Self-organization of rod–coil *tri*- and *tetra*-arm star metallo-supramolecular block copolymers in selective solvents†

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Rod–coil *tri*- and *tetra*-arm star metallo-supramolecular block copolymers have been synthesized by *bis*-complex formation between a ω-terpyridine ruthenium(II) *mono*-complex poly(ethylene glycol) (PEG) and either a *tris*-terpyridine or a *tetra*-terpyridine functionalized conjugated rigid core. This leads to amphiphilic star copolymers in which the *tris*-terpyridine or the *tetra*-terpyridine rigid core can be considered as hydrophobic central block and the complexed PEG blocks as hydrophilic segments. The self-assembly of these two metallo-supramolecular star block copolymers has been investigated by dynamic and static light scattering as well as by cryo-transmission electron microscopy in acetone and acetone/water mixtures.

Introduction

Rod–coil block copolymers are of special interest considering self-assembly either in bulk or in selective solvents. Indeed, it has been demonstrated that the conformational rigidity of the rigid block results in an increase of the Flory–Huggins parameter in comparison with coil–coil copolymers.[1] As a result, phase-separated structures can be observed at lower molar mass for rod–coil copolymers than for coil–coil ones.[2] Moreover, in such systems, the aggregation of the rigid segments into (liquid-)crystalline domains competes with the phase-separation between the blocks during the self-assembly process, eventually leading to very complex morphologies in the bulk.[3] Rod–coil block copolymers have thus been considered as valuable precursors for micelles with peculiar morphologies. Rod-like blocks generally consist in either helical structures like polypeptides,[4] polyisocyanates,[5] polyisocyanides,[6] and polycarbodiimides,[7] or π-conjugated polymers such as poly(*p*-phenylene)s,[8,9] poly(thiophene)s,[10] and poly(phenylquinoline)s.[11] Selected examples include the combination of an α-helical polypeptide block with a second coil-forming polymer block, as illustrated by *e.g.* the work of Lecommandoux and coworkers who prepared pH-sensitive vesicles from a poly(butadiene)-*block*-poly(glutamic acid) copolymer,[12] and by Klok *et al.* who studied the aggregation in PEG-polypeptide block copolymers.[13] As far as π-conjugated polymers are concerned, selected examples can be found in the work of Jenekhe and Chen who prepared poly(phenylquinoline)-*block*-polystyrene copolymers that form spherical and tubular aggregates with a large hollow cavity,[11] and of Müllen and coworkers who prepared micrometer-long fibrils consisting of nanophase separated ribbons of poly(*p*-phenyleneethynylene)-*block*-poly(dimethylsiloxane) oligomers.[14] Also relevant to this field is the work of Stupp and coworkers who synthesized a "miniaturized" triblock terpolymer containing polystyrene and polyisoprene oligomeric blocks linked to a third rod-like block formed by biphenyl esters and ended by a phenolic residue.[15] Interestingly, these copolymers self-assemble into non-centrosymmetric nanostructures highly regular in size and shape. These nanostructures are characterized by a mushroom shape which is thought to result from the frustrated crystallization of the rod blocks. Hockey-puck micelles have been reported by Kilbinger and coworkers from oligo(*p*-benzamide)-*block*-PEG copolymers in which strong directional hydrogen bonds were responsible for the formation of well-defined supramolecular structures.[16] In most of these examples, the rigid rod block is not strictly speaking a polymer but rather an oligomer that is further combined with a flexible polymer block. Nevertheless, the accordingly formed rod–coil macromolecules are coined block copolymers.

All these observations motivated us to combine our metallo-supramolecular block copolymer concept[17] with rod–coil architectures. Metallo-supramolecular block copolymers are block copolymers in which metal–ligand complexes have been introduced in well-defined locations of the macromolecular chain, *e.g.* in one of the blocks[18] or at the junction between the blocks.[19,20] Such metallo-supramolecular block copolymers have been further dissolved in a selective solvent for one of the blocks giving rise to micellar structures in which metal–ligand complexes are located in the micellar core,[18,21] in the micellar corona[22] or at the core-corona interface[23–25] depending on the used metallo-supramolecular block copolymers. Further details on metallo-supramolecular block copolymers and associated micelles can be found in recent reviews.[26,27] In the following, we will focus on

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metallo-supramolecular block copolymers in which the metal–ligand is located at the block junction.

Very recently, we reported on the synthesis and aggregation behavior in water of coil-rod–coil ABA triblock copolymers containing PEG as hydrophilic A block and different conjugated rod-like ditopic terpyridyl ligands as hydrophobic B segment, linked to A *via bis*-terpyridine ruthenium(II) complexes.[28] The self-assembly of these materials was studied in water by cryo-transmission electron microscopy and dynamic light scattering, demonstrating a significant influence of the various middle B segments on the size of the obtained micelles. In the current paper, we report on the synthesis of a *tris*-terpyridine and a *tetra*-terpyridine functionalized conjugated rigid cores as hydrophobic central blocks, which are linked to PEG hydrophilic arms *via bis*-terpyridine ruthenium(II) complexes. The self-assembly of the resulting star like rod–coil metallo-supramolecular block copolymers is investigated in detail in acetone and acetone/water mixtures.

Materials and methods

All chemicals were of reagent grade and used as received unless otherwise specified. $AgSbF_6$ was purchased from Aldrich. $Ru(DMSO)_4Cl_2$ was prepared according to literature procedures.[29] The *mono*-terpyridine PEG_{44} **1**, the *mono*-complex PEG_{44}-[$RuCl_2$(DMSO) **2** and the model complex PEG_{44}-[Ru]-PEG_{44} **3** were synthesized and characterized as described in a previous study.[28] Moreover, the preparation and full characterization of the *tris*-terpyridine **4** and *tetra*-terpyridine **6** functionalized rigid cores is described elsewhere.[30] Preparative size-exclusion chromatography was performed on BioBeads S-X1 columns using acetone as eluent.

Instrumentation

Size-exclusion chromatograms (SEC) were measured on a Waters SEC system consisting of an isocratic pump, a solvent degasser, a column oven, a 2996 photodiode array (PDA) detector, a 2414 refractive index detector, a 717 plus autosampler, and a Waters Styragel HT 4 GPC column (with 10 μm particles) with a precolumn installed. The eluent was *N*,*N*-dimethylformamide (DMF) containing 5 mM NH_4PF_6 as additive at a flow rate of 0.5 mL/min. Linear poly(ethylene glycol) with a narrow polydispersity and with a M_w range from 970 to 40 000 Da were used as standards. The column temperature was set to 323 K. Nuclear magnetic resonance spectra were recorded on a Varian Gemini 400 MHz spectrometer at 298 K. Chemical shifts are reported in parts per million (δ) downfield from an internal standard, tetramethylsilane (TMS) in CD_3CN. UV-vis spectra were recorded on a Perkin-Elmer Lamda-45 (1 cm cuvettes, CH_3CN or CH_2Cl_2).

Synthesis of the tri-arm star block copolymer 5

A suspension of the *mono*-complex PEG_{44}-[$RuCl_2$(DMSO) **2** (3 eq.) and $AgSbF_6$ (4 eq.) was refluxed overnight in acetone, followed by filtration of the formed AgCl. The PEG_{44}-[Ru(II)(DMSO)-$(OCMe_2)_2]^{2+}(SbF_6^-)_2$ solution was then added to a solution of the *tris*-terpyridine ligand **4** (1 eq., 0.03 mmol) in acetone. The reaction mixture was heated under reflux for 48 h. After cooling to ambient temperature, the reaction mixture was filtered through Celite and subsequently purified by preparative size exclusion chromatography (BioBeads SX-1, acetone). Three fractions were isolated that correspond to the totally complexed arms of the *tris*-terpyridine ligand **4** namely *tris*-(**5F1**) and to the partially complexed ligand **4** namely *bis*-(**5F2**) and *mono*-(**5F3**) adducts, respectively.

5F1 (fraction 1): Yield: 15%. ^{1}H-NMR (400 MHz, CD_3CN, 298 K): δ (ppm) = 9.07 (s, 6H; $H_{3'}$, $H_{5'}$), 8.70 (m, 12H; H_3, $H_{3''}$), 8.55 (m, 12H; H_4, $H_{4''}$), 8.41 (m, 6H; $H_{3'}$, $H_{5'}$), 8.38 (m, 6H; H_{aryl}), 8.27 (m, 6H; H_{aryl}), 8.09 (m, 3H; H_{olefin}), 7.9 (m, 24H; H_5, $H_{5''}$, H_6, $H_{6''}$), 7.46 (m, 2H; H_{aryl}), 7.41 (m, 4H; H_{olefin}), 7.20 (m, 4H; H_{aryl}), 7.16 (m, 4H; H_{aryl}), 4.73 (m, 6H), 4.14 (m, 6H; H_{alkyl}), 3.96 − 3.19 (m, 550H; $H_{PEG\text{-}backbone}$), 1.78 (m, 12H; H_{aryl}), 1.56 (m, 12H; H_{alkyl}), 1.29 (m, 48H; H_{alkyl}), 0.89 (m, 24 H; H_{alkyl}). UV-Vis (CH_3CN): λ_{max}: 272, 305, 405, 497.

Synthesis of the tetra-arm star block copolymer 7

Analog to **5** using the following: 4 eq. PEG_{44}-$RuCl_2$(DMSO), 5 eq. $AgSbF_6$ and 1 eq. *tetra*-terpyridine ligand **6**. Final purification was performed by preparative size exclusion chromatography (BioBeads SX-1, acetone). Yield: 28%. ^{1}H-NMR (400 MHz, CD_3CN, 298 K): δ (ppm) = 9.07 (s, 8H; $H_{3'}$, $H_{5'}$), 8.69 (m, 16H; H_3, $H_{3''}$), 8.52 (m, 16H; H_4, $H_{4''}$), 8.43 (m, 8H; $H_{3'}$, $H_{5'}$), 8.39 (m, 8H; H_{aryl}), 8.28 (m, 8H; H_{aryl}), 8.09 (m, 4H; H_{olefin}), 7.9 (m, 32H; H_5, $H_{5''}$, H_6, $H_{6''}$), 7.46 (m, 2H; H_{aryl}), 7.41 (m, 4H; H_{olefin}), 7.20 (m, 4H; H_{aryl}), 7.16 (m, 4H; H_{aryl}), 4.73 (m, 8H), 4.07 (m, 8H), 4.44 − 3.57 (m, 730H; $H_{PEG\text{-}backbone}$), 1.78 (m, 16H; H_{aryl}), 1.56 (m, 16H; H_{alkyl}), 1.29 (m, 64H; H_{alkyl}), 0.89 (m, 24H; H_{alkyl}). UV-Vis (CH_3CN): λ_{max}: 273, 305, 496.

Micelle formation

The *tri*- and *tetra*-arm star metallo-supramolecular block copolymers were directly dissolved in acetone at room temperature. The obtained solutions were filtrated through a 0.2 μm syringe filter. Known amounts of distilled water (5 and 10 vol%) were further added to the acetone solutions.

Dynamic light scattering

The hydrodynamic radius, R_h, of the micellar structures were measured by dynamic light scattering (DLS). The experimental autocorrelation function, $g(t)$, is commonly expressed in the form of a cumulant expansion:

$$g(t) = \exp\left[-\Gamma_1 t + \left(\frac{\Gamma_2}{2!}\right)t^2 - \left(\frac{\Gamma_3}{3!}\right)t^3 + \ldots \right]$$

where Γ_i is the ith cumulant, and $\Gamma_1 = Dq^2$ where D is the translational diffusion coefficient and q is the absolute value of the scattering vector. The diffusion coefficient is related to the hydrodynamic radius R_h by the Stokes–Einstein equation:

$$R_h = \frac{k_B T}{6\pi\eta D}$$

where k_B is the Boltzmann constant and η the viscosity of the solvent.

DLS measurements were performed on a Malvern CGS-3 apparatus equipped with a He–Ne laser with a wavelength of

632.8 nm. The temperature was controlled at 25 °C, and the measurements were done at various angles. DLS results were analyzed by the cumulant method, while size distribution histograms were obtained by the CONTIN method. The polydispersity index (PDI) of the micelles was estimated from the Γ_2/Γ_1^2 ratio in which Γ_1 and Γ_2 represent the first and second cumulant, respectively.

SLS was performed in acetone with concentrations ranging from 0.2 to 1.6 g/L. The analysis of the scattering intensities using a Zimm plot yields the weight averaged molar mass, $M_{w,app}$, and the *z*-averaged radius of gyration, R_g. An estimation of the aggregation number of the micelle, N_{agg}, is obtained by dividing the apparent molar mass of the micelle by the molar mass of the corresponding block copolymer. The variation of the index of refraction *n* as a function of the polymer concentration, d*n*/d*c*, was experimentally measured with a Mettler-Toledo RE40D refractometer.

Cryo-transmission electron microscopy

Cryo-TEM measurements were performed on a FEI Tecnai 20, type Sphera TEM operating at 200 kV (LaB6 filament). Images were recorded with a bottom mounted 1k × 1k Gatan CCD camera. A Gatan cryo-holder operating at −174 °C was used for the cryo-TEM measurements. TEM grids, both 200 mesh carbon coated copper grids and R2/2 Quantifoil Jena grids were purchased from SPI. Prior to blotting the grids were made hydrophilic by surface plasma treatment using a Cressington 208 carbon coater operating at 5 mA for 40 seconds. For conventional sample preparation 3 μL aliquots were applied to a 200 mesh carbon coated copper grid and subsequently excess liquid was quickly manually blotted away with filter paper. Cryo-TEM specimens were prepared within the environmental chamber (22 °C, relative humidity 100%) of an automated vitrification robot (FEI Vitrobot Mark III). Excess liquid was blotted away (−2 mm offset, 2 s) with filter paper within the environmental chamber of the Vitrobot. The grids were subsequently shot through a shutter into melting ethane placed just outside the environmental chamber. Vitrified specimens were stored under liquid nitrogen before imaging.

Results and discussion

In this paper, we have synthesized original amphiphilic macromolecular structures that combine either a *tri*-arm or *tetra*-arm, conjugated, rigid core with flexible PEG coil blocks. The synthesis of those structures relies on the formation of heteroleptic *bis*-terpyridine ruthenium(II) complexes between the terpyridine-functionalized rigid cores and *mono*-terpyridine functionalized PEG chains (see Fig. 1). The synthesis and characterization of the terpyridine functionalized rigid cores has been recently reported in detail and will not be discussed here.[30] A *mono*-terpyridine PEG with M_n = 2200 g/mol has been utilized as hydrophilic block. The coupling of this PEG block to the terpyridine rigid core has been achieved by using a sequential self-assembly process. The synthesis of the *tri*- and *tetra*-arm star metallo-supramolecular block copolymers can be selectively achieved by first preparing the PEG-[Ru(II) *mono*-complex, which is further reacted under the appropriate

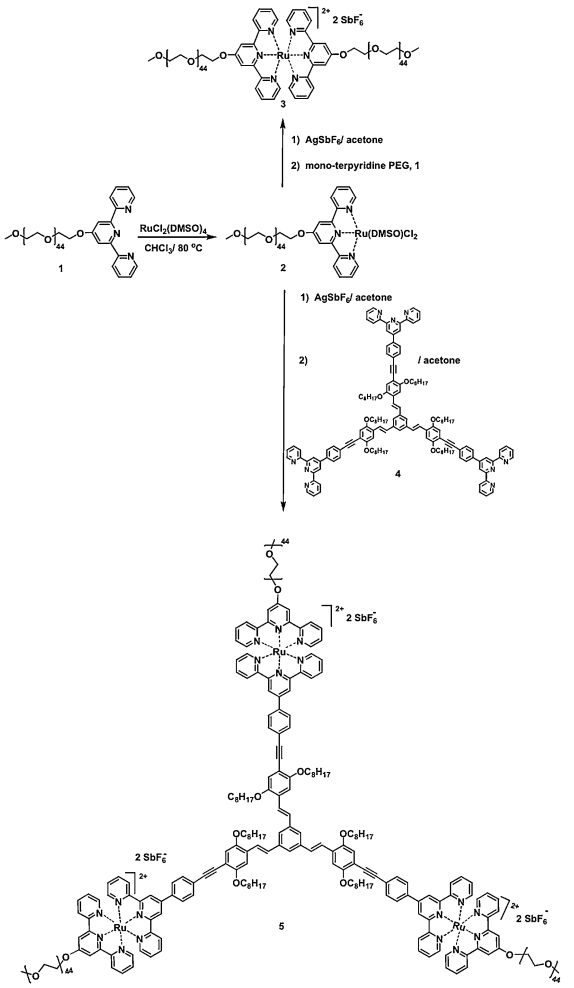

Fig. 1 Schematic representation of the synthesis of the PEG_{44}-[Ru(DMSO)Cl_2 *mono*-complex **2**, Ru(II) model complex **3** and *tri*-arm star metallo-supramolecular block copolymer **5**.

conditions with the terpyridine-functionalized rigid core to form the desired AB copolymers. The high selectivity of this two-step process was previously demonstrated.[29] Furthermore, the high stability of the *bis*-2,2′:6′,2″-terpyridine-ruthenium(II) complexes allows to keep the integrity of the block copolymers in various environments, such as organic solvents or water, which is a prerequisite for their use in micellization studies.[31]

Practically, the synthesis of the *tri*-arm star metallo-supramolecular block copolymer **5** was performed by synthesizing first a PEG-[Ru(II)Cl_2DMSO *mono*-complex **2** (see structure in Fig. 1). This *mono*-complex **2** was further activated with $AgSbF_6$ in acetone under reflux followed by the subsequent addition of the *tris*-terpyridine rigid rod core **4** (Fig. 1). The molar ratio between the PEG-[Ru(II)Cl_2DMSO **2** and the *tris*-terpyridine rigid rod core **4** was 3:1, since the rigid core has three available terpyridine units per molecule for the metallo-complexation process.

In case of the *tetra*-arm metallo-supramolecular block copolymer **7** (Fig. 2) this molar ratio was set to 4:1. Unfortunately, these complexation reactions did not yield pure *tri*-arm and

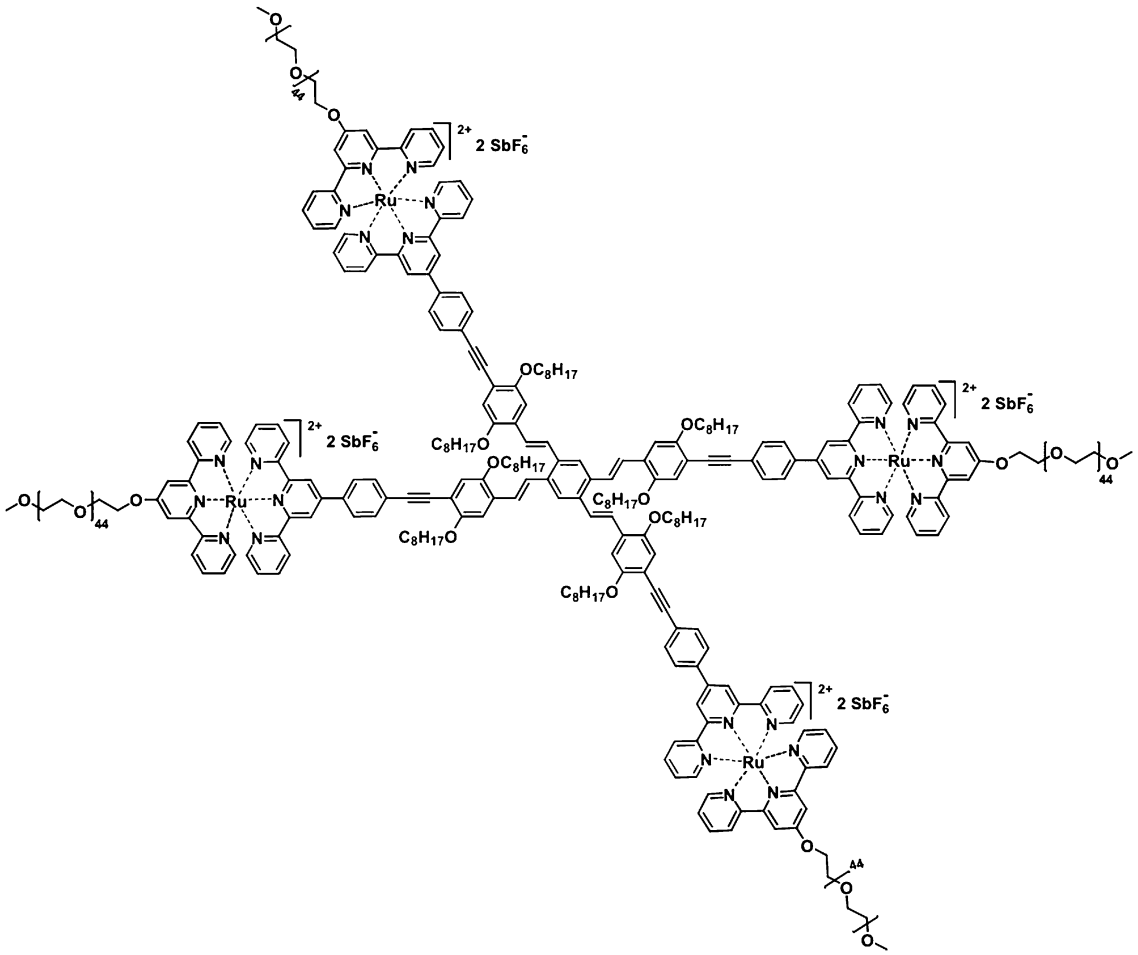

Fig. 2 Schematic representation of the *tetra*-arm star metallo-supramolecular copolymer **7**.

tetra-arm star copolymers but rather mixtures of *mono*-arm, *di*-arm, *tri*-arm and/or *tetra*-arm complexed products. Those mixtures could be successfully purified by preparative SEC using BioBeads columns (see Experimental Part) to yield the desired *tri*-arm **5F1** or *tetra*-arm star **7** copolymers. In case of the *tri*-arm copolymer **5**, the *mono*-(**5F3**) and *bis*-adducts (**5F2**) were isolated from the desired *tri*-arm star block copolymer (**5F1**) in sufficient amounts to be characterized (see ESI†). It was not possible to characterize the *mono*-, *bis*- and *tris*-adducts for the *tetra*-arm star copolymers **7** due to insufficient amounts of isolated pure materials. Sufficient amount of *tetra*-block copolymer **7** was, however, collected to allow subsequent micellization studies.

That indeed *tri*- **5F1** and *tetra*-star **7** block copolymers have been isolated at the end of these purification processes has been also ascertained by SEC (see Figs. 3 and 4; for the conditions used, see also ref. 32). The SEC traces of either the *tri*- and *tetra*-arm star block copolymers have been compared to those of the starting PEG-[Ru(II)Cl_2DMSO *mono*-complex **2** and PEG_{44}-[Ru]-PEG_{44} **3** model compound (Figs. 3 and 4). A clear shift towards higher molar masses is observed for the *tri*- and *tetra*-arm star block copolymers compared to the starting *mono*-complex **2**. Moreover, the star copolymers are not contaminated by the PEG_{44}-[Ru]-PEG_{44} *bis*-complex. In addition, the SEC traces of the two other fractions (*mono*-and *bis*-adducts) isolated after purification of the *tri*-arm star block copolymers have been also added to Fig. 3.

It is clear that fraction **5F1** has a higher molar mass and corresponds to the *tri*-arm star block copolymer (Fig. 3). Additional information about the characterization of the **5F1**, **5F2**

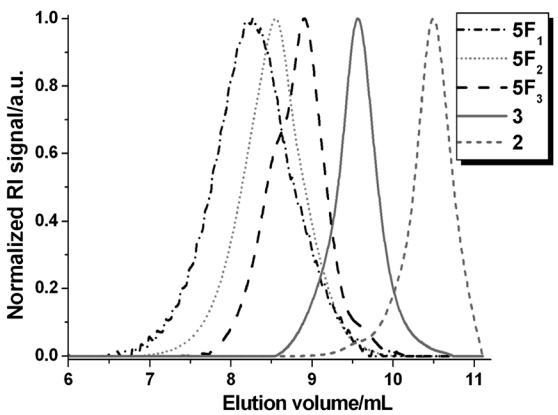

Fig. 3 Size-exclusion elution curves (RI detector) of the different fractions of the *tri*-arm star metallo-supramolecular block copolymer **5F1**, **5F2**, **5F3** in comparison to the PEG_{44}-[Ru(DMSO)Cl_2 *mono*-complex **2** and the PEG_{44}-[Ru]-PEG_{44} dimer **3**.

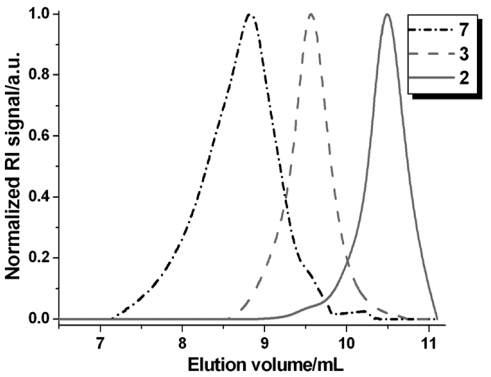

Fig. 4 Size-exclusion elution curves (RI detector) of the *tetra*-arm star metallo-supramolecular copolymer **7** in comparison to the PEG_{44}-[$Ru(DMSO)Cl_2$ *mono*-complex **2** and the PEG_{44}-[Ru]-PEG_{44} dimer **3**.

and **5F3** fractions as well as the **7** compound is available in the ESI†.

Although they contain PEG outer chains, the *tri*- **5F1** and *tetra*-arm **7** star block copolymers were not directly soluble in water. Their association behavior was thus investigated in acetone, which is a good solvent for the PEG blocks and a bad solvent for the *tri*- and *tetra*-arm cores. Different associating behavior can be anticipated. The *tri*- and *tetra*-arm star block copolymers could either behave as isolated chains, the central core of one macromolecule being stabilized by the outer PEG blocks, or different macromolecules could aggregate into micelles consisting of a core containing the *tri*-arm and *tetra*-arm surrounded by the coronal PEG chains. The morphology of such micelles is difficult to predict. One could, however, speculate about the formation of a rod-like morphology in the case of the *tri*-arm star block copolymer since the conjugated *tri*-arm central part is supposed to adopt a planar conformation, as evidenced by the extended conjugation in the the *tri*-terpyridine core **4**.[30] Planes of *tri*-arm star block copolymers could then stack to form rod-like micelles. The stacking will, however, be strongly perturbed by the presence of the charged and bulky octahedral Ru(II) *bis*-terpyridine complexes that are located at each extremity of the conjugated *tri*-arm central block. The picture is even more complicated for the *tetra*-arm star block copolymer since the conformation of the central part is expected to be not totally planar but distorted.[25] In conclusion, it seems difficult to predict the morphology of the aggregates formed by the *tri*-(**5F1**) and *tetra*-arm (**7**) star block copolymers in acetone by those simple geometrical arguments. The accordingly obtained aggregates have been therefore experimentally investigated by dynamic and static light scattering as well as cryo-TEM in order to elucidate their morphology.

Firstly, the characteristic features of the aggregates formed by the *tri*-arm star block copolymer **5F1** have been investigated by dynamic light scattering (DLS) in acetone at different concentrations (from 0.2 g/L to 1.6 g/L) and at different angles (from 50° to 130°). The apparent *z*-average diffusion coefficient, $D_z(c)$, was determined from the slope of the evolution of Γ, determined by the cumulant method, *versus* q^2 (Fig. 5, left). Fitting these data provides a clear linear correlation passing through the origin, indicating that only translational diffusion occurs. Then $D_z(c)$ was plotted against the concentration and the *z*-average diffusion

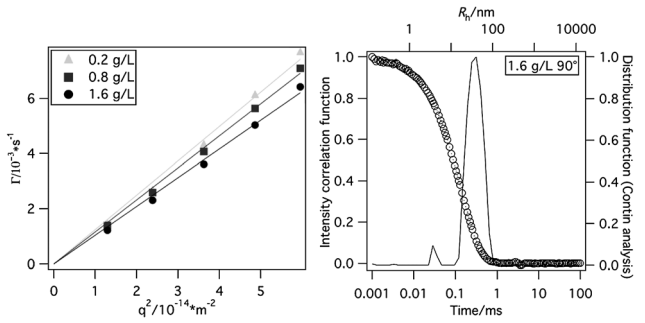

Fig. 5 Dynamic light scattering data for the aggregates formed by the *tri*-arm star metallo-supramolecular copolymer **5F1** in acetone: Dependence of the first cumulant frequency (Γ) with the square magnitude of the scattering vector (q^2) at different concentrations (left) and intensity autocorrelation functions and CONTIN analysis in acetone solution at a concentration of 1.6 g/L (right).

coefficient was determined by extrapolating $D_z(c)$ to $c = 0$. Finally, the *z*-average hydrodynamic radius R_h has been calculated from the Stokes–Einstein equation. A R_h of 52 nm was calculated. The DLS data were also analyzed using the CONTIN method to determine the size distribution. The experimental autocorrelation function $g(q,t)$ and the particle size distribution obtained by the CONTIN analysis of the DLS data are shown in Fig. 5 (right). This graph reveals a bimodal distribution. The presence of unimers in solution could be responsible for the first minor population.

In addition to DLS, static light scattering (SLS) was performed in acetone with concentrations ranging from 0.2 to 1.6 g/L. The analysis of the scattering intensities using a Zimm plot (Fig. 6) yielded a weight averaged molar mass, $M_{w;app}$, of 9.75×10^6 Da and a *z*-averaged radius of gyration, R_g, of 55 nm. By comparing this value to the previously determined R_h (52 nm), a R_g/R_h ratio of 1.06 is found, which is close to the value expected for vesicles. In fact, the R_g/R_h ratio (also called ρ-parameter) is a structure-sensitive property reflecting the radial density distribution of the scattering particle.[33] A ρ value close to 1 is characteristic of hollow spheres such as vesicles.[33] An estimation of the aggregation number of the micellar aggregates, N_{agg}, has been obtained by dividing the apparent molar mass as determined by SLS, by the molar mass of the corresponding polymer.

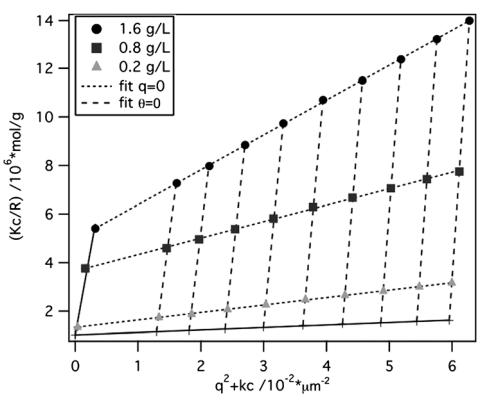

Fig. 6 Zimm plot of the *tri*-arm star metallo-supramolecular copolymer **5F1** in acetone.

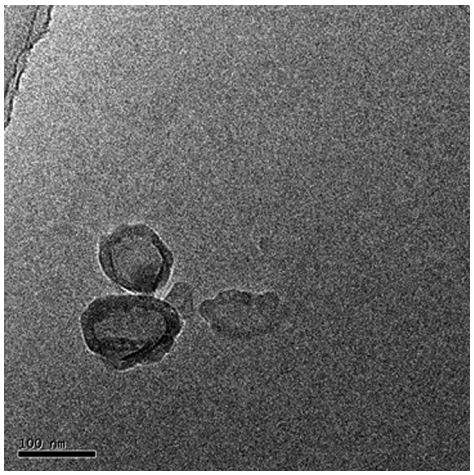

Fig. 7 Cryo-TEM picture of the aggregates formed by the *tri*-arm star metallo-supramolecular copolymer **5F1** in acetone.

A value of 970 was calculated for N_{agg}. Such a high N_{agg} value is also in agreement with the formation of vesicles.

Cryo-TEM was then performed in order to visualize the aggregates formed by the *tri*-arm-star block copolymer **5F1**. A typical cryo-TEM image is shown in Fig. 7. Vesicles are clearly seen, with a diameter close to 100 nm. However, those vesicles were damaged during cryo-TEM sample preparation from acetone solutions resulting in collapsed structures (Fig. 7).

In a recent paper, Tew and coworkers reported on the formation of vesicles with thin walls from molecules possessing a *tri*-arm structure.[34] The molecules did not self-assemble following the common bilayer structure found in vesicular walls because of steric constraints resulting from their peculiar shape. Those observations are in line with our TEM images and a packing of the *tri*-arm star block copolymer chains similar to the one previously proposed by Tew and coworkers could be proposed, in which the vesicular wall is formed by the rigid cores and both its inner and outer surfaces are decorated with the PEG blocks (Fig. 8). In a final experiment, water was added to the vesicles formed by the *tri*-arm star-block copolymer in acetone. The vesicles were found to be stable after addition of 5 wt% of water and kept the same structure as in pure acetone. Further additions of water resulted in unstable solutions.

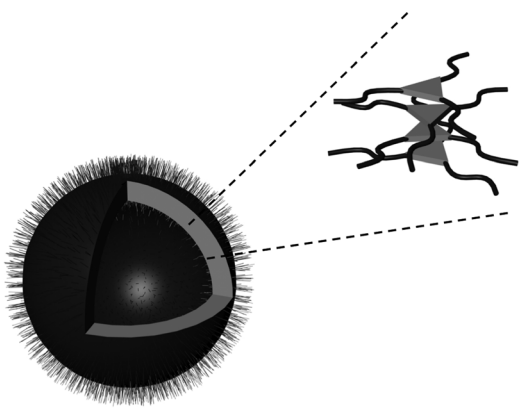

Fig. 8 Schematic representation of a vesicle formed from the *tri*-arm star metallo-supramolecular copolymer **5F1** in acetone.

In a second step, the self-assembly of the *tetra*-arm star block copolymer **7** was investigated in acetone. No scattering signal was detected for those solutions (at least for concentrations up to 2 g/L), indicating that no aggregation is taking place for this copolymer in acetone. Therefore, it can be assumed that the *tetra*-arm metallo-supramolecular block copolymers behave as isolated chains in acetone. The enhanced solubility in acetone of the *tetra*-arm block copolymer compared to the *tri*-arm counterpart could be explained by the larger fraction of PEG blocks in the *tetra*-arm. The non-planar conformation of the *tetra*-arm core could also play a role as discussed before.

In order to trigger aggregation in this system, small amounts of water (5 and 10 vol%) were added to the initial acetone solution of the *tetra*-arm star block copolymer. The addition of water should reduce the solubility of the central conjugated part of the sample and promote the formation of micellar aggregates. The sample with 5 vol% of water was investigated by DLS (Fig. 9). A well-defined intensity autocorrelation function was detected, evidencing aggregation of the *tetra*-arm star block copolymer chains. The evolution of Γ *versus* q^2 was linear and passed through the origin, indicating that only translational diffusion occurs (not shown). The CONTIN size distribution histogram (Fig. 9, left) revealed the presence of two populations, one at 15 nm and one centered around 150 nm. The first population can be attributed to the aggregates formed by the *tetra*-arm star block copolymer while the second one could result from either the presence of superaggregates or transient species in which the free *tetra*-arm star block copolymer chains are not yet compacted into aggregated structures but are rather loosely interacting in solution. If it is the case, addition of more water should result in the shrinking of these loose species into defined aggregates with a smaller size. The CONTIN size distribution histogram of the *tetra*-arm metallo-supramolecular block copolymers in acetone with 10 vol% water is shown in Fig. 9 (right). Two populations are again observed in this histogram. However, the relative intensity of the population corresponding to the smaller objects (R_h of 35 nm) is dramatically enhanced compared to the second population (R_h of 150 nm). This observation strengthens our hypothesis that the second population observed in the CONTIN histogram corresponds to loose structures that further generate the more compact aggregates assigned to the first population.

Further addition of water led to unstable solutions that were not further investigated. Because aggregates and loose aggregates are coexisting in water/acetone solutions of the *tetra*-arm star

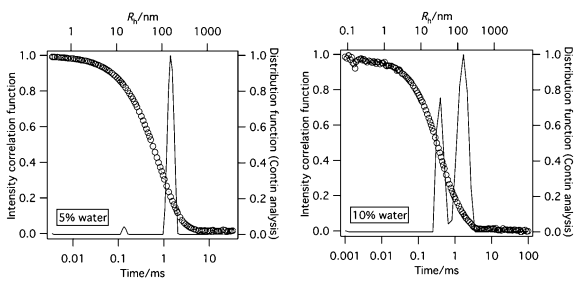

Fig. 9 Intensity autocorrelation functions and CONTIN analysis for the aggregates formed at a concentration of 1 g/L by the *tetra*-arm star metallo-supramolecular copolymer **7** in acetone/water 95:5 v/v (left) and 90:10 v/v mixtures (right).

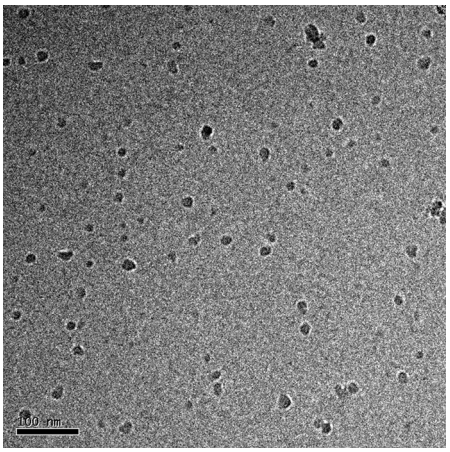

Fig. 10 Cryo-TEM picture of the aggregates formed by the *tetra*-arm star metallo-supramolecular copolymer **7** in an acetone/water 90:10 v/v mixture.

block copolymer, SLS is not an useful technique to obtain information on the aggregates corresponding to the first population since the observed signal will be a mix of both populations. However, cryo-TEM imaging could be successfully applied on the *tetra*-arm star block copolymer in a 90:10 v/v acetone/water solution (Fig. 10). Micelles with a diameter around 20 to 30 nm were observed. The shape of those micelles is ill-defined, ranging from spheres to more elongated structures. Those micelles are thought to result from the precipitation of the *tetra*-arm cores into ill-defined doamins stabilized by PEG chains. Since the measured sizes are different from the R_h corresponding to the first population measured in the CONTIN histogram, one could consider that the CONTIN algorithm could not totally resolve single micelles from aggregated micelles, as previously reported for other micellar systems.[35]

Conclusions

In this contribution, we have demonstrated that metal–ligand complexation can be successfully used to synthesize complex *tri*-arm and *tetra*-arm macromolecular architectures in which a conjugated rigid core has been coupled to flexible PEG blocks through *bis*-terpyridine ruthenium(II) complexes. Moreover, the accordingly obtained macromolecules can be seen as amphiphilic star block copolymers since the size of the central rigid cores extended by the bulky *bis*-terpyridine ruthenium complexes is not negligible compared to the low molar mass PEG segments. Although the metal–ligand complexation did not proceed quantitatively in either *tri*-arm or *tetra*-arm star block copolymers, preparative size-exclusion chromatography was successfully applied to isolate the desired products.

The associating behavior of the *tri*-arm and *tetra*-arm star block copolymers was further investigated in acetone. Formation of well-defined vesicles was observed for the *tri*-arm system in pure acetone and acetone/water 95:5 v/v mixtures. In sharp contrast, no aggregation was noted for the *tetra*-arm system in pure acetone. Addition of small amounts of water to the latter did, however, trigger the formation of spherical micelles. This different behavior is thought to be related to the higher content of the hydrophilic block in the *tetra*-arm copolymer compared to the *tri*-arm one as well as to the different conformation of the *tri*-arm core (planar) compared to the *tetra*-arm one (non-planar).

Finally, the formation of aggregated structures from those star-like systems with conjugated rigid cores characterized by interesting photophysical properties could be considered appealing synthons for the construction of functional metallo-supramolecular assemblies with potential applications, *e.g.* in optoelectronics as well as redox-responsive materials.

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