. The residue was then purified by silica gel chromatography (eluents: toluene/EtOH 95:5 up to 9:1) and by precipitation from MeOH, affording pure **170** as dark brown solid (0.02 g, 85%). C₁₂₆H₇₂N₆O₃, MW: 1717.33 g/mol. M.p. > 250 °C. $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2952.72, 2897.32, 2862.0, 1670.0, 1361.71, 1266.0, 802.80, 727.27, 530.90. UV-Vis (CH₂Cl₂, 25 °C) $\lambda_{\max}(\epsilon, \text{mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1})$ 255 (120000), 420 (590624), 517 (23310), 553 (14682), 592 (7230). $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 8.87 (s, 8H, *H*_{d,e}), 8.13-8.11 (m, 10H, *H*_{c,f,g}), 7.76-7.75 (m, 6H, *H*_b), 5.94 (s, 1H, *H*_p), 5.16-5.04 (m, 2H, *H*_i), 4.12-4.10 (m, 4H, *H*_{n,o}), 3.85-3.76 (m, 4H, *H*_{j,k}), 3.62-3.61 (m, 2H, *H*_m), 3.35-3.47 (m, 2H, *H*_l), 2.98 (m, 1H, *H*_h), 1.96 (s, 3H, *H*_q), 1.60 (s, 27H, *H*_a). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 170.0, 156.02, 153.42, 153.21, 152.58, 150.50, 146.83, 146.30, 146.0, 145.93, 145.81, 145.80, 145.70, 145.64, 145.48, 145.41, 145.32, 145.25, 145.05, 144.95, 144.91, 144.88, 144.70, 144.67, 144.63, 144.22, 143.90, 143.56, 142.73, 142.55, 142.42, 142.30, 142.16, 142.0, 142.95, 141.83, 141.77, 161.67, 141.64, 141.60, 141.51, 141.50, 141.43, 141.33, 141.20, 141.15, 139.80, 139.76, 139.35, 139.20, 139.11, 139.0, 138.83, 138.0, 136.63, 136.56, 136.22, 135.20, 135.15, 134.43, 123.70, 120.54, 120.34, 119.10, 82.10, 70.53, 70.42, 70.01, 68.85, 52.34, 39.33, 34.90, 31.70, 23.35 (peaks are missing due to overlaps). MALDI-HRMS: calc. 1716.5666, *m/z*: 1716.5659 ($[M]^+$, C₁₂₆H₇₂N₆O₃⁺).

Oxidized CNTs (ox-DWCNTs)



***p*-DWCNTs** (200 mg, Nanocyl 2100, lot n° 080526) were sonicated for 5 min in H₂O₂ (15% solution, 200 ml), and then heated for 3h at 100 °C. The resulting suspension was then poured in H₂O (1 l) and then filtered through a 0.4 µm polycarbonate filter. The black precipitate obtained was washed several times with H₂O (200 ml), and then with MeOH to ease the drying under reduced pressure. This procedure was repeated two times. Thus, starting with an overall amount of 600 mg of ***p*-DWCNTs**, 252 mg of a black powder were collected. The product was then dispersed in 50 ml of a 2N HCl solution through sonication (5 min) and then stirred for additional 10 min at rt. The resulting suspension was then filtered through 0.4 µm polycarbonate filters allowing the collection of black pellets of CNTs. These were heated at 450 °C under air for 45 min affording 175 mg of oxidized material, which was subsequently dispersed in 200 ml of a 3:1 H₂SO₄ conc. (95%) HNO₃ conc. (65%) aqueous solution through 2 min of sonication. The resulting black dispersion was stirred at for 1h at rt. The reaction mixture was then poured into 1l of H₂O and again filtered through a 0.4 µm polycarbonate filters. The black precipitate was then washed several times with H₂O (200 ml), and MeOH, affording desired **ox-DWCNTs** (134 mg, 22% w/w) as black powder. The complete characterization of this material is presented in section 3.2.5.

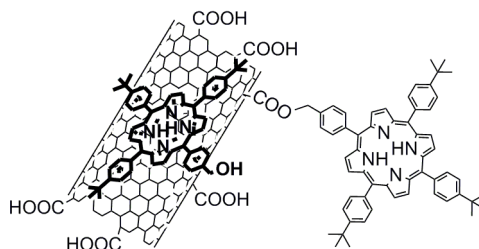
163-DWCNTs



ox-DWCNTs (50 mg) were dispersed in DMF (10 ml) through continuous sonication. After 20 min pyridine (1 ml) and HOBt (100 mg, 750 µmol) were sequentially added to the dispersion. After two cycles of 35 min and 50 min of sonication, EDC (88 mg, 540 µmol) and a solution of **163** (100 mg, 122 µmol) in DMF (5 ml) were respectively added. The reaction was then sonicated for further 30 min and then stirred for 48h at rt. The resulting dispersion was precipitated in H₂O (100 ml) and then filtered through a 0.4 µm polycarbonate filter. The black powder obtained was then washed with several additions of H₂O (200 ml) and MeOH to ease the drying under reduced pressure. The powder was then dispersed in DMF (5 ml), precipitated in CHCl₃ (100 ml) and then filtered through a 0.45 µm polytetrafluoroethylene filter. The dispersion/precipitation in CHCl₃ was repeated 5 times, until the filtered solution

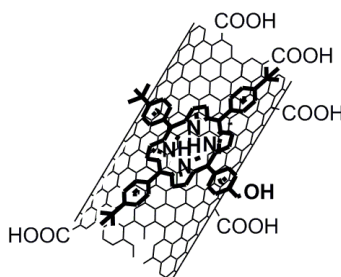
was completely colorless, affording desired **163-DWCNTs** (43 mg) as a black powder. The complete characterization of this material is presented in *section 3.2.5*.

163@(163-DWCNTs)



ox-DWCNTs (30 mg) were dispersed in DMF (5 ml) under sonication for 10 min. Subsequently, pyridine (500 μ l) was added. After two cycles of 20 min and 35 min of continuous sonication, NHS (100.3 mg, 854 μ mol) and EDC (88 mg, 540 μ mol) were sequentially added. The dispersion was then sonicated for 45 min, and a solution of **163** (80 mg, 98 μ mol) in DMF (5 ml) was added. The reaction was further sonicated for further 30 min and then stirred for 48h at rt. The reaction was then precipitated in H₂O (200 ml) and the resulting black-violet suspension was filtered through a 0.2 μ m polycarbonate filter. The black precipitate obtained was extensively washed through additions of H₂O (200 ml) and acetone (400 ml). The black powder was then redispersed in DMF (5 ml), once again precipitated in acetone (200 ml) and then filtered through a 0.45 μ m polytetrafluoroethylene filter affording desired **163@(163-DWCNTs)** (25 mg) as a black powder. The complete characterization of this material is presented in *section 3.2.5*.

163@DWCNTs



ox-DWCNTs (50 mg) were dispersed in DMF (10 ml) through continuous sonication. After 20 min pyridine (1 ml) and HOBt (100 mg, 750 μ mol) were sequentially added. After 50 min of sonication a solution of **163** (100 mg, 122 μ mol) in DMF (5 ml) was added. The reaction was further sonicated for 30 min and then stirred for 48h at rt. The resulting dispersion was precipitated in H₂O (100 ml) and then filtered through 0.4 μ m polycarbonate filter. The powder was washed with H₂O (200 ml) and MeOH to ease the drying under reduced pressure. The precipitate was then dispersed in DMF (5 ml), precipitated in CHCl₃ (100 ml) and then filtered through 0.45 μ m polytetrafluoroethylene filter. The dispersion/precipitation in CHCl₃ was repeated 5 times, until the filtered solution was completely colorless, affording the desired **163@DWCNTs** (40 mg) as a black powder. The complete characterization of this material is presented in *section 3.2.5*.

Appendix

Crystal Structure Data (Chapter 2)

X-Ray Analysis of 42

Crystal Data

Identification Code: 42
 Empirical Formula: $C_{16}H_8F_3NO$
 Formula Weight: 287.23
 Temperature: 293 K
 Crystal system, space group: Triclinic, P-1
 Unit cell dimensions:
 $a = 7.1907(4) \text{ \AA}$, $\alpha = 99.062(4)^\circ$
 $b = 7.7186(3) \text{ \AA}$, $\beta = 94.542(4)^\circ$
 $c = 13.0947(3) \text{ \AA}$, $\gamma = 113.830(5)^\circ$
 Volume: $648.27(6) \text{ \AA}^3$
 Z , Calculated density: 2, 1.472 g/cm^3
 $F(000)$: 292
 Crystal Size: $0.05 \times 0.20 \times 0.40 \text{ mm}$

Data Collection

Radiation: $1.54184 \text{ \AA}$
 θ range for data collection: 3.5 to 67.5°
 Dataset: $-8: 7; -7: 9; -15: 15$
 Total, Unique Data, $R(\text{int})$: 5207, 2312, 0.012
 Observed data [$I > 2.0 \sigma(I)$]: 2076

Refinement

SHELXS-86 program
 Refinement method: F^2 using SHELXL-97 software
 N_{ref} , N_{par} : 2312, 200
 R , wR_2 , S : 0.0559, 0.1677, 1.10
 $w = 1/[\sigma^2(F_o^2) + (0.0940P)^2 + 0.1158P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 Max. and Av. Shift/Error: 0.00, 0.00
 Min. and Max. Resd. Dens: $-0.27, 0.22 \text{ \AA}^{-3}$

Table 1. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for 42. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
F1*	1.4877(3)	1.1010(5)	0.88050(19)	0.1151(9)
F2*	1.2810(4)	1.0891(6)	0.98437(17)	0.1292(12)
F3*	1.4166(6)	1.3362(3)	0.9210(3)	0.1393(10)
O1	0.1557(2)	0.6498(2)	0.43231(12)	0.0791(5)
N1	0.3499(2)	0.5974(2)	0.31581(13)	0.0666(5)
C1	0.1492(3)	0.5310(3)	0.26454(15)	0.0646(6)
C2	0.0663(4)	0.4476(3)	0.16031(18)	0.0824(8)
C3	-0.1406(4)	0.3984(3)	0.1337(2)	0.0897(9)
C4	-0.2590(4)	0.4289(3)	0.2058(2)	0.0897(9)
C5	-0.1770(3)	0.5128(3)	0.3090(2)	0.0829(9)
C6	0.0302(3)	0.5627(3)	0.33593(16)	0.0641(6)
C7	0.3411(3)	0.6648(3)	0.41289(17)	0.0690(7)

Appendix

C8	0.5121(3)	0.7487(3)	0.49427(17)	0.0743(7)
C9	0.6563(3)	0.8191(3)	0.56322(16)	0.0705(7)
C10	0.8277(3)	0.9041(3)	0.64683(15)	0.0627(6)
C11	1.0179(3)	0.9110(3)	0.63052(15)	0.0687(7)
C12	1.1811(3)	0.9909(3)	0.71145(16)	0.0679(6)
C13	1.1561(3)	1.0648(3)	0.80976(15)	0.0611(6)
C14	0.9673(3)	1.0598(3)	0.82667(16)	0.0730(7)
C15	0.8035(3)	0.9792(3)	0.74601(17)	0.0745(7)
C16	1.3312(3)	1.1498(3)	0.89877(17)	0.0716(7)
F3*	1.3524(17)	1.0363(10)	0.9487(9)	0.1393(10)
F1*	1.2939(12)	1.2678(16)	0.9744(6)	0.1151(9)
F2*	1.4959(12)	1.257(2)	0.8768(6)	0.1292(12)

Table 2. Hydrogen Atom Positions and Isotropic Displacement Parameters ($\text{\AA}^2$) for **42**.

Atom	x	y	z	U(iso)
H2	0.14540	0.42610	0.11120	0.0990
H11	1.03570	0.86140	0.56440	0.0820
H12	1.30870	0.99500	0.69990	0.0820
H14	0.95070	1.11100	0.89270	0.0880
H15	0.67600	0.97500	0.75790	0.0890
H3	-0.20240	0.34260	0.06440	0.1080
H4	-0.39840	0.39170	0.18410	0.1080
H5	-0.25630	0.53460	0.35790	0.1000

Table 3. (An)isotropic displacement parameters for **42**.

Atom	U(1,1)	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
F1*	0.0825(13)	0.169(2)	0.0916(14)	-0.0145(14)	-0.0192(10)	0.0719(14)
F2*	0.0975(15)	0.211(3)	0.0673(12)	0.0501(16)	0.0050(10)	0.0473(17)
F3*	0.144(2)	0.0681(12)	0.158(2)	-0.0109(12)	-0.082(2)	0.0286(12)
O1	0.0710(9)	0.0886(10)	0.0693(9)	0.0086(7)	0.0069(7)	0.0290(7)
N1	0.0525(8)	0.0785(10)	0.0616(9)	0.0058(7)	0.0018(7)	0.0249(7)
C1	0.0593(10)	0.0638(10)	0.0652(11)	0.0098(8)	0.0000(8)	0.0235(8)
C2	0.0852(15)	0.0831(14)	0.0688(13)	0.0042(10)	-0.0001(11)	0.0319(12)
C3	0.0856(16)	0.0760(14)	0.0848(15)	0.0105(11)	-0.0239(13)	0.0204(11)
C4	0.0615(12)	0.0799(14)	0.114(2)	0.0281(13)	-0.0162(13)	0.0187(10)
C5	0.0612(12)	0.0850(14)	0.1044(18)	0.0260(12)	0.0104(11)	0.0309(10)
C6	0.0574(10)	0.0625(10)	0.0677(11)	0.0138(8)	0.0023(8)	0.0220(8)
C7	0.0603(11)	0.0689(11)	0.0683(12)	0.0129(9)	-0.0005(9)	0.0202(9)
C8	0.0655(12)	0.0778(13)	0.0693(13)	0.0129(10)	0.0016(10)	0.0224(10)
C9	0.0626(12)	0.0728(12)	0.0680(12)	0.0133(9)	0.0022(9)	0.0225(9)
C10	0.0599(11)	0.0601(10)	0.0622(11)	0.0112(8)	0.0031(8)	0.0213(8)

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C11	0.0687(12)	0.0781(12)	0.0557(10)	0.0047(9)	0.0074(9)	0.0311(10)
C12	0.0595(10)	0.0807(12)	0.0636(11)	0.0106(9)	0.0086(8)	0.0315(9)
C13	0.0616(10)	0.0595(10)	0.0586(10)	0.0119(8)	0.0053(8)	0.0228(8)
C14	0.0724(12)	0.0858(13)	0.0579(11)	0.0044(9)	0.0107(9)	0.0342(10)
C15	0.0577(11)	0.0904(14)	0.0732(13)	0.0083(10)	0.0099(9)	0.0323(10)
C16	0.0749(13)	0.0719(12)	0.0628(11)	0.0124(9)	0.0020(9)	0.0280(10)
F3*	0.144(2)	0.0681(12)	0.158(2)	-0.0109(12)	-0.082(2)	0.0286(12)
F1*	0.0825(13)	0.169(2)	0.0916(14)	-0.0145(14)	-0.0192(10)	0.0719(14)
F2*	0.0975(15)	0.211(3)	0.0673(12)	0.0501(16)	0.0050(10)	0.0473(17)

Table 4. Bond lengths (Å) for **42**.

Bond	Å	Bond	Å
F1-C16	1.350(4)	C8-C9	1.195(3)
F1*-C16	1.356(10)	C9-C10	1.433(3)
F2-C16	1.304(4)	C10-H11	1.382(3)
F2*-C16	1.228(12)	C10-H15	1.390(3)
F3-C16	1.288(3)	C11-H12	1.376(3)
F3*-C16	1.221(10)	C12-H13	1.380(3)
O1-C7	1.339(3)	C13-H14	1.379(3)
O1-C6	1.386(3)	C13-H16	1.495(3)
N1-C1	1.392(3)	C14-H15	1.376(3)
N1-C7	1.312(3)	C2-H2	0.9300
C1-C2	1.385(3)	C3-H3	0.9300
C1-C6	1.375(3)	C4-H4	0.9300
C2-C3	1.378(4)	C5-H5	0.9300
C3-C4	1.375(4)	C11-H11	0.9300
C4-C5	1.372(4)	C12-H12	0.9300
C5-C6	1.379(3)	C14-H14	0.9300
C7-C8	1.414(3)	C15-H15	0.9300

Table 4. Bond angles (°) for **42**.

Angle	°	Angle	°
C6-O1-C7	103.85(17)	F1-C16-F3	104.1(3)
C1-N1-C7	103.91(17)	F1-C16-C13	113.3(2)
N1-C1-C2	130.1(2)	F2-C16-F3	108.1(3)
N1-C1-C6	108.60(17)	F2-C16-C13	113.3(2)
C2-C1-C6	121.3(2)	F3-C16-C13	114.0(3)
C1-C2-C3	115.9(2)	F1*-C16-C13	109.6(4)
C2-C3-C4	122.4(2)	F2*-C16-C13	114.5(4)
C3-C4-C5	121.8(3)	F3*-C16-C13	116.0(5)
C4-C5-C6	116.0(2)	F1*-C16-F2*	103.3(7)

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O1-C6-C1	107.92(19)	F1*-C16-F3*	100.4(7)
O1-C6-C5	129.5(2)	F2*-C16-F3*	111.4(8)
C1-C6-C5	122.6(2)	C1-C2-H2	122.00
O1-C7-N1	115.72(19)	C3-C2-H2	122.00
O1-C7-C8	120.32(19)	C2-C3-H3	119.00
N1-C7-C8	124.0(2)	C4-C3-H3	119.00
C7-C8-C9	179.8(2)	C3-C4-H4	119.00
C8-C9-C10	179.3(2)	C5-C4-H4	119.00
C9-C10-C11	120.75(19)	C4-C5-H5	122.00
C9-C10-C15	120.1(2)	C6-C5-H5	122.00
C11-C10-C15	119.2(2)	C10-C11-H11	120.00
C10-C11-C12	120.41(19)	C12-C11-H11	120.00
C11-C12-C13	120.2(2)	C11-C12-H12	120.00
C12-C13-H14	119.8(2)	C13-C12-H12	120.00
C12-C13-H16	120.8(2)	C13-C14-H14	120.00
C14-C13-H16	119.34(18)	C15-C14-H14	120.00
C13-C14-H15	120.1(2)	C10-C15-H15	120.00
C10-C15-H14	120.3(2)	C14-C15-H15	120.00
F1-C16-F2	103.1(2)		

Table 5. Torsion angles (°) for **42**.

Torsion Angle	°	Torsion Angle	°
C6-O1-C7-N1	-0.2(2)	C4-C5-C6-O1	179.5(2)
C6-O1-C7-C8	179.89(19)	C9-C10-C11-C12	-179.3(2)
C7-O1-C6-C1	0.0(2)	C15-C10-C11-C12	0.1(3)
C7-O1-C6-C5	-179.6(2)	C9-C10-C15-C14	179.6(2)
C1-N1-C7-O1	0.3(2)	C11-C10-C15-C14	0.2(3)
C7-N1-C1-C2	178.9(2)	C10-C11-C12-C13	0.1(3)
C1-N1-C7-C8	-179.8(2)	C11-C12-C13-C14	-0.5(3)
C7-N1-C1-C6	-0.3(2)	C11-C12-C13-C16	179.2(2)
N1-C1-C6-O1	0.2(2)	C12-C13-C14-C15	0.8(3)
N1-C1-C6-C5	179.8(2)	C16-C13-C14-C15	-178.9(2)
N1-C1-C2-C3	-179.5(2)	C12-C13-C16-F1	-16.3(3)
C6-C1-C2-C3	-0.4(3)	C12-C13-C16-F2	-133.3(3)
C2-C1-C6-O1	-179.08(19)	C12-C13-C16-F3	102.5(3)
C2-C1-C6-C5	0.5(3)	C14-C13-C16-F1	163.4(2)
C1-C2-C3-C4	-0.3(3)	C14-C13-C16-F2	46.4(3)
C2-C3-C4-C5	0.8(4)	C14-C13-C16-F3	-77.8(3)
C3-C4-C5-C6	-0.6(3)	C13-C14-C15-C10	-0.6(3)
C4-C5-C6-C1	-0.1(3)		

X-Ray Analysis of 43

Crystal Data

Identification Code: **43**
 Empirical Formula: $C_{24}H_{12}N_2O_2$
 Formula Weight: 360.37
 Temperature: 293 K
 Crystal system, space group: Monoclinic, P21/c
 Unit cell dimensions:
 $a = 15.416(3) \text{ \AA}$, $\alpha = 90^\circ$
 $b = 4.7521(11) \text{ \AA}$, $\beta = 98.518(18)^\circ$
 $c = 11.923(3) \text{ \AA}$, $\gamma = 90^\circ$
 Volume: $863.8(3) \text{ \AA}^3$
 Z, Calculated density: 2, 1.385 g/cm³
 F(000): 372
 Crystal Size: 0.05×0.10×0.50 mm

Data Collection

Radiation: 0.71073 Å
 θ range for data collection: 3.5 to 25.0°
 Dataset: −18: 18; −3: 5; −14: 11
 Total, Unique Data, R(int): 3391, 1527, 0.084
 Observed data [$I > 2.0 \sigma(I)$]: 477

Refinement

SHELXS-86 program
 Refinement method: F^2 using SHELXL-97 software
 Nref, Npar: 1527, 127
 R, wR2, S: 0.0588, 0.1496, 0.72
 $w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 Max. and Av. Shift/Error: 0.00, 0.00
 Min. and Max. Resd. Dens: −0.25, 0.20 Å^{−3}

CCDC 818510 contains the crystallographic data for this molecule and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for **43**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
O1	0.28140(18)	0.1237(8)	0.2292(3)	0.0647(14)
N1	0.2030(2)	0.1385(8)	0.0549(3)	0.0444(14)
C1	0.2713(3)	0.2303(11)	0.1225(4)	0.0537(19)
C2	0.2129(3)	−0.0655(10)	0.2269(4)	0.0427(16)
C3	0.1899(3)	−0.2398(10)	0.3101(4)	0.0563(19)
C4	0.1188(3)	−0.4053(11)	0.2832(4)	0.0581(19)
C5	0.0679(3)	−0.4002(12)	0.1746(4)	0.062(2)
C6	0.0920(3)	−0.2233(11)	0.0921(4)	0.059(2)
C7	0.1645(3)	−0.0536(10)	0.1201(4)	0.0433(19)
C8	0.3309(3)	0.4338(11)	0.0952(4)	0.0543(19)
C9	0.3810(3)	0.6024(11)	0.0665(4)	0.0503(19)
C10	0.4411(3)	0.8058(10)	0.0334(4)	0.0494(19)
C11	0.4317(3)	0.9033(12)	−0.0772(4)	0.0589(19)
C12	0.5114(3)	0.9012(12)	0.1101(4)	0.0588(19)

Appendix

Table 2. Hydrogen Atom Positions and Isotropic Displacement Parameters ($\text{\AA}^2$) for **43**.

Atom	x	y	z	U(iso)
H3	0.22230	-0.24310	0.38240	0.0680
H4	0.10280	-0.52650	0.33780	0.0700
H5	0.01860	-0.51450	0.15860	0.0750
H6	0.05990	-0.21910	0.01960	0.0710
H11	0.38610	0.83520	-0.13000	0.0710
H12	0.52010	0.83270	0.18400	0.0700

Table 3. (An)isotropic displacement parameters for **43**.

Atom	U(1,1)	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
O1	0.0615(19)	0.080(3)	0.052(2)	-0.004(2)	0.0064(16)	-0.0170(19)
N1	0.054(2)	0.050(3)	0.028(2)	-0.002(2)	0.0026(18)	-0.0071(19)
C1	0.073(3)	0.058(4)	0.036(3)	0.003(3)	0.028(3)	0.001(3)
C2	0.044(2)	0.044(3)	0.041(3)	0.001(3)	0.009(2)	-0.009(2)
C3	0.051(3)	0.075(4)	0.043(3)	0.010(3)	0.007(2)	-0.003(3)
C4	0.062(3)	0.061(4)	0.056(3)	0.001(3)	0.024(3)	-0.007(3)
C5	0.062(3)	0.072(4)	0.054(4)	-0.015(4)	0.014(3)	-0.017(3)
C6	0.063(3)	0.079(5)	0.034(3)	-0.010(3)	0.001(2)	-0.012(3)
C7	0.048(3)	0.051(4)	0.030(3)	-0.004(3)	0.003(2)	0.000(2)
C8	0.065(3)	0.058(4)	0.041(3)	0.004(3)	0.012(2)	0.002(3)
C9	0.057(3)	0.055(4)	0.039(3)	0.004(3)	0.007(2)	0.012(2)
C10	0.047(3)	0.064(4)	0.038(3)	0.006(3)	0.009(2)	0.002(2)
C11	0.055(3)	0.081(4)	0.038(3)	0.003(3)	-0.002(2)	-0.012(3)
C12	0.063(3)	0.074(4)	0.038(3)	0.007(3)	0.003(2)	0.001(3)

Table 4. Bond lengths ($\text{\AA}$) for **43**.

Bond	$\text{\AA}$	Bond	$\text{\AA}$
O1-C1	1.357(6)	C8-C9	1.197(7)
O1-C2	1.384(6)	C9-C10	1.434(7)
N1-C1	1.303(6)	C10-C11	1.385(7)
N1-C7	1.388(6)	C10-C12	1.387(7)
C1-C8	1.405(7)	C11-C12	1.374(7)
C2-C3	1.378(7)	C3-H3	0.9300
C2-C7	1.378(7)	C4-H4	0.9300
C3-C4	1.349(7)	C5-H5	0.9300
C4-C5	1.411(7)	C6-H6	0.9300
C5-C6	1.386(7)	C11-H11	0.9300
C6-C7	1.379(7)	C12-H12	0.9300

Appendix

Table 4. Bond angles (°) for **43**.

Angle	°	Angle	°
C1-O1-C2	104.1(4)	C9-C10-C11	120.5(4)
C1-N1-C7	104.3(4)	C9-C10-C12	120.8(4)
O1-C1-N1	115.2(4)	C11-C10-C12	118.7(4)
O1-C1-C8	119.1(4)	C10-C11-C12	121.1(4)
N1-C1-C8	125.7(4)	C10-C12-C11	120.2(4)
O1-C2-C3	130.8(4)	C2-C3-H3	121.00
O1-C2-C7	107.4(4)	C4-C3-H3	121.00
C3-C2-C7	121.9(4)	C3-C4-H4	119.00
C2-C3-C4	117.8(4)	C5-C4-H4	119.00
C3-C4-C5	122.0(5)	C4-C5-H5	120.00
C4-C5-C6	119.4(5)	C6-C5-H5	120.00
C5-C6-C7	118.4(4)	C5-C6-H6	121.00
N1-C7-C2	109.1(4)	C7-C6-H6	121.00
N1-C7-C6	130.4(4)	C10-C11-H11	119.00
C2-C7-C6	120.6(4)	C12-C11-H11	120.00
C1-C8-C9	176.7(5)	C10-C12-H12	120.00
C8-C9-C10	179.3(5)	C11-C12-H12	120.00

Table 5. Torsion angles (°) for **43**.

Torsion Angle	°	Torsion Angle	°
C2-O1-C1-N1	2.4(5)	C3-C2-C7-C6	-1.7(7)
C2-O1-C1-C8	179.7(4)	C3-C2-C7-N1	-180.0(4)
C1-O1-C2-C7	-1.9(5)	C2-C3-C4-C5	-1.0(7)
C1-O1-C2-C3	179.1(5)	C3-C4-C5-C6	1.0(8)
C7-N1-C1-C8	-178.9(5)	C4-C5-C6-C7	-1.2(7)
C7-N1-C1-O1	-1.8(5)	C5-C6-C7-C2	1.6(7)
C1-N1-C7-C2	0.5(5)	C5-C6-C7-N1	179.4(5)
C1-N1-C7-C6	-177.6(5)	C9-C10-C11-C12	179.8(5)
O1-C2-C3-C4	-179.8(5)	C12-C10-C11-C12	-2.5(8)
O1-C2-C7-C6	179.2(4)	C9-C10-C12-C11	-179.8(5)
C7-C2-C3-C4	1.4(7)	C11-C10-C12-C11	2.4(8)
O1-C2-C7-N1	0.9(5)	C10-C11-C12-C10	2.5(8)

X-Ray Analysis of 44

Crystal Data

Identification Code: **44**
 Empirical Formula: C₂₄H₁₂N₂S₂
 Formula Weight: 392.48
 Temperature: 293 K
 Crystal system, space group: Monoclinic, P2₁/c
 Unit cell dimensions:
 $a = 15.4225(7) \text{ \AA}$, $\alpha = 90^\circ$
 $b = 5.0284(3) \text{ \AA}$, $\beta = 98.247(4)^\circ$
 $c = 11.9017(6) \text{ \AA}$, $\gamma = 90^\circ$
 Volume: 913.44(8) Å³
 Z, Calculated density: 2, 1.427 g/cm³
 F(000): 404
 Crystal Size: 0.01×0.08×0.09 mm

Data Collection

Radiation: 1.54184 Å
 θ range for data collection: 2.9 to 67.6°
 Dataset: -18: 17; -5: 6; -13: 14
 Total, Unique Data, R(int): 3881, 1631, 0.031
 Observed data [$I > 2.0 \sigma(I)$]: 1266

Refinement

SHELXS-86 program
 Refinement method: F² using SHELXL-97 software
 Nref, Npar: 1631, 133
 R, wR₂, S: 0.0393, 0.1039, 1.03
 $w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.1291P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 Max. and Av. Shift/Error: 0.00, 0.00
 Min. and Max. Resd. Dens: -0.20, 0.15 Å⁻³

CCDC 818509 contains the crystallographic data for this molecule and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for **44**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
*S1	0.70541(5)	0.85001(17)	0.74176(6)	0.0652(3)
*N1	0.79386(15)	0.8484(5)	0.94488(18)	0.0580(8)
C1	0.72694(13)	0.7420(4)	0.88084(17)	0.0541(7)
C2	0.79379(13)	1.0593(4)	0.77022(18)	0.0570(7)
C3	0.82288(18)	1.2392(6)	0.6959(2)	0.0748(9)
C4	0.89384(18)	1.3918(5)	0.7345(2)	0.0784(10)
C5	0.93644(16)	1.3680(5)	0.8437(2)	0.0753(10)
C6	0.90795(16)	1.1902(5)	0.9182(2)	0.0721(9)
C7	0.83516(13)	1.0357(4)	0.88161(17)	0.0558(7)
C8	0.67049(14)	0.5453(5)	0.91662(19)	0.0622(8)
C9	0.62030(14)	0.3819(5)	0.94145(19)	0.0604(7)
C10	0.55933(13)	0.1875(4)	0.97081(18)	0.0548(7)
C11	0.56104(15)	0.1086(5)	1.0833(2)	0.0678(8)
C12	0.49794(15)	0.0771(5)	0.88855(19)	0.0666(8)

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*S1	0.8128(3)	0.8164(10)	0.9834(3)	0.0652(3)
*N1	0.7211(6)	0.886(3)	0.7764(7)	0.0580(8)

Table 2. Hydrogen Atom Positions and Isotropic Displacement Parameters ($\text{\AA}^2$) for **44**.

Atom	x	y	z	U(iso)
H3	0.79470	1.25540	0.62170	0.0900
H4	0.91400	1.51480	0.68590	0.0940
H5	0.98510	1.47360	0.86750	0.0900
H6	0.93710	1.17410	0.99190	0.0870
H11	0.60220	0.18160	1.13960	0.0810
H12	0.49630	0.12840	0.81320	0.0800

Table 3. (An)isotropic displacement parameters for **44**.

Atom	U(1,1)	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
S1	0.0614(4)	0.0665(5)	0.0673(4)	0.0060(4)	0.0079(3)	-0.0149(3)
N1	0.0587(14)	0.0559(14)	0.0602(14)	0.0006(11)	0.0116(10)	-0.0040(11)
C1	0.0540(11)	0.0460(11)	0.0656(12)	0.0014(9)	0.0198(9)	-0.0008(10)
C2	0.0519(11)	0.0525(12)	0.0688(13)	-0.0034(10)	0.0162(9)	-0.0021(10)
C3	0.0831(17)	0.0759(17)	0.0678(14)	0.0083(12)	0.0194(12)	-0.0080(14)
C4	0.0884(18)	0.0641(16)	0.0930(18)	0.0007(13)	0.0482(15)	-0.0131(14)
C5	0.0654(14)	0.0669(16)	0.1000(19)	-0.0216(14)	0.0342(13)	-0.0193(12)
C6	0.0665(14)	0.0776(17)	0.0729(14)	-0.0136(13)	0.0121(11)	-0.0096(13)
C7	0.0581(12)	0.0484(12)	0.0647(12)	-0.0021(10)	0.0223(9)	0.0003(10)
C8	0.0607(13)	0.0521(13)	0.0775(14)	0.0032(11)	0.0229(10)	-0.0001(11)
C9	0.0578(12)	0.0516(13)	0.0746(13)	0.0037(10)	0.0196(10)	-0.0010(10)
C10	0.0516(11)	0.0443(12)	0.0721(13)	0.0041(10)	0.0209(9)	0.0007(9)
C11	0.0671(14)	0.0672(15)	0.0690(13)	0.0063(11)	0.0090(10)	-0.0149(12)
C12	0.0708(14)	0.0665(15)	0.0642(12)	0.0114(11)	0.0159(11)	-0.0097(12)
*S1	0.0614(4)	0.0665(5)	0.0673(4)	0.0060(4)	0.0079(3)	-0.0149(3)
*N1	0.0587(14)	0.0559(14)	0.0602(14)	0.0006(11)	0.0116(10)	-0.0040(11)

Table 4. Bond lengths ($\text{\AA}$) for **44**.

Bond	$\text{\AA}$	Bond	$\text{\AA}$
S1-C1	1.728(2)	C5-C6	1.375(3)
S1-C2	1.717(2)	C6-C7	1.383(3)
*S1-C7	1.710(5)	C8-C9	1.195(3)
*S1-C1	1.709(5)	C9-C10	1.434(3)
N1-C1	1.306(3)	C10-C11	1.393(3)
N1-C7	1.413(3)	C10-C12	1.377(3)
*N1-C1	1.430(11)	C11-C12	1.378(3)

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*N1-C2	1.430(12)	C3-H3	0.9300
C1-C8	1.423(3)	C4-H4	0.9300
C2-C3	1.384(3)	C5-H5	0.9300
C2-C7	1.391(3)	C6-H6	0.9300
C3-C4	1.361(4)	C11-H11	0.9300
C4-C5	1.375(3)	C12-H12	0.9300

Table 5. Bond angles (°) for **44**.

Angle	°	Angle	°
C1-S1-C2	88.03(10)	C2-C7-C6	119.51(19)
C1-*S1-C7	81.34(19)	*S1-C7-C2	28.2(2)
C1-N1-C7	109.92(19)	C1-C8-C9	176.6(2)
C1-*N1-C2	113.7(6)	C8-C9-C10	179.4(2)
S1-C1-N1	117.21(17)	C9-C10-C11	120.5(4)
S1-C1-C8	117.61(16)	C9-C10-C12	120.8(4)
*N1-C1-C8	130.3(5)	C11-C10-C12	118.7(4)
N1-C1-C8	125.2(2)	C10-C11-C12	121.1(4)
*S1-C2-C8	112.5(2)	C10-C12-C11	120.2(4)
*S1-C1-*N1	117.1(5)	C2-C3-H3	121.00
S1-C2-C7	112.23(15)	C4-C3-H3	121.00
C3-C2-C7	121.2(2)	C3-C4-H4	119.00
*N1-C2-C7	98.9(4)	C5-C4-H4	119.00
*N1-C2-C3	139.4(4)	C4-C5-H5	120.00
S1-C2-C3	126.55(18)	C6-C5-H5	120.00
C2-C3-C4	118.1(2)	C5-C6-H6	121.00
C3-C4-C5	121.5(2)	C7-C6-H6	121.00
C4-C5-C6	120.8(2)	C10-C11-H11	119.00
C5-C6-C7	118.8(2)	C12-C11-H11	120.00
N1-C7-C2	112.61(18)	C10-C12-H12	120.00
N1-C7-C6	127.9(2)	C11-C12-H12	120.00
*S1-C7-C6	112.1(2)		

Table 6. Torsion angles (°) for **44**.

Torsion Angle	°	Torsion Angle	°
C2-S1-C1-N1	-0.17(19)	C3-C2-C7-C6	-1.5(3)
C2-S1-C1-C8	179.69(18)	C3-C2-C7-N1	177.9(2)
C1-S1-C2-C7	0.57(16)	C2-C3-C4-C5	0.6(4)
C1-S1-C2-C3	-178.1(2)	C3-C4-C5-C6	-0.7(4)
C7-N1-C1-C8	179.9(2)	C4-C5-C6-C7	-0.3(4)
C7-N1-C1-S1	-0.3(3)	C5-C6-C7-C2	1.4(3)
C1-N1-C7-C2	0.7(3)	C5-C6-C7-N1	-177.9(2)

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C1-N1-C7-C6	-179.9(2)	C9-C10-C11-C12	179.6(2)
S1-C2-C3-C4	179.1(2)	C12-C10-C11-C12	0.0(3)
S1-C2-C7-C6	179.73(18)	C9-C10-C12-C11	-179.6(2)
C7-C2-C3-C4	0.5(4)	C11-C10-C12-C11	0.0(3)
S1-C2-C7-N1	-0.9(2)	C10-C11-C12-C10	0.0(4)

X-Ray Analysis of 45

Crystal Data

Identification Code: 45
 Empirical Formula: $C_{24}H_{12}N_2Se_2$
 Formula Weight: 486.28
 Temperature: 293 K
 Crystal system, space group: Monoclinic, P21/c
 Unit cell dimensions:
 $a = 10.1702(10) \text{ \AA}$, $\alpha = 90^\circ$
 $b = 5.2571(3) \text{ \AA}$, $\beta = 98.598(5)^\circ$
 $c = 11.5250(5) \text{ \AA}$, $\gamma = 90^\circ$
 Volume: $929.98(9) \text{ \AA}^3$
 Z , Calculated density: 2, 1.737 g/cm^3
 $F(000)$: 476
 Crystal Size: $0.01 \times 0.05 \times 0.07 \text{ mm}$

Data Collection

Radiation: $1.54184 \text{ \AA}$
 θ range for data collection: 2.3 to 67.6°
 Dataset: $-22: 17$; $-5:46$; $-13: 13$
 Total, Unique Data, $R(\text{int})$: 3567, 1659, 0.040
 Observed data [$I > 2.0 \text{ sigma}(I)$]: 1388

Refinement

SHELXS-86 program
 Refinement method: F^2 using SHELXL-97 software
 N_{ref} , N_{par} : 1659, 127
 R , wR_2 , S : 0.0527, 0.1364, 1.04
 $w = 1/[\sigma^2(F_o^2) + (0.0839P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 Max. and Av. Shift/Error: 0.00, 0.00
 Min. and Max. Resd. Dens: $-0.54, 1.06 \text{ \AA}^{-3}$

CCDC 818511 contains the crystallographic data for this molecule and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Table 1. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for 45U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Se1	0.22017(3)	0.21381(14)	0.18713(4)	0.0549(2)
N1	0.2720(2)	0.1937(11)	0.4214(4)	0.0546(14)
C1	0.2187(2)	0.1067(12)	0.3465(4)	0.0502(14)
C2	0.3074(2)	0.3981(12)	0.2452(4)	0.0480(14)
C3	0.3538(3)	0.5559(13)	0.1847(4)	0.0577(16)
C4	0.4143(3)	0.6705(14)	0.2469(6)	0.0627(17)
C5	0.4304(3)	0.6296(14)	0.3675(5)	0.0632(16)

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C6	0.3844(3)	0.4735(14)	0.4266(4)	0.0598(14)
C7	0.3221(2)	0.3566(12)	0.3663(4)	0.0498(14)
C8	0.1611(3)	−0.0620(13)	0.3815(4)	0.0547(16)
C9	0.1127(3)	−0.1969(13)	0.4142(4)	0.0542(16)
C10	0.0558(2)	−0.3515(12)	0.4565(4)	0.0488(14)
C11	0.0505(3)	−0.3420(13)	0.5761(4)	0.0527(16)
C12	0.0046(3)	−0.5116(12)	0.3821(4)	0.0545(16)

Table 2. Hydrogen Atom Positions and Isotropic Displacement Parameters ($\text{\AA}^2$) for **45**.

Atom	x	y	z	U(iso)
H3	0.34390	0.58280	0.10380	0.0690
H4	0.44580	0.77920	0.20760	0.0760
H5	0.47240	0.70830	0.40790	0.0760
H6	0.39500	0.44590	0.50730	0.0720
H11	0.08450	−0.23610	0.62770	0.0640
H12	0.00750	−0.52040	0.30230	0.0660

Table 3. (An)isotropic displacement parameters for **45**.

Atom	U(1,1)	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Se1	0.0493(4)	0.0754(4)	0.0395(3)	0.0035(2)	0.0047(2)	−0.0092(2)
N1	0.049(2)	0.075(3)	0.042(2)	−0.0005(18)	0.0139(17)	0.0035(19)
C1	0.046(2)	0.063(3)	0.043(2)	−0.001(2)	0.0111(18)	0.004(2)
C2	0.044(2)	0.058(3)	0.042(2)	−0.002(2)	0.0068(17)	−0.001(2)
C3	0.056(3)	0.070(3)	0.049(2)	0.004(2)	0.014(2)	−0.007(2)
C4	0.051(3)	0.070(3)	0.068(3)	0.003(3)	0.012(2)	−0.008(2)
C5	0.045(2)	0.074(3)	0.068(3)	−0.010(3)	0.000(2)	−0.001(3)
C6	0.049(2)	0.080(3)	0.049(2)	−0.009(2)	0.003(2)	0.000(2)
C7	0.044(2)	0.061(3)	0.045(2)	−0.002(2)	0.0083(18)	0.005(2)
C8	0.052(3)	0.067(3)	0.046(2)	0.001(2)	0.010(2)	0.004(2)
C9	0.053(3)	0.068(3)	0.043(2)	0.003(2)	0.012(2)	0.004(2)
C10	0.048(2)	0.057(3)	0.044(2)	0.003(2)	0.0157(19)	0.005(2)
C11	0.051(3)	0.065(3)	0.041(2)	0.001(2)	0.0036(19)	−0.004(2)
C12	0.064(3)	0.065(3)	0.037(2)	0.002(2)	0.016(2)	−0.001(2)

Table 4. Bond lengths ($\text{\AA}$) for **45**.

Bond	$\text{\AA}$	Bond	$\text{\AA}$
Se1-C1	1.897(5)	C8-C9	1.199(8)
Se1-C2	1.878(4)	C9-C10	1.421(7)
N1-C1	1.289(6)	C10-C11	1.398(6)
N1-C7	1.410(6)	C10-C12	1.383(7)

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C1-C8	1.425(7)	C11-C12	1.374(8)
C2-C3	1.384(7)	C3-H3	0.9300
C2-C7	1.393(6)	C4-H4	0.9300
C3-C4	1.360(8)	C5-H5	0.9300
C4-C5	1.389(9)	C6-H6	0.9300
C5-C6	1.365(8)	C11-H11	0.9300
C6-C7	1.382(7)	C12-H12	0.9300

Table 5. Bond angles (°) for **45**.

Angle	°	Angle	°
C1-Se1-C2	84.07(19)	C9-C10-C11	119.8(4)
C1-N1-C7	111.4(4)	C9-C10-C12	121.7(4)
Se1-C1-N1	117.0(3)	C11-C10-C12	118.5(4)
Se1-C1-C8	121.3(3)	C10-C11-C12	120.4(5)
N1-C1-C8	121.7(4)	C10-C12-C11	121.2(4)
Se1-C2-C7	109.9(3)	C2-C3-H3	121.00
C3-C2-C7	121.2(4)	C4-C3-H3	121.00
Se1-C2-C3	129.0(4)	C3-C4-H4	119.00
C2-C3-C4	118.1(5)	C5-C4-H4	119.00
C3-C4-C5	121.8(5)	C4-C5-H5	120.00
C4-C5-C6	119.8(5)	C6-C5-H5	120.00
C5-C6-C7	119.9(5)	C5-C6-H6	121.00
N1-C7-C2	117.7(4)	C7-C6-H6	121.00
N1-C7-C6	123.1(4)	C10-C11-H11	119.00
C2-C7-C6	119.2(4)	C12-C11-H11	120.00
C1-C8-C9	177.7(5)	C10-C12-H12	120.00
C8-C9-C10	178.1(5)	C11-C12-H12	120.00

Table 6. Torsion angles (°) for **45**.

Torsion Angle	°	Torsion Angle	°
C2-Se1-C1-N1	0.0(4)	C3-C2-C7-C6	-0.5(8)
C2-Se1-C1-C8	179.9(4)	C3-C2-C7-N1	179.9(5)
C1-Se1-C2-C7	0.1(4)	C2-C3-C4-C5	0.7(9)
C1-Se1-C2-C3	-179.9(5)	C3-C4-C5-C6	-0.7(9)
C7-N1-C1-C8	-180.0(5)	C4-C5-C6-C7	0.1(9)
C7-N1-C1-Se1	-0.1(6)	C5-C6-C7-C2	0.5(8)
C1-N1-C7-C2	0.1(6)	C5-C6-C7-N1	-179.8(5)
C1-N1-C7-C6	-179.6(5)	C9-C10-C11-C12	179.5(5)
Se1-C2-C3-C4	179.8(4)	C12-C10-C11-C12	-0.2(8)
Se1-C2-C7-C6	179.6(4)	C9-C10-C12-C11	-179.5(5)
C7-C2-C3-C4	-0.2(8)	C11-C10-C12-C11	0.2(8)

Se1-C2-C7-N1	-0.1(6)	C10-C11-C12-C10	0.2(8)
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Additional Information (Chapter 2)

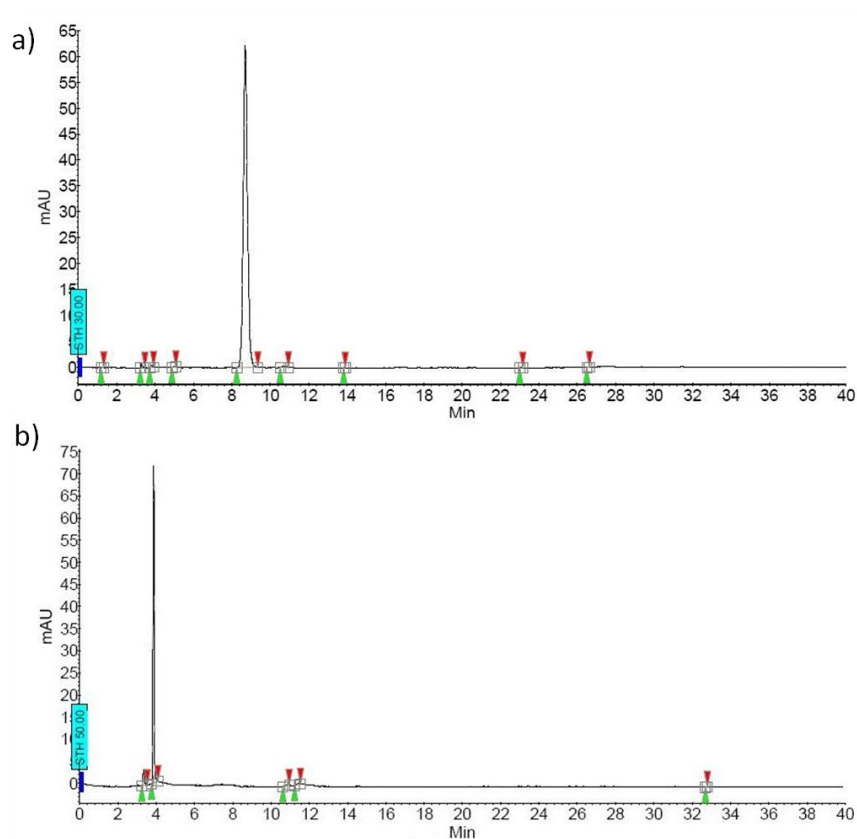


Figure A1. HPLC chromatograms of modules **43** (a) and **44** (b) after purification. The analysis was performed using isocratic eluent (CH_3CN).

Additional Information (Chapter 3)

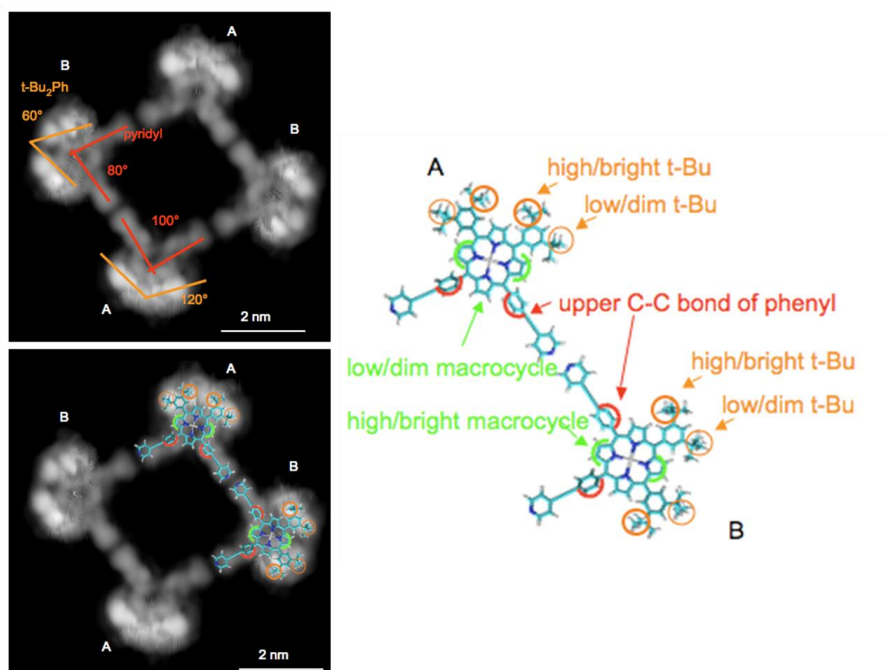


Figure A2. The opening angle of the t-Bu₂Ph groups is linked to the opening angle of the pyridyl legs by a saddle-shaped macrocycle deformation. The two lobes of each t-Bu leg have not the same apparent height (brightness): dihedral angle of phenyl ring of t-Bu₂Ph group not 0°. Conformation A has a 120° opening angle of the t-Bu₂Ph pumps and the two *inner* t-Bu groups are brighter/higher. Conformation B has a 60° opening angle of the tBP pumps and the two *outer* t-Bu groups are brighter/higher.

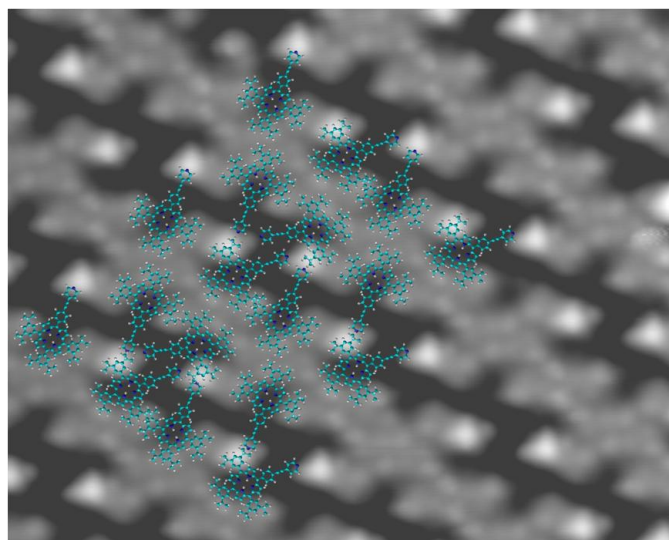


Figure A3. Porphyrin module **109** on the weakly interacting Ag(111) surface without Cu adatoms: formation of dense-packed islands at low sub-monolayer coverages, no Pyridyl head to head coupling (see overlaid models).

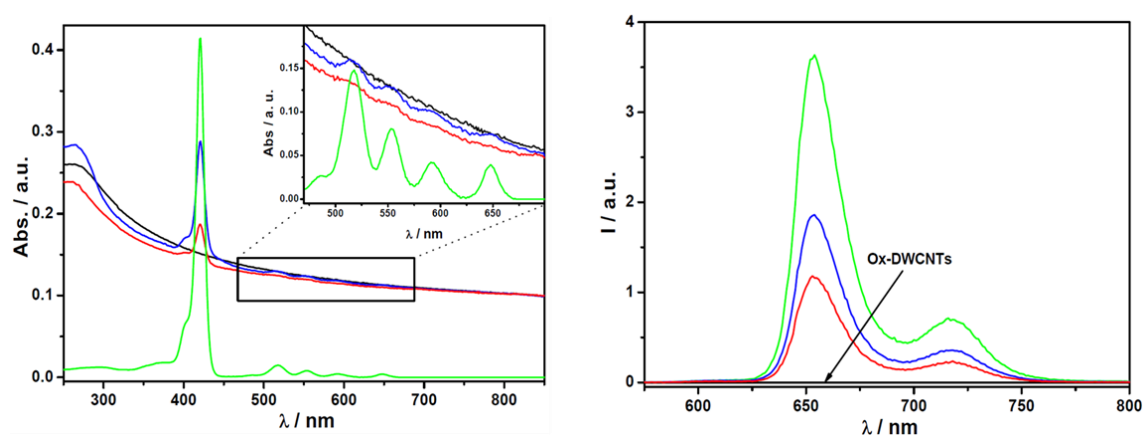


Figure A4. Left: Electronic absorption spectra of **163** (green), **ox-DWCNTs** (black), **163-DWCNTs** (blue) and **163@DWCNTs** (red) in CHCl_3 . Inset: expanded Q-band region of all the materials. Spectra of samples containing carbon nanotubes are normalized at 850 nm. Right: Emission spectra of **163** (green), **ox-DWCNTs** (black), **163-DWCNTs** (blue) and **1@DWCNTs** (red) upon excitation at 420 nm in CHCl_3 . Note: the qualitative trend of emission intensities is that observed experimentally (**163** > **163-DWCNTs** > **163@DWCNTs**) but the intensity ratios must not be taken for quantitative comparisons (see text).

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Curriculum Vitae

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2004-2006	Università degli Studi di Roma 'La Sapienza' Master in Chemistry
2006	Università degli Studi di Roma 'La Sapienza' Master diploma work under the supervision of <i>Prof. Dr. Osvaldo Lanzalunga</i> 'Racemization of aromatic chiral sulfoxides by an electron transfer mechanism. Configurational stability of aromatic sulfoxide radical cations'
2007-2011	Université Notre-Dame de la Paix (FUNDP), Namur, Belgium PhD in Organic Chemistry under the supervision of <i>Prof. Dr. Davide Bonifazi</i> 'Synthesis, self-assembly and optoelectronic properties of heteroaromatic chromophores'
2010	Technical University of Munich (TUM), Munich, Germany Research in the STM group of <i>Prof. Dr. Johannes Barth</i> 'Surface-Templated Engineering of Porphyrin-Based Molecules'
2009-2010	Supervision diploma work 'Bidimensional expansion of porphyrin cores' by <i>Daphné Stassen</i>
2011	Post-doctorate at Imperial College of London, Department of Materials

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