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Synthetic platform for mono-functionalised tridentate macrocycles as key precursors of mechanically-linked macromolecular systems

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Atul Kumar Sharma,[a] Jagadeesh Malineni,[a] Simon Box,[a] Sina Ghiassinejad,[a] Evelyne van Ruymbeke,[a] Charles-André Fustin[a]*

We report here a synthetic platform toward mono-functionalized tridentate macrocycles based on a pyridine-2,6-bis-carboxamide motif. These macrocycles bear a variety of functional groups at the fourth position of the pyridine, giving access to a wide range of synthetic methods for further derivatisation or preparation of more complex structures such as mechanically interlocked molecules or polymer materials. To illustrate the potential of this family of macrocycles a series of square planar palladium complex-based pseudorotaxanes, containing different axles and functional groups on the ring, are synthesised, and then use to prepare a macro-pseudorotaxane, i.e. a polymer containing a rotaxane junction, and mechanically-linked gels by a one-pot and a polyrotaxane approach.

Introduction

In the last few decades, mechanically interlocked molecules (MIMs) have attracted great interest due to their unique dynamics, and consequently, a wide range of interlocked molecules and materials have been reported.[1-5] Typical examples of MIMs are rotaxanes and catenanes. These interlocked systems exhibit exceptional properties which are not accessible with covalent systems. For example, they can alter the reactivity of moieties embedded in their structure thanks to the higher steric hindrance in the interlocked systems,[6-9] or they can be used as 'on' and 'off' catalysts thanks to the stimulus induced translocation of the macrocycle between two binding sites on the axle.[10-13] The idiosyncratic characteristics of MIMs were also utilised to develop artificial molecular machines such as molecular pumps, motors, clocks, and switches.[14-17] The field of polymer chemistry was also attracted by the intriguing characteristics of mechanical links to produce interesting mechanically interlocked polymers (MIPs), such as polycatenanes[18-20] and polyrotaxanes.[21-23] On the other hand, slide-ring networks obtained from the cross-linking of polyrotaxanes by linking the rings two-by-two show much better (mechanical) properties compared to traditional physical or chemical networks such as high extensibility, extreme swelling and high mechanical strength.[24-26]

Interlocked systems are efficiently formed thanks to the template effect that can exploit many kinds of (supramolecular) interactions such as π–π stacking, hydrogen bonds, electrostatic interactions, solvophobic effects,…[1-5] Among these, the metal coordination template is particularly interesting due to its high versatility, practicality and reliability.[27-30] Different systems such as rotaxanes, catenanes, and 3-dimensionally interlocked networks were developed using this template with various transition metal ions.[27-30] Among these, the palladium(II)-based square planar complex, formed by the 3+1 approach between a tridentate and a monodentate ligand, has been found to be a very interesting candidate for the formation of interlocked systems.[31-37]

It is interesting to note that all the molecules discussed above have a common structural feature: the presence of at least one cyclic component. It won't be wrong to say that the whole concept of mechanical linking in these molecules and materials depends mainly on macrocycles. Depending on the synthetic strategies, rings such as crown ethers, cucurbiturils, cyclodextrins, and so on have been utilised to produce various mechanically interlocked systems.[1-5] However, many of the rings utilised to develop mechanically interlocked systems, especially in the field of polymeric materials, are formed by repeating units, resulting either in too many identical functional groups or no functional groups on the macrocycles, which may limit their solubility or even induce their aggregation. Strategies to introduce a single functional group on these types of macrocycles exist, but they are not always straightforward.[38,39] Controlling precisely the number of functionalities on the macrocycle is also

[a] *Institute of Condensed Matter and Nanosciences (IMCN), Bio- and Soft Matter Division (BSMA), Université catholique de Louvain, Place Pasteur 1, 1348, Louvain-la-Neuve, Belgium*
Email- charles-andre.fustin@uclouvain.be
Electronic Supplementary Information (ESI) available: full details on synthesis and characterization of the compounds]. See DOI: 10.1039/x0xx00000x

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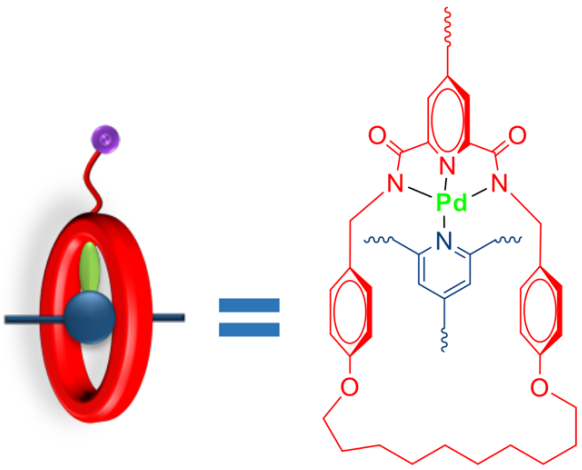


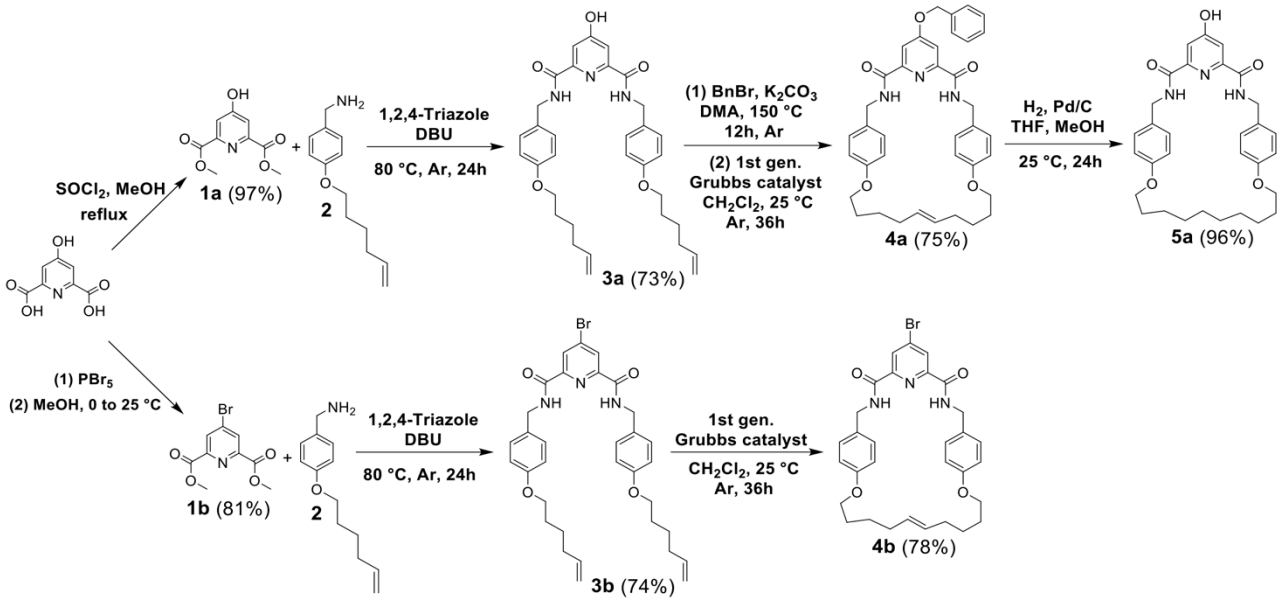
Figure 1. General chemical and cartoon presentation of a palladium-based pseudorotaxane.

crucial for the development of various types of interlocked systems and to gain good control over their properties.[40-42]

Considering the importance of controlling the number of functions on the macrocycle and the advantages of the palladium-based 3+1 approach for preparing MIMs, we report here on a synthetic platform toward mono-functionalized tridentate macrocycles based on a pyridine-2,6- bis-carboxamide motif. These macrocycles bear a variety of functional groups at the fourth position of the pyridine, giving access to a wide range of synthetic methods, e.g. C-C bond formation, Cu catalysed alkyne-azide cycloaddition (CuAAC click reaction), substitution reactions, controlled or uncontrolled radical polymerisation, for further derivatisation or preparation of more complex structures such as MIMs. In this respect, the formation of pseudorotaxanes based on palladium(II) complexes (Figure 1) from these tridentate macrocycles is also demonstrated using different pyridine derivatives as monodentate ligand. Finally, to illustrate the usefulness of these functionalised pseudorotaxanes in the polymer field, several materials bearing mechanical links are synthesised such as a macro-pseudorotaxane, i.e., a polymer containing a rotaxane junction, a polyrotaxane, and mechanically cross-linked three-dimensional polymeric networks.

Results and discussion

To access a greater range of synthetic methodologies in the area of mechanically interlocked molecules and materials, we have developed mono-functional macrocycles bearing different functional groups such as terminal alkynes, aryl and alkyl halides, aromatic and aliphatic alcohols, aliphatic azide, functional groups suitable for substitution reactions, and functional groups suitable for free or controlled radical polymerisation. As starting points for all these macrocycles, we have selected an alcohol and a bromide functionalized macrocycle because of the versatility offered by these two functional groups. Scheme 1 illustrates the synthesis of the two starting macrocycles, inspired by the work of D.A. Leigh,[31,34] that will be later derivatised. Compounds **1a** and **1b** were first synthesised from the commercially available chelidamic acid. In the first case, the carboxylic acid groups of chelidamic acid were esterified with the help of thionyl chloride and methanol at the refluxing temperature of methanol to obtain compound **1a,** while in the second case the chelidamic acid was first brominated by phosphorus pentabromide to replace all the hydroxyl functional groups by a bromide, and then esterified by methanol in one-pot to produce compound **1b.** Compound **2** was synthesised by a two-step procedure reported in literature.[31,32] The U-shaped compounds **3a** and **3b** were formed by the condensation reaction between the ester groups of **1a** and **1b** and the primary amine group of compound **2** in a solvent-free reaction in the presence of a catalytic amount of DBU and 1,2,4-triazole. Finally, the cyclisation of the U-shaped molecules was executed by ring-closing olefin metathesis (RCM), which was carried out in the presence of Grubbs 1st-generation catalyst in dry



Scheme 1. Synthesis of the macrocycles containing two different functional groups at the fourth position of pyridine.

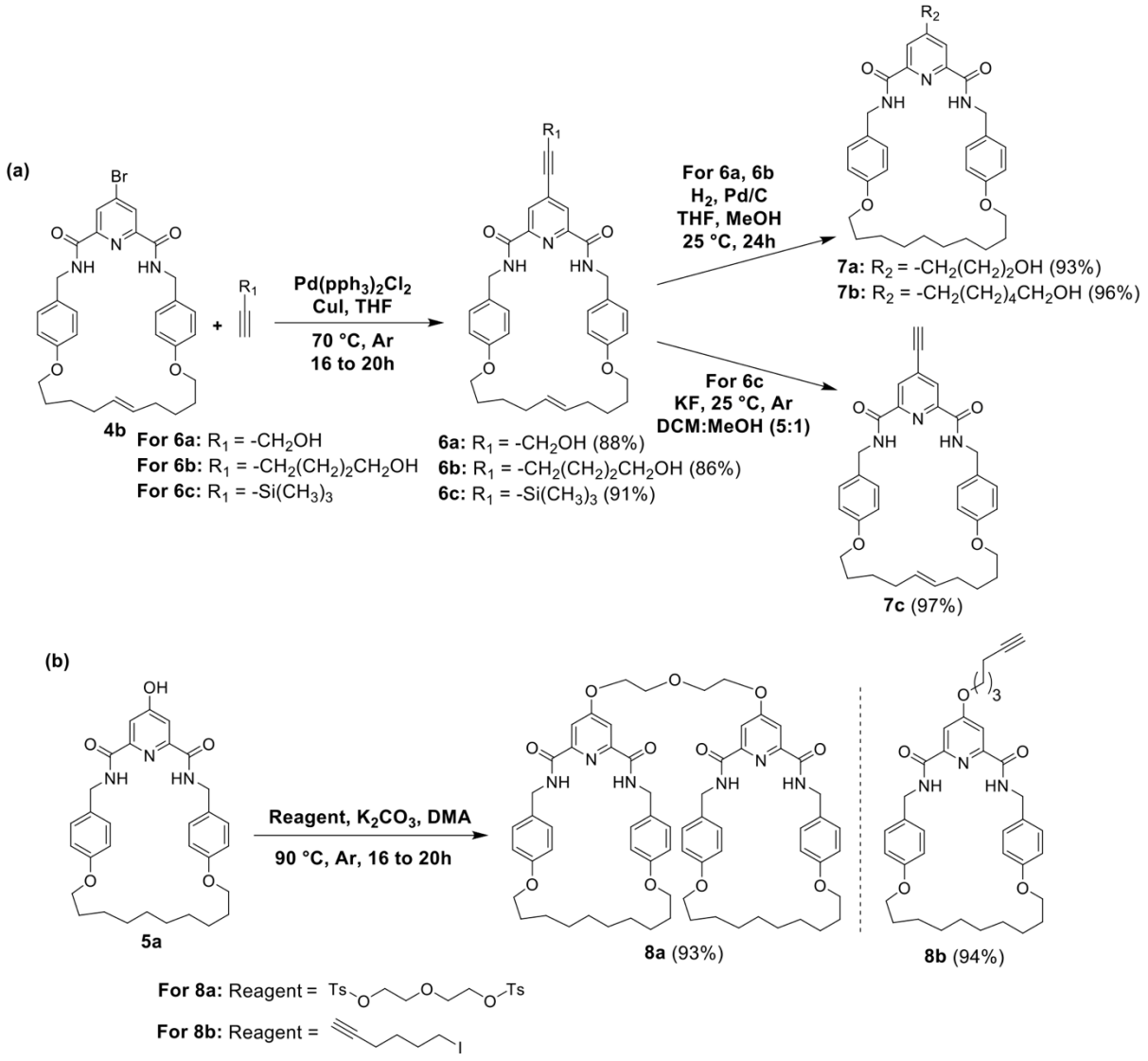
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dichloromethane at a concentration of 1.6 mmolar under an inert atmosphere. Compound **4b** was obtained in 78% yield while the RCM on compound **3a** yielded only 10% of the desired cyclised product. This lack of productivity is attributed to the presence of the hydroxyl functionality. Reports have indeed shown that the Grubbs 1st-generation catalyst can be sensitive to the presence of alcohols.[43,44] During the course of the metathesis reaction in the presence of alcohols, it is reported that a ruthenium hydride complex, which is inactive for the metathesis reaction, may be formed. Therefore, after the investigation of the variety of protecting groups, benzylic ether provided a significant increase in reactivity to obtain compound **4a** in 75% yield. The benzyl bromide protection was also selected because the reduction of the isolated double bond on the ring and deprotection of the benzyl group of **4a** can be done in a single step to afford compound **5a**.

With the mono-functionalised pivotal intermediates **4b** and **5a** in hand, different macrocycle derivatives can be prepared (Scheme 2). As demonstrated in Scheme 2a, three derivatives **7a**, **7b** and **7c** were obtained from **4b**. Compound **7a** and **7b** contain a hydroxyl functionality which can be further utilised for nucleophilic substitution, selective protection and deprotection, or can be converted to an electrophile by replacing it by a good leaving group. On the other hand, the terminal alkyne function of **7c** can be utilised for C-C cross-coupling, or Cu-catalysed alkyne-azide cycloaddition (CuAAC). The aryl bromide position of compound **4b** is suitable for the C-C bond formation by palladium catalysed reactions. Thus, different alkyne groups were grafted at the fourth position of the pyridine by utilising the Sonogashira reaction. After examining various palladium complexes and a range of bases, all the reactions were performed in the presence of a catalytic amount of the palladium complex [$Pd(PPh_3)Cl_2$] and CuI at 70 °C under an inert atmosphere. We demonstrate here the attachment of three different alkyne groups, starting from propargyl alcohol to the longer chain 5-hexyn-1-ol, and the mono-silyl protected trimethylsilylacetylene. All these molecules were easily purified by column chromatography to isolate the products in very good yield



Scheme 2. Exploitation of two different mono-functional groups present at the 4th position of the macrocycle's pyridine (a) Demonstration of C-C coupling (Sonogashira) with different substrates in the first step, followed by the reduction of non-aromatic unsaturated bonds (7a, 7b) and deprotection of silyl group (7c). (b) Demonstration of nucleophilic substitution reactions.

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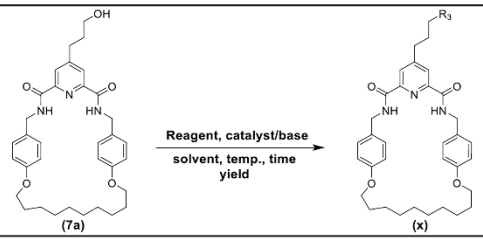
(Scheme 2, **6a**, **6b**, **6c**). The alkyne triple bond and the isolated double bond of the macrocycle (Scheme 2, **6a**, **6b**) were reduced by the traditional palladium on charcoal method in a hydrogen atmosphere, in a 1:1 ratio of tetrahydrofuran and methanol, to yield compounds **7a** and **7b**. The silyl protection of compound **6c** was easily removed with the help of potassium fluoride to produce compound **7c** (Scheme 2a).

From intermediate **5a**, compound **8a,** which is a double macrocycle, and compound **8b**, a derivative containing a six-carbon chain terminated by an acetylene group have been produced (Scheme 2b). The double macrocycle **8a** can be employed as a direct cross-linker for the preparation of 3-dimensional polyrotaxane networks (see below). On the other hand, compound **8b** can be utilised for transition metal-mediated C-C cross-couplings or as a suitable component for the CuAAC click reaction. Compound **8a** was produced by connecting two molecules of **5a** by a small triethylene glycol linker which was activated by a tosyl group at both ends. The reaction proceeded with 2:1 ratio of **5a** and tosylated triethylene glycol in dimethylacetamide (DMA) at 90 °C, aided by one equivalent of potassium carbonate, to obtain **8a** in good yield after column chromatography. In a similar way, compound **8b** was formed through the substitution reaction between the commercially available 6-iodo-1-hexyne and compound **5a**, promoted by potassium carbonate as a base at 90 °C in DMA.

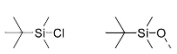
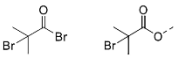
Compound **7a** was selected for further derivatisation to yield a diverse range of useful functionalities on the macrocycle (Table 1). The hydroxyl function of **7a** was activated with mesyl chloride or tosyl chloride to produce compounds **7a-1** and **7a-2,** respectively. The mesyl and tosyl intermediates can be further used for reaction with various nucleophiles. For example, compound **7a-1** was treated with lithium bromide in acetonitrile at 80 °C to give compound **7a-6** in 93% yield. Similarly, compound **7a-2** was used to illustrate the replacement of the tosyl group by an azide to afford compound **7a-7** in excellent yield. This compound could be further exploited for the CuAAC click reaction, which has been reported as a useful tool to develop various interlocked systems and networks,[45] or converted to a primary amine by the Staudinger reaction for example.

Incorporation of interlocked architectures or coordinating macrocycles in polymer-based materials can yield materials with unique or improved physical and chemical properties as discussed earlier. However, there are few reports where interlocked architectures are used in conjunction with polymers synthesised by controlled radical polymerisation.[32,46-49] Controlled radical polymerisations are useful tools to obtain polymers of variable architectures (linear, star, branched, block copolymers…) with narrow molar mass distribution in a broad range of molar masses. Hence, controlled radical polymerisation can also provide an interesting way to incorporate mechanically interlocked systems in polymers. Therefore, intermediate **7a** was reacted with α-bromoisobutyryl bromide in the presence of Et_3N to afford compound **7a-5** which could be used as an initiator to generate a range of polymers by Atom Transfer Radical Polymerization (ATRP)[50] or Single Electron Transfer- Living Radical Polymerization (SET-LRP)[51]. Alternatively, to obtain a macrocycle able to participate as a monomer in radical polymerisation, macrocycle **7a-4**, bearing an acrylate group, was produced by the reaction of acryloyl chloride with compound **7a**. This acrylate functionalised macrocycle could be an interesting constituent for the development of various side-chain polyrotaxanes, or slide-ring networks generated by radical polymerisation. Moreover, the acrylate functional group could also be further exploited for a palladium-catalysed Heck reaction or a Michael addition. Finally, it is worth mentioning that the hydroxyl group of **7a** could be oxidised to attain groups such as an aldehyde or a carboxylic acid to exploit reactions such as Wittig or amide formation.

Table 1. Synthesis of diverse functional groups as derivatives of the macrocycle (**7a**)[a]



(7a) (x)

Comp.(x)	Reagent	R_3	Cat./ Base	Solvent	Temp. (°C)	Time (h)	Yield(%)[b]
7a-1			Et_3N	DCM	25	16	96
7a-2			Et_3N	DCM	25	24	94[c]
7a-3			Et_3N	DCM	25	16	96[d]
7a-4			Et_3N	DCM	25	6	94
7a-5			Et_3N	DCM	25	4	90
7a-6 From 7a-1	LiBr	---Br	-	CH_3CN	80	6	93[e]
7a-7 From 7a-2	NaN_3	---N_3	-	DMA	40	24	92[f]

[a]All the reactions were performed using **7a** (0.1 mmol), Reagent (0.3 mmol) and triethylamine (0.6 mmol) under inert atmosphere unless otherwise stated. [b]Isolated yield, [c]TsCl (0.8 mmol) and triethylamine (1.2 mmol), [d]TBDMSCl (0.15 mmol) and imidazole (0.15 mmol), [e]LiBr (1.0 mmol), [f]NaN_3 (1.0 mmol) were used.

As mentioned earlier, these macrocycles have the ability to act as a tridentate ligand and can form a square planar palladium complex with a complementary monodentate ligand such as pyridine. These palladium-based macrocyclic complexes can be, for example, integrated in different types of polymers to form mechanically interlocked polymers. In order to have access to different polymerisation mechanisms, two different pyridine derivatives were used as monodentate ligands to form various Pd-complexes (Scheme 3). These palladium complexes could be considered as pseudorotaxanes because the pyridine derivative

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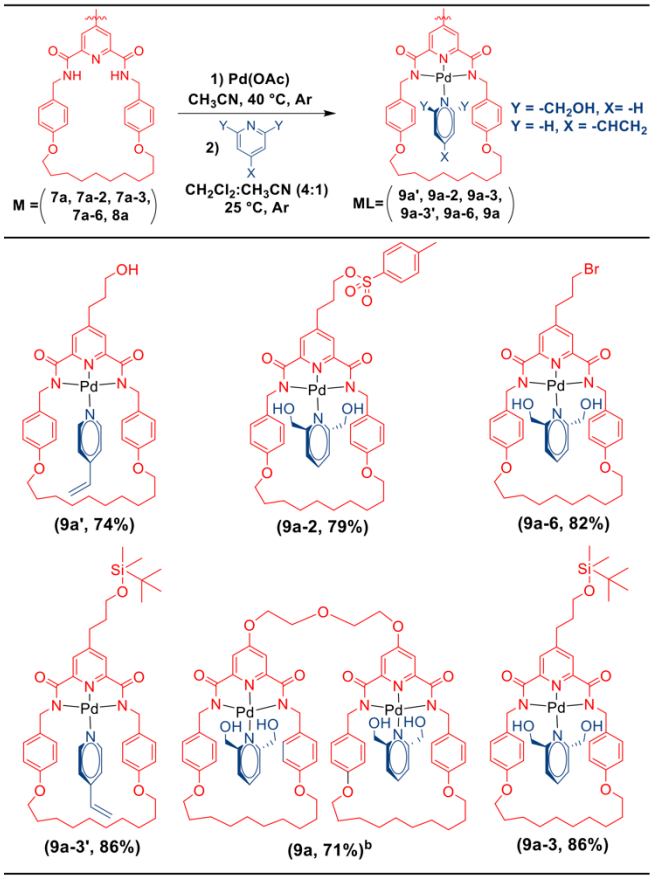
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present in the cavity of the macrocycle can be seen as a small axle. 4-vinylpyridine gives us access to radical polymerisation, while 2,6-pyridinedimethanol gives us access to polyaddition or polycondensation. A pseudorotaxane containing a 4-vinyl pyridine has been reported previously, and it was shown that the vinyl bond of the pyridine is indeed accessible for radical polymerization.[35-37] The threading of the macrocycle onto the pyridine axles is clearly evidenced by ^{1}H NMR (see ESI). Indeed, the aromatic protons of the 2,6-substituted pyridine axles experience a deshielding effect while the protons of the two benzylic rings of the macrocycle experience a strong shielding, indicating that the axle is located in the cavity of the macrocycle. Moreover, the –CH_2– groups attached to the 2 and 6 positions of the pyridine experience a strong shielding effect. For the vinyl pyridine axle, the protons of the benzylic rings of the macrocycle also experience a shielding effect. These typical signatures of the threading have been previously reported for similar (pseudo)rotaxanes.[31,34,52] In the following, selected examples of polymers containing mechanical link(s) obtained by controlled radical polymerization and polyaddition are reported to illustrate the usefulness of this family of macrocycles.

Synthesis of macro-pseudorotaxane

Different research groups have investigated the incorporation of a rotaxane junction in polymers.[46,49,53,54] The mechanical bond of the rotaxane junction potentially allows the controlled large motion of the ring along the polymer thread, which leads to a change in the relative position of the ring with respect to the long polymeric axle. This motion of the ring can change the shape of the rotaxane containing polymer and may significantly modify rheological, mechanical, dynamic and thermal properties of the polymers.[32,46,47,53,54] Thus, an example of the synthesis of a polymer containing a rotaxane junction is demonstrated in this work. This macro-pseudorotaxane (Scheme 4) was prepared from pseudorotaxane **9b-1** bearing an ATRP/SET-LRP initiator group both on the macrocycle and at the end of the axle. Here also, the pseudorotaxane structure of **9b-1** is clearly confirmed by ^{1}H NMR. As discussed above, the aromatic protons and the –CH_2– protons of the pyridine axle are respectively deshielded and shielded when in the cavity of the macrocycle (see ESI). This behaviour is very similar to the one of a [2]rotaxane reported by Leigh et al.[34] Another very typical behaviour is the conversion of the two benzylic peaks of the macrocycle into a significantly shielded (≈1 ppm) multiplet in the 3+1 palladium interlocked complex.[31,34]

The dual initiator **9b-1** can thus be used to efficiently grow polymer chains of different nature by controlled radical polymerisation simultaneously on the macrocycle and on the axle. To exemplify this, a macro-pseudorotaxane based on methyl acrylate was synthesised by SET-LRP. This polymerisation method was chosen because it proceeds at room temperature, insuring thereby to keep the integrity of the pseudorotaxane dual initiator **9b-1** during polymerisation.

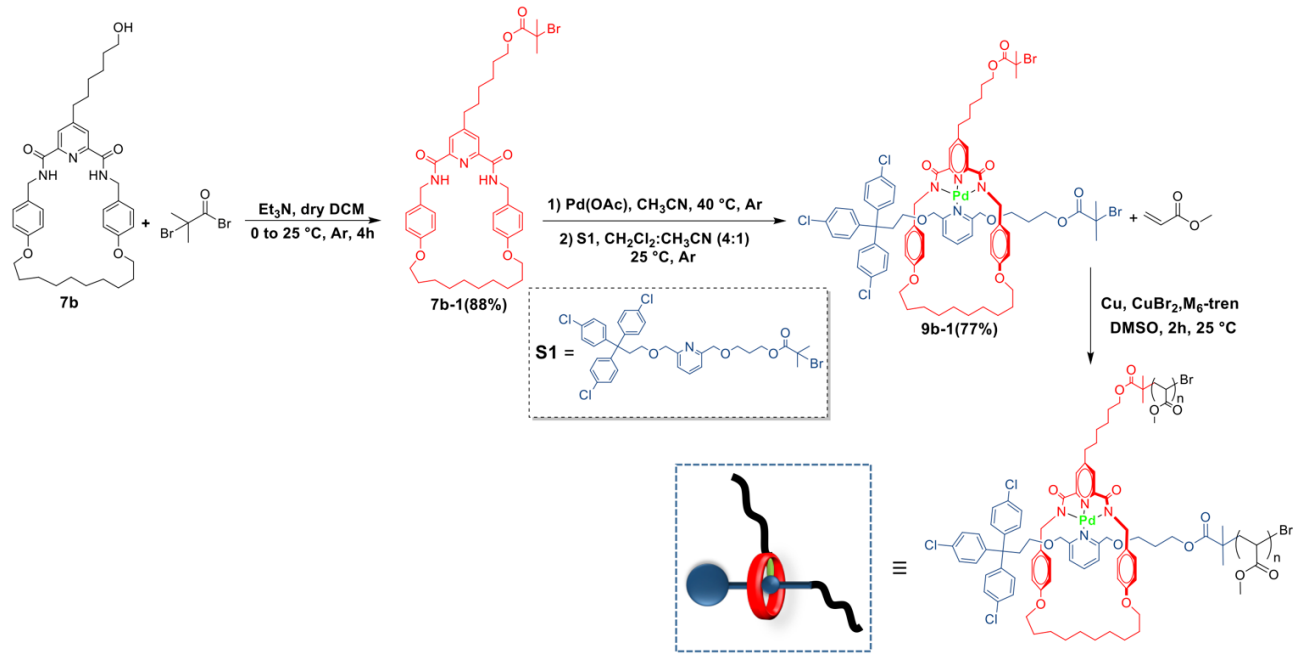


Scheme 3. Scope of different pseudorotaxanes from different macrocycles. [a]All the reactions were performed using M (0.1 mmol), $Pd(OAc)_2$ (0.11 mmol) and pyridine derivatives (0.1 mmol) in a minimum amount of solvent for 16h in the first step and 24h in the second step; Overall isolated yield after column chromatography; [b]A mixture of THF and CH_3CN in 1:3 ratio was used as the solvent in the first step.

The synthesis of the macro-pseudorotaxane is shown in Scheme 4, which started with intermediate **7b**. Compound **7b** was reacted with α-bromoisobutyryl bromide in presence of Et_3N to afford compound **7b-1** which was further treated with $Pd(OAc)_2$ in acetonitrile at 40 °C to produce the square planar palladium complex. The pyridine of axle **S1** (see ESI) then replaced the weak acetonitrile ligand in a 4:1 mixture of dichloromethane and acetonitrile to obtain the pseudorotaxane **9b-1**. The SET-LRP reaction was performed for 2 hours in the presence of Cu(0), $CuBr_2$ and M_6-TREN (Tris[2-(dimethylamino)ethyl]amine) in DMSO at 25 °C under inert conditions to grow the two poly(methyl acrylate) chains to obtain the macro-pseudorotaxane. Size exclusion chromatography (SEC) revealed that a well-defined macro-pseudorotaxane was obtained with a number averaged molar mass of 21000 g/mol and a molar mass dispersity of 1.1.

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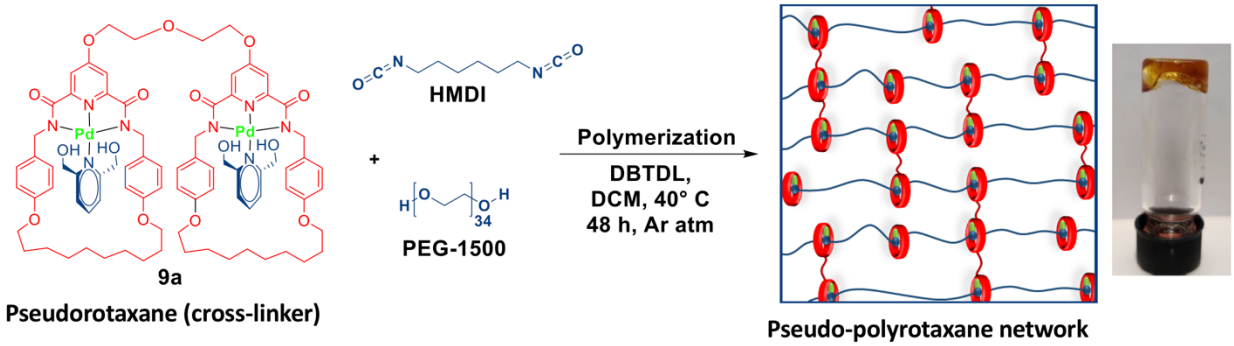


Scheme 4. Synthesis of a macro-pseudorotaxane by controlled radical polymerisation (SET-LRP).

Synthesis of the interlocked networks

To further demonstrate the possibilities of application of the macrocycles and pseudorotaxanes, two different interlocked network systems have also been prepared by two different strategies. The first network (gel) was synthesised by a direct one-pot approach by using the double macrocycle bis-pseudorotaxane **9a** (Scheme 5) as a cross-linker. This pseudorotaxane indeed bears four alcohol groups that can be exploited in a polyaddition approach with a diisocyanate to prepare polyurethanes. Hexamethylene diisocyanate (HMDI) and a poly(ethylene glycol) spacer with a Mn of 1500 g/mol (PEG-1500) were used to this effect. The reaction was performed under mild conditions in dry dichloromethane with a catalytic amount of dibutyltin dilaurate under inert atmosphere. The respective amounts of the three building blocks were 0.2 eq. of bis-pseudorotaxane, 0.6 eq. of PEG-1500, and 1 eq. of HMDI, to respect the balance between OH and isocyanate groups. The reaction between the difunctional PEG and HMDI leads to linear chains while the tetrafunctional bis-pseudorotaxane will induce cross-linking, giving the network as shown in Scheme 5. The obtained one-pot gel can swell in the presence of solvents. However, on excessive dilution, the gel swells to its maximum extent and then slowly turns into a solution. This process indicates that the rings started to move due to internal tensions (sufficiently large to break the Pd complexes) caused by the large swelling, and then started to unthread because stoppers are not present at the chain-ends to prevent their unthreading. This leads to a loss of cross-links, and finally to a dissolution of the polymer chains when a sufficient number of cross-links has been lost. This gel-sol transition induced by swelling is typical of physical gels based on non-covalent interactions, as it is indeed the case here.[55,56]

The second approach is termed the polyrotaxane approach because in this case, a polyrotaxane is first synthesised and then cross-linked to produce the three-dimensional network (Scheme 6). In this case as well, we used polyurethane chemistry with the same chain extenders, i.e., PEG-1500 and HMDI, to produce the polymer chains. The average concentration of rings in each polyrotaxane can be controlled simply by changing the amount of pseudorotaxane **9a-**

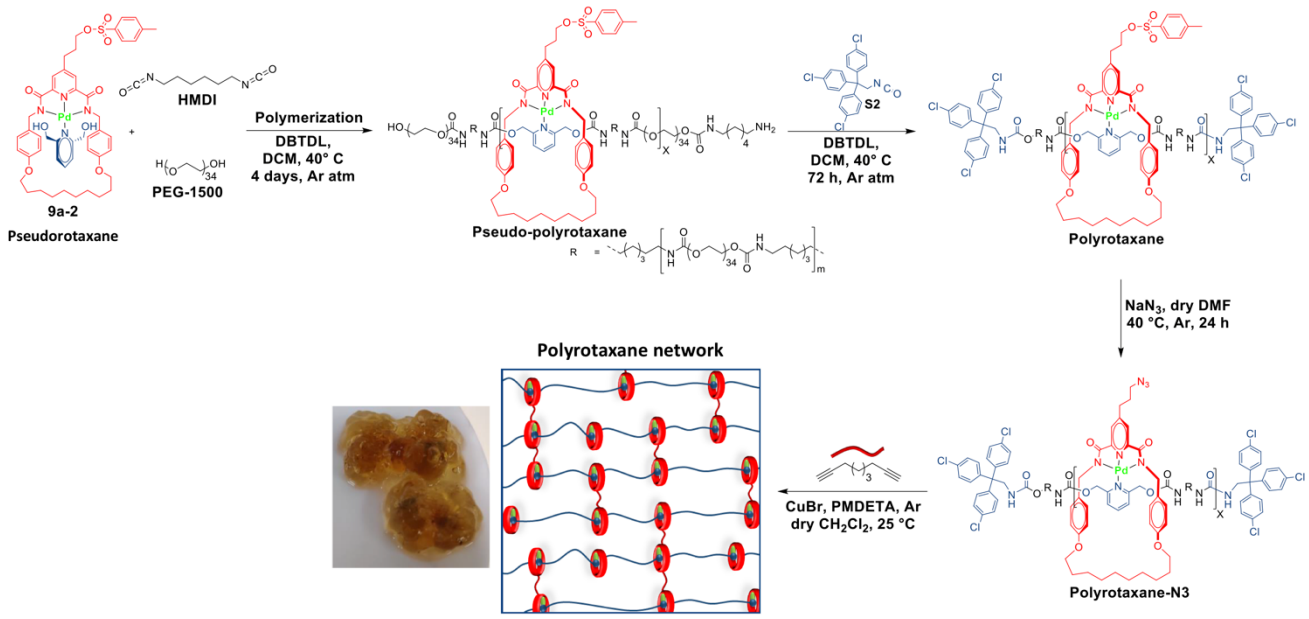


Scheme 5. Synthesis of a one-pot pseudo-polyrotaxane network.

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Scheme 6. Synthesis of the polyrotaxane network. The picture shows the gel swollen to equilibrium in DCM.

2 at the beginning of the reaction. However, the positioning and spacing between the rings are completely random due to the random incorporation of the PEG spacer and pseudorotaxane during polymerisation. The reaction was performed in dry dichloromethane under an inert atmosphere in the presence of a catalytic amount of dibutyltin dilaurate (Scheme 6). The reaction was quenched with a 2:8 mixture of water/acetone to convert all the isocyanate chain-ends to primary amines. The polypseudorotaxane was then purified by precipitation in 30% ethyl acetate/hexane mixture, and treated with an excess of isocyanate functionalised bulky stopper **S2** (see ESI) to achieve the desired polyrotaxane. By using this process, we synthesised a polyrotaxane having 0.4 eq. pseudorotaxanes and 0.6 eq. of PEG-1500 with respect to the 1 eq. of HMDI. The molar mass of the obtained polyrotaxane was approximately 21000 g/mol (Mn) with a molar mass dispersity of 1.9 as determined by SEC using a PEG calibration, in good agreement with the molar mass determined by ^{1}H-NMR (26000 g/mol).

All the tosyl groups on the macrocycles were then substituted by azide functions by treating the polyrotaxane with an excess of sodium azide in DMF at 40 °C, which was confirmed by infrared spectroscopy. This azide substituted polyrotaxane was then cross-linked by the CuAAC click reaction, using an aliphatic dialkyne as cross-linker and a copper complex as catalyst, to produce a three-dimensional interlocked network (Scheme 6). The obtained gel was cleaned by swelling it for a few hours in dichloromethane to remove possible free chains, and was then transferred to a saturated EDTA solution in 1:1 water/methanol for 24 hours. This yellowish-brown material was kept in water for 24 hours to remove the EDTA, transferred to methanol for a few hours, and finally transferred to dichloromethane. With this approach, we obtained a stable gel as confirmed by the fact that it can resist swelling for several days in a large amount of dichloromethane and various other solvents. This stability is due to the presence of the bulky stoppers at the polymer chain-ends, which prevent the unthreading of the rings and preserve the network stability. Preliminary rheological characterizations of the one-pot and polyrotaxane gels have been performed, and clearly confirmed their cross-linked nature. The elastic modulus G' is indeed well above the loss modulus G'', and shows no evolution over the investigated frequency range (see Figures S1 in ESI).

Conclusions

In this work, we have reported on the synthesis of a number of tridentate macrocycles bearing different functional groups which could be useful for the development of various molecular or macromolecular interlocked systems based on the palladium template 3+1 approach. Many well-known organic synthetic methods such as electrophilic or nucleophilic substitution, Copper catalysed azide-alkyne cycloaddition, metal catalysed C-C bond formation, radical polymerisation and so on could be used to further derivatize these macrocycles or incorporate them into polymeric materials. To illustrate the potential of this family of macrocycles a series of palladium-based pseudorotaxanes, containing different axles and functional groups on the ring, were synthesised and some were used to prepare mechanically interlocked polymers and networks. In this way, a macro-pseudorotaxane, i.e., a polymer containing a rotaxane junction, was prepared by using controlled radical polymerisation from a pseudorotaxane dual initiator, and 3D mechanically linked gels were prepared by a one-pot and a polyrotaxane approach.

This work does not claim to be comprehensive, but aims at illustrating the potential and robustness of mechanical links exploiting the palladium template 3+1 approach based on a tridentate macrocycle, especially for the less-explored polymer material field. We hope that the examples shown here can stimulate

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other studies to further expand the potential of this family of macrocycles.

Conflicts of interest

There are no conflicts to declare

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