Metallo-supramolecular diblock copolymers based on heteroleptic cobalt(III) and nickel(II) *bis*-terpyridine complexes†

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Amphiphilic metallo-supramolecular diblock copolymers containing either a reversible cobalt(III) or nickel(II) heteroleptic *bis*-terpyridine complex at the junction between a polystyrene and a poly(ethylene oxide) block have been successfully prepared.

In recent years, metallo-supramolecular block copolymers, in which metal–ligand complexes are used to hold together different polymer blocks, have gained increasing interest because they combine the characteristic features of block copolymers (*e.g.* microphase separation between immiscible constituent blocks) with those of supramolecular polymers (*e.g.* reversibility and tunability of the supramolecular bonds).[1] The integrity of the block copolymer, and thus its self-assembly properties, are directly related to the supramolecular linker. The metal–ligand coordination bond is highly interesting because of the large range of interaction strength, directionality, and reversibility, accessible by tuning the ligand or the metal centre. Moreover, the presence of a metal complex in the copolymer structure may introduce additional electrochemical, photophysical, catalytic and magnetic properties.

Until now, heteroleptic *bis*(2,2′:6′,2″-terpyridine) ruthenium(II) complexes (-[Ru]-) have been essentially used as the supramolecular connection between two polymer blocks.[2] This situation results from the fact that a two-step self-assembly process is required to specifically form heteroleptic complexes, and such a requirement can be met with the ruthenium(III)/ruthenium(II) system. In this respect, ruthenium(III) chloride is first reacted with a terpyridine end-functionalized polymer block (A-[) leading to a stable A-[$RuCl_3$ *mono*-complex that can be isolated and purified.[2] In a second step, the A-[$RuCl_3$ *mono*-complex is reacted with a different terpyridine end-functionalized polymer block (B-[) under reducing conditions to allow the reduction of ruthenium(III) to ruthenium(II) and the subsequent formation of an heteroleptic A-[Ru]-B *bis*-complex. These complexes were observed to be highly stable and were able to preserve the structural integrity of the formed A-[Ru]-B metallo-supramolecular block copolymers.[3] Consequently, they were not prone to ligand exchange and it was demonstrated that harsh conditions were required to open such complexes.[4] This last point is certainly a severe limitation of A-[Ru]-B metallo-supramolecular block copolymers in the context of smart switchable materials and motivates the quest towards less stable heteroleptic complexes to be introduced in metallo-supramolecular block copolymers. A very interesting step in this direction has been recently introduced by O'Reilly and coworkers and is based on the use of palladium(II) and of the so-called SCS pincer as the metal–ligand complex bridging the two different polymer blocks.[5] In this case the reversibility of the metal–ligand complex can be more easily manipulated than in the case of -[Ru]- complexes.

We are particularly interested in the terpyridine ligand because it can bind to a large range of metal ions, giving rise to complexes with vastly different binding constant and half-life, and can moreover be rather easily functionalized, allowing its incorporation into the desired architecture.[2,6] In this contribution, we have prepared for the first time metallo-supramolecular block copolymer based on heteroleptic *bis*(2,2′:6′,2″-terpyridine) cobalt(III) and nickel(II) complexes. These complexes are stable enough to preserve the integrity of the block copolymer architecture, but are much more easily opened compared to the ruthenium(II) parent compounds, being thus better candidates for smart switchable materials. Metallo-supramolecular block copolymers based on polystyrene (PS) and poly(ethylene oxide) (PEO) have been targeted with the aim of preparing PS-[Co]-PEO and PS-[Ni]-PEO amphiphilic block copolymers (Fig. 1) that could be easily compared to the extensively characterized PS-[Ru]-PEO system.[1–4]

The terpyridine ligand was attached to the PEO_{230} block by polymer end-group modification as reported elsewhere,[7] while the PS_{240}-[block was prepared by nitroxide mediated controlled radical polymerization of styrene using a terpyridine-functionalized initiator.[8] The accordingly obtained PEO_{230}-[and PS_{240}-[blocks exhibited narrow polydispersity indices of 1.07 and 1.10, respectively. Cobalt(II) and nickel(II) chloride were selected as initial salts, and *N*,*N*-dimethylformamide (DMF) as solvent because it has been reported that these metal ions form a soluble complex in DMF, in which the metal centre is coordinated by the solvent molecules in a mainly octahedral geometry.[9] Moreover, DMF is known to be a good solvent for both PEO and PS blocks and is thus an appropriate

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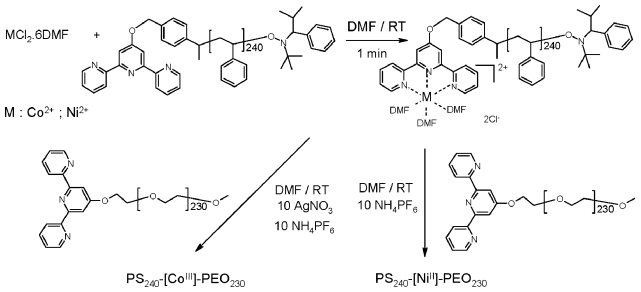

Fig. 1 Synthetic scheme towards the formation of PS_{240}-[Co]-PEO_{230} and PS_{240}-[Ni]-PEO_{230} metallo-supramolecular block copolymers (the subscript numbers represent the average degree of polymerization of each polymer block).

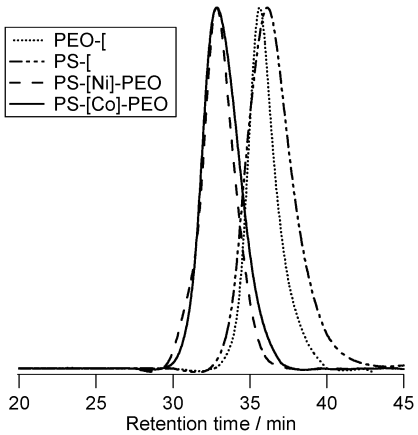

Fig. 2 SEC traces (eluent: 5 mM NH_4PF_6 in DMF, the intensities of the elution peaks have been normalized for reasons of clarity) of the metallo-supramolecular block copolymers (PS_{240}-[Co^{III}]-PEO_{230} and PS_{240}-[Ni^{II}]-PEO_{230}) and of the corresponding starting blocks (PS_{240}-[and PEO_{230}-[).

medium in which to perform the complexation reactions. As stated above, the first step towards metallo-supramolecular block copolymers consists of forming a *mono*-complex between the metal ion and one of the terpyridine-functionalized polymer blocks. In this work, the PS_{240}-[block was added to the precursor complex of cobalt(II) and nickel(II) ions in DMF to yield the PS_{240}-[Co^{II} and PS_{240}-[Ni^{II} *mono*-complexes, respectively. The PEO_{230}-[block was subsequently added *in situ* to the intermediate *mono*-complexes to form the heteroleptic PS_{240}-[Co^{II}]-PEO_{230} and PS_{240}-[Ni^{II}]-PEO_{230} *bis*-complexes (Fig. 1). The PS_{240}-[Ni^{II}]-PEO_{230} *bis*-complex exhibits a stability sufficient to maintain the integrity of the block copolymer, in agreement with previous results on *bis*-terpyridine nickel(II)-based complexes.[10] However this situation does not prevail for the PS_{240}-[Co^{II}]-PEO_{230} system because of the labile character of *bis*-terpyridine cobalt(II) complexes.[11] This drawback can be circumvented by oxidation of the labile *bis*-terpyridine cobalt(II) complex into a kinetically inert *bis*-terpyridine cobalt(III) by addition of an excess of silver nitrate (Fig. 1). Finally, the chlorine counter ions were exchanged for hexafluorophosphate ones to improve the solubility of the *bis*-complexes in organic solvent. The synthesis of the PS_{240}-[Co^{III}]-PEO_{230} *bis*-complex has been followed by UV-Vis spectroscopy. The spectra clearly show the expected changes resulting from the oxidation of Co^{II} into Co^{III} (see ESI†). The synthesis of the nickel-based copolymer was not followed by UV-Vis spectroscopy because nickel-terpyridine complexes do not show easily detectable characteristic bands.[12]

After synthesis the copolymers were purified by successive extractions with water, a selective solvent for PEO, and with diethyl ether, a selective solvent for PS. It was indeed previously demonstrated for ruthenium(II)-based copolymers that this procedure is efficient in yielding pure metallo-supramolecular block copolymers.[13] These purified PS-[Ni^{II}]-PEO and PS-[Co^{III}]-PEO copolymers were then analyzed by size-exclusion chromatography (SEC). The SEC traces of both compounds clearly show a shift toward lower retention times compared to the starting PEO-[and PS-[blocks (Fig. 2). Moreover, no shoulders corresponding to remaining PEO-[and PS-[blocks were observed in the chromatograms of the copolymers. These results clearly demonstrate the successful preparation of pure PS-[Ni^{II}]-PEO and PS-[Co^{III}]-PEO copolymers.

In addition, ^{1}H-NMR spectroscopy confirmed the formation of the PS_{240}-[Co^{III}]-PEO_{230} and PS_{240}-[Ni^{II}]-PEO_{230} heteroleptic *bis*-complexes (Fig. 3). The measured integration ratio of PS and PEO characteristic signals corresponds to the expected ratio calculated from the copolymer composition. Moreover, signals characteristic of the diamagnetic *bis*-terpyridine cobalt(III) complexes were clearly observed (Fig. 3a) and their integration matched the expected value, evidencing the complete oxidation of the starting *bis*-terpyridine cobalt(II). Due to the paramagnetic character of the *bis*-terpyridine nickel(II) complexes, no terpyridine signals could be detected (Fig. 3b).

In order to unambiguously prove that amphiphilic metallo-supramolecular block copolymers have indeed been obtained, micelles have been prepared in a selective solvent for the PEO block. Since the copolymers have a rather large hydrophobic fraction, they cannot be dissolved directly in water. They were thus first dissolved in DMF, a good solvent for both the PS

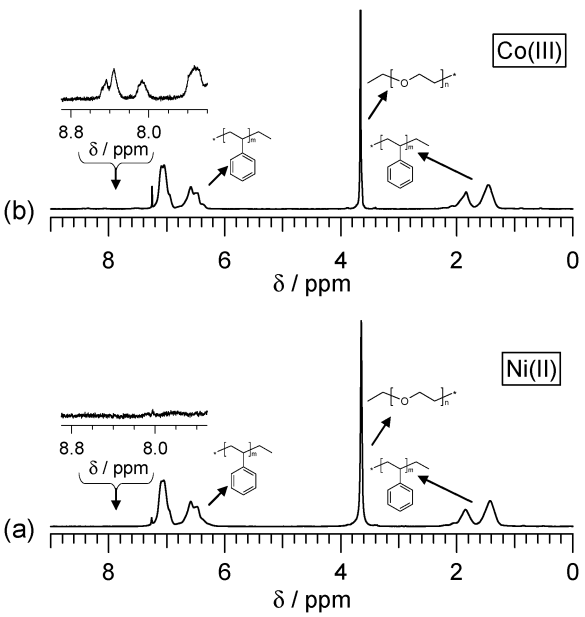

Fig. 3 ^{1}H-NMR spectra of PS_{240}-[Ni^{II}]-PEO_{230} (a) and PS_{240}-[Co^{III}]-PEO_{230} (b) metallo-supramolecular block copolymers in $CDCl_3$.

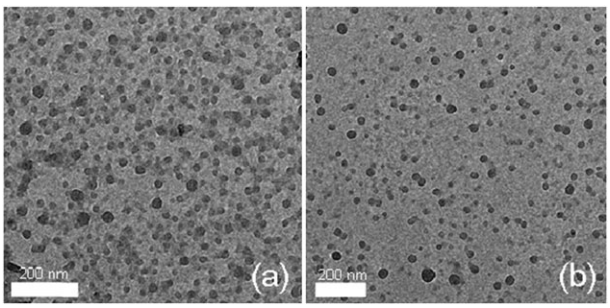

Fig. 4 TEM pictures (without staining) of micelles prepared from PS_{240}-[Co^{III}]-PEO_{230} (a) and PS_{240}-[Ni^{II}]-PEO_{230} (b) metallo-supramolecular block copolymers.

and PEO blocks, and water, a selective solvent for PEO, was then added dropwise to reach a 1 : 1 v/v DMF–water ratio. The opalescence characteristic of micelle formation was observed upon addition of water. The two micellar solutions were subsequently investigated by transmission electron microscopy (TEM) without staining. According to TEM pictures (Fig. 4), spherical micelles with an average radius of 15 nm and 17 nm were observed for the PS_{240}-[Ni^{II}]-PEO_{230} and PS_{240}-[Co^{III}]-PEO_{230} samples, respectively. In these TEM images, the electronic contrast mainly originates from the nickel(II) and cobalt(III) ions. The nature of the metal ion present in the copolymer seems to have no significant influence on the size of the micelles since essentially the same radii have been observed for both samples.

In a final step, the possibility of opening the *bis*-terpyridine cobalt(III) and nickel(II) complexes upon application of a chemical stimulus to the micellar solutions of the PS_{240}-[Co^{III}]-PEO_{230} and PS_{240}-[Ni^{II}]-PEO_{230} metallo-supramolecular block copolymers has been tested. In the case of the PS_{240}-[Co^{III}]-PEO_{230} sample, one molar equivalent of *N*-ethylmorpholine compared to the *bis*-terpyridine cobalt(III) was added to the micellar solution in presence of 0.01 M HCl. The reduction of cobalt(III) into labile cobalt(II) complex and the protonation of the terpyridines due to the HCl resulted in the opening of the *bis*-complexes, and led to the loss of the PEO stabilizing chains in the micellar corona. This immediately resulted in the macroscopic precipitation of the PS micellar cores that were no longer stabilized (see ESI† and Fig. 5). In the case of the PS_{240}-[Ni^{II}]-PEO_{230} sample, the opening of the *bis*-terpyridine nickel(II) complexes was achieved by adding a slight molar excess of potassium cyanide to the micellar solution. This resulted in the formation of $[Ni(CN)_4]^{2-}$, a more stable complex than the *bis*-terpyridine-nickel(II). The cleavage of the latter complexes resulted again in the loss of the PEO stabilizing coronal chains and in the precipitation of the PS micellar cores (see ESI† and Fig. 5).

In conclusion, the first synthesis of amphiphilic metallo-supramolecular block copolymers containing either *bis*-terpyridine cobalt(III) or nickel(II) complexes is presented. The obtained PS_{240}-[Co^{III}]-PEO_{230} and PS_{240}-[Ni^{II}]-PEO_{230} metallo-supramolecular block copolymers have the advantage of offering a supramolecular junction stable enough to maintain the integrity of the block copolymer structure but that can

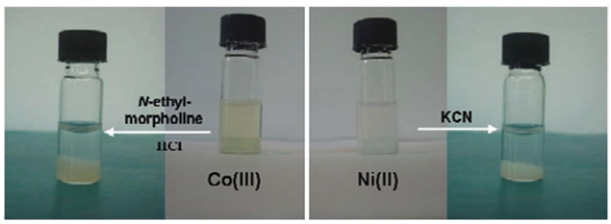

Fig. 5 Micellar core precipitation induced by opening the *bis*-terpyridine cobalt(III) and nickel(II) complexes in PS_{240}-[Co^{III}]-PEO_{230} and PS_{240}-[Ni^{II}]-PEO_{230} micelles.

be easily opened upon application of an adequate chemical stimulus. The strategy reported here could be generalized to other copolymers, thanks to the terpyridine functionalized NMP initiator used here, or the RAFT initiator reported by Harruna and coworkers.[14] Such copolymers, bearing an easily addressable junction, have interesting potential to build hollow structures such as nanoporous films, or nanocages.

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