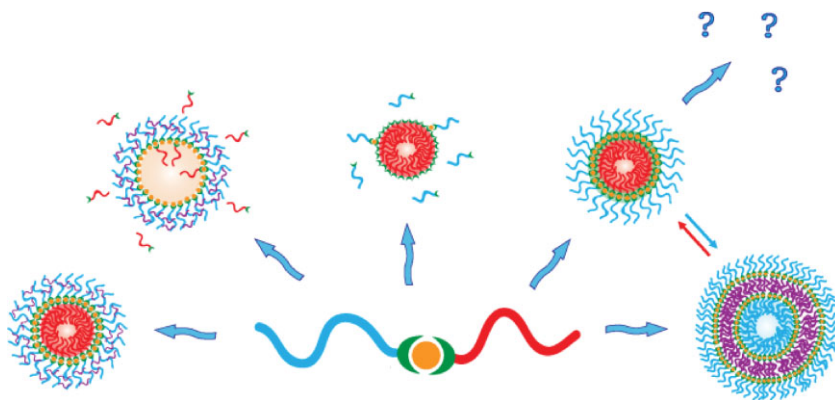


Using Metallo-Supramolecular Block Copolymers for the Synthesis of Higher Order Nanostructured Assemblies

Adam O. Moughton, Rachel K. O'Reilly*

Many research groups have explored the properties and solution self-assembly of main chain metallo-supramolecular multiblock copolymers. Until recently, these metal complexes have been used to prepare mainly micelle type structures. However, the self-assembly of such copolymers has been exploited further to create more advanced architectures which utilize the reversible supramolecular linkage of their building blocks as a key component in their synthesis. Furthermore, the incorporation of multiple orthogonal interactions and stimuli responsive polymers into their design, enables more precise external control of their properties. This feature article discusses recent developments and provides an insight into their potential exploitation and development for the creation of novel, smart, and responsive nanostructures.



Introduction

The desire to control the structure and function of nanostructured materials for use in novel applications

has driven scientists to employ a host of synthetic strategies for their creation.^[1,2] In particular, the self-assembly of amphiphilic diblock copolymers in solution has facilitated access to various well-defined nanosized architectures.^[3–9] For this purpose, typically block copolymers covalently connected at their homopolymer junction are employed, which readily undergo phase separation in a selective solvent for one or more of the homopolymer blocks. This gives rise to various morphologies with typically predictable sizes and shapes, which contain distinct nanosized polymeric domains whose characteristics are defined, and can be tuned by the polymer's composition and properties.^[10–16]

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Imparting further complexity and functionality into such architectures via the selective incorporation of non-covalent interactions onto the constituent polymers is particularly desirable toward advancing the goal of making these materials more functionally complex and/or responsive.^[17–20] Of the many potential non-covalent bonding motifs to choose from, hydrogen bonding^[21–25] and metal–ligand interactions^[26–30] are particularly appealing choices since they can exhibit specific binding via complementary interactions or preferred coordination geometry respectively, and may impart exploitable properties such as reversibility into the final nanostructured assemblies.^[31,32] Recently, researchers have incorporated both non-covalent motifs into polymer architectures to potentially utilize their unique properties, in an attempt to achieve further advanced architectures and applications.^[33–35]

Metal–ligand coordination is a particularly attractive motif since the interaction is highly specific and directional, and its relative binding strength can be readily tuned via metal and ligand selection from a host of well-studied systems.^[19,30,36] Moreover, transition metals also offer photophysical, electrochemical, catalytic, and magnetic properties which may further enhance their use and potential application in this field.^[30] Research in recent years has shown that transition metal complexing ligands capable of selective binding can be incorporated onto the side chain and chain end of polymers and have proven to be useful building blocks for the creation of a wide range of metallo-supramolecular assemblies, which combine the characteristic properties of block copolymers with that of supramolecular chemistry.^[27,36,37] The area of H-bonding directed self-assembly of copolymers is a burgeoning field and a distinct area of research in its own right and will not be covered in this feature article.^[19,38]

Block copolymers which are formed via a supramolecular transition metal complex linkage between the homopolymer segments have shown particular research interest.^[27,29,36] This is perhaps owing to their ability to undergo conventional self-assembly into various morphologies, as for covalent block copolymers, yet still retain supramolecular reversibility and the unique properties of transition metal complexes, thus offering many advantages over conventionally synthesized architectures.^[39–44]

Moreover, in recent years, researchers have begun to pre-design and manipulate such metallo-supramolecular block copolymers to target specific nanostructures whereby a key design feature in their synthesis is utilized after self-assembly has occurred; viz, the supramolecular linkage can be selectively cleaved to remove the attached polymer blocks, thus producing novel functional architectures from tailor made parent self-assembled structures.^[31,45–48]

In this feature article, we will provide a brief introduction to the field of main chain metallo-supramolecular block



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Rachel O'Reilly is currently an EPSRC career acceleration fellow in the Chemistry Department at the University of Warwick. She graduated from the University of Cambridge in 1999 and went on to complete her PhD at Imperial College, London in 2003 under the supervision of Professor Vernon C. Gibson. In 2003 she moved to the US to work on the functionalisation of polymeric nanoparticles using 'Click' chemistry, at the IBM Almaden research center in San Jose California and Washington University in Saint Louis, Missouri, under the joint direction of Professors Craig J. Hawker and Karen L. Wooley. In 2004 she was awarded a research fellowship from the Royal Commission for the Exhibition for 1851 and moved back to the UK in 2005. At this time she took up a Royal Society Dorothy Hodgkin Fellowship in the Chemistry Department at the University of Cambridge and in 2009 she moved to take up her current position at Warwick. Her current research focuses on bridging the interface between creative synthetic, polymer and catalysis chemistry, to allow for the development of materials that are of significant importance in medical, materials and nanoscience applications.

copolymers and evaluate recent literature on the topic of their specific design to undergo self-assembly to form tuneable and stimuli responsive higher order structures. We will also discuss their possible future development for use in novel applications which utilize these key design features. For a more comprehensive background on main chain metallo-supramolecular polymers, the reader is directed toward several excellent reviews on the subject.^[29–30,37] Furthermore, in this highlight we will only cover metallo-supramolecular polymers containing one metal–ligand complex which serves as a linkage between homo- and copolymers and therefore we will not be covering literature on multiple complex containing metallo-polymers in detail, or the broader topic of metal containing polymers. Once more, the reader is directed toward several excellent and comprehensive reviews on these topics.^[30,49–51]

Metallo-Supramolecular Block Copolymers

Metallo-supramolecular polymers can be defined as having metal–ligand interactions in the main chain of a copolymer, specifically located at the junction between polymer blocks, and are formed via the coordinative bonding of polymer chain end bound ligands to transition metal ions. Various metallo-supramolecular interactions can be used to link different homo- or copolymer building blocks together, through various different binding modes, resulting in a wide range of achievable copolymers or multiblock copolymers respectively, and in turn enabling the synthesis of various novel supramolecular polymer architectures with interesting and tuneable self-assembly behavior. The key features of these metallo-polymer systems include their specificity, directionality, and opportunity to exploit the tuneable binding strength and reversibility of the metal–ligand interaction (Figure 1).^[29,37]

Linear metallo-supramolecular di- and tri-block copolymers with symmetrical or asymmetrical metal–ligand interactions, i.e., either having the same or different ligands

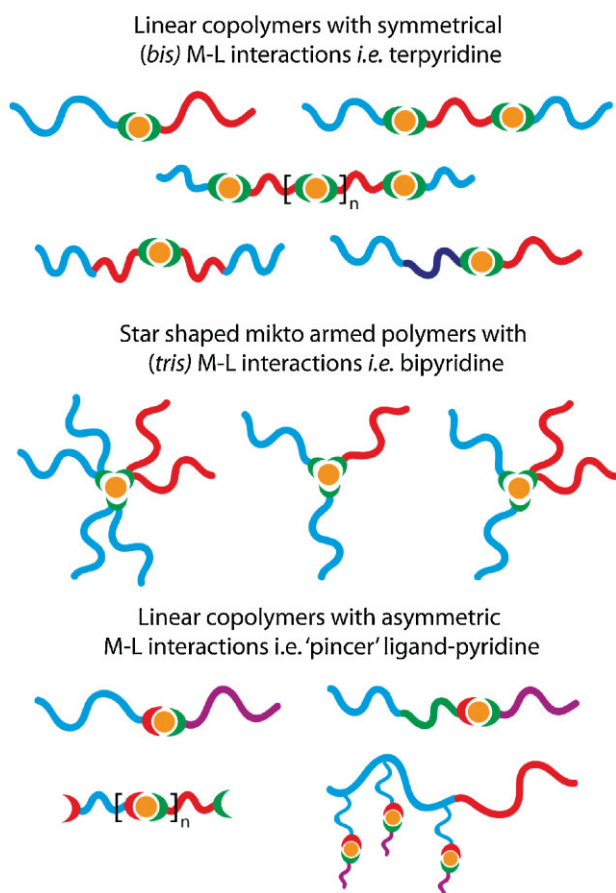


Figure 1. Schematic representation of the three main classes of metallo-supramolecular block copolymer architectures studied in recent years.

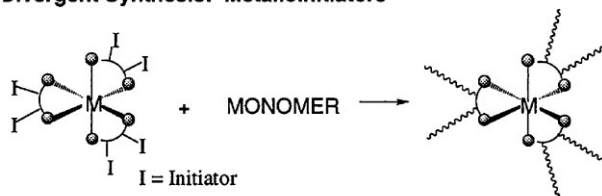
bound to one metal center, have been intensively studied in the past decade in particular. This is perhaps owing to their facile and versatile synthesis, similarity to conventional copolymers, and great promise for self-assembly into interesting and useful architectures.

However, it should be first noted that initial work in this field targeted star shaped metallo-supramolecular polymers. This pioneering work in combining metal–ligand interactions with polymers to form the first examples of metallo-copolymer architectures was by Wu and Fraser,^[52] and first highlighted that such copolymers were possible via divergent or convergent approaches (Figure 2). In their first reports, Fraser and coworkers^[26,52–60] utilized the *tris* binding of bipyridine to iron (II) and ruthenium (II) in particular, in the targeted synthesis of symmetrical star shaped metallo-supramolecular polymers.

Fraser and coworkers^[61–69] have produced further reports based on the binding of many different polymers, end functionalized with bipyridine and β -diketonate ligands to various metal centers, including later transition metals such as europium (III). The polymer architectures produced, utilized the desire of these bidentate ligands to coordinate in an octahedrally arranged *tris*-binding mode to earlier transition metal ions such as iron and ruthenium, thus producing mikto-armed complex centered stars, with a tuneable number of polymer chains per complexing ligand. Furthermore, the binding of these ligand bound polymers to europium (III), enabled the formation of stars with four ligand attachment points with five polymer arms in total, due to the higher coordination sphere of the lanthanide metal center, thus expanding the scope of achievable architectures through the coordination preference of a metal center and its oxidation state.^[62]

The higher coordination number of lanthanide metal centers in combination with ligand functionalized

Divergent Synthesis: Metalloinitiators



Convergent Synthesis: Macroligand Chelation

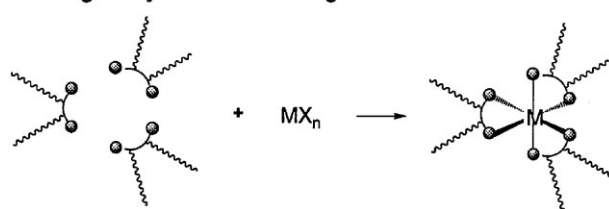


Figure 2. Formation of metallo-supramolecular star shaped polymers.^[52]

polymers has been further explored by Rowan and coworkers^[70–72]. They utilized the binding of 2,6-bis-(benzimidazolyl)-4-hydroxypyridine end functionalized poly(ethylene glycol) (PEG) chains to cobalt (II) or zinc (II) and added 3% lanthanum (III) or europium (III) respectively, to cross-link the polymer network and forming thermal, mechanical, chemo-, and photoresponsive luminescent gels. Rowan and coworkers^[73] have also investigated this ligand binding motif to synthesize conjugated metallo-supramolecular polymers from ditopic ligand functionalized conjugated monomers via coordination with Zn^{2+} , resulting in materials with interesting optical properties.

As mentioned previously, linear metallo-supramolecular di- and tri-block copolymers have shown particular research progress, both in terms of their synthesis and in their utilization as building blocks in self-assembly.

Thus, given such progress and the closely related topic of this feature article, the concept is introduced and given due priority as a subject matter here, but this is by no means an extensive introduction, given the large magnitude of papers detailing the many aspects of their synthesis and properties. Once more, it is important to stress that the reader should be referred to several excellent reviews on such linear metallo-polymers.^[29,36,37,74]

Compared to covalently linked block copolymers, linear metallo-supramolecular block copolymers offer many advantages that are not observed in their analogous covalent counterparts, offering the advantages of both the metal complexes and the copolymers, and resulting in useful and tuneable building blocks for self-assembly, whose properties can easily be exploited for advanced nanoscience applications (Figure 3).^[27,30,36,74] For example, a very recently published paper described the preparation and use of a novel metallopolymer, based on a silver (I) carbene catalyst, which could be activated via ultrasound.^[75]

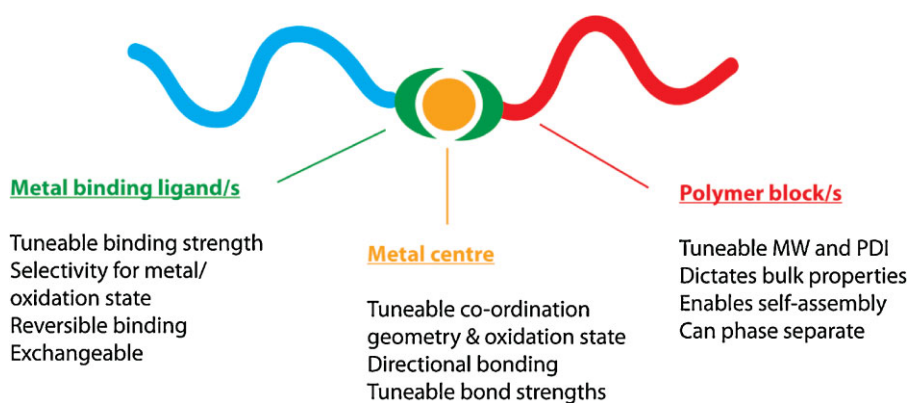
It has been shown in recent years by Schubert and coworkers^[30,36,74] that homopolymer chains end func-

ionalized with terpyridine ligands can bind to various metal centers, forming linear metallo-supramolecular block copolymers. The first example of their preparation in 2002 was by Lohmeijer and Schubert,^[76] who utilized ruthenium(II) complexation to bind two terpyridine functionalized homopolymers together. This symmetrical bis-terpyridine based connection strategy has been shown to effectively and efficiently bind together many different homo- and copolymers to create various di- and tri-block metallo-copolymer systems.^[29,30,36,74] Furthermore, a library of 13 different metallo-supramolecular block copolymers based on terpyridine functionalized polystyrene and poly(ethylene oxide) (PEO) blocks has subsequently been synthesized^[77] and shown to be useful building blocks for self-assembly.^[77]

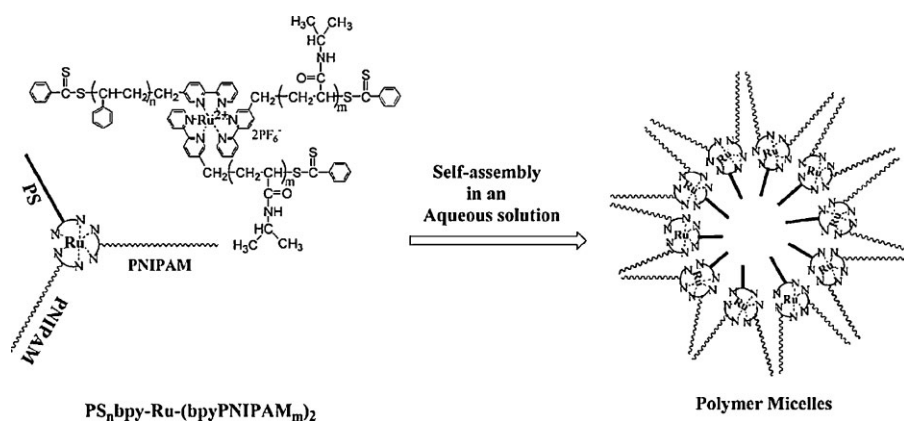
More recently Harruna and coworkers^[78,79] have also researched the synthesis and binding of bipyridine functionalized polymers such as poly(styrene) (PS) and poly(*N*-isopropylacrylamide) (PNIPAM) chains to ruthenium(II) to produce thermoresponsive mikto-armed ruthenium(II) complex centered stars (Figure 4).

These reports include the self-assembly of such stars into interesting architectures and thus illustrates how the coordination geometry of a metal complex (dictated by the coordination preference of the transition metal ion and its oxidation state) can influence the morphology of the final self-assembled structure in solution. As shown previously by Fraser et al.^[62] such factors can influence the copolymer architecture achieved and hence this is expected. However, of particular interest would be to try and influence the architecture of a metallo copolymer and hence preferred morphology of a self-assembled metallo-supramolecular polymer in situ, via a change in the coordination geometry of the transition metal. For instance, it is known that changing the oxidation state of ruthenium can alter its preferred coordination geometry and hence binding mode when self-assembled in the solid state; but to the author's knowledge, little has been achieved in altering the coordination geometry of a transition metal which links a metallo-supramolecular polymer when self-assembled in solution.

In Nature, the influence of the coordination geometry of a transition metal in solution has an important and direct impact on the chemical reactivity of the active site in metallo-enzymes and can give rise to structural changes in the enzyme itself and vice versa. For example, in the oxygen transporting metallo-enzyme, hemoglobin, a change in the oxidation state and hence coordination geometry of iron in the enzyme bound



■ Figure 3. Properties of linear metallo-supramolecular block copolymers.



■ Figure 4. Formation of micelles from amphiphilic star-shaped metallopolymers.^[78]

porphyrin complex, upon binding to oxygen, gives rise to a conformational change in the tetrameric hemoglobin protein complex. In turn, this enables for an increased affinity for oxygen by the other heme subunits in a cooperative process.^[80] Furthermore, the coordination geometry of a metal center in a metallo-enzyme can be influenced by the folding of the protein around the complex by imposing constraints on the bond angles and lengths and hence bond strengths (e.g., selective uptake of copper by an albumin protein via the ligand-field Jahn–Teller effect). Moreover, in metal ion uptake, a protein fold can alter its coordination environment such that it can distinguish between the coordination requirements of iron(II) and iron(III) by a factor of 1×10^5 .^[80]

Using elaborate natural systems as a source of inspiration, chemists might be able to begin manipulating the structure and reactivity of the “active sites” of self-assembled metallo-supramolecular polymers by changing their oxidation state and/or preferred coordination geometry. This could give rise to a change in preferred morphology of the polymer in solution due to a change in the location or relative proximity of incompatible polymer chains, or it could give rise to a change in the polymer architecture via a reduced coordination sphere driven removal of ligand bound polymer chains, i.e. enabling the selective removal of specific polymer chains.

Analogous to metallo-enzymes, applying conformational or structural changes to a homopolymer in a self-assembled metallo-supramolecular polymer, may also impose coordination requirements on the polymer bound metal complex, thus becoming metal ion (coordination geometry/oxidation state) selective. It should be noted that the structure of such a metallo-supramolecular polymer may not resemble existing literature examples. However, conformational changes in polymers are well known, particularly stimuli induced changes, for example the thermoresponsive coil to globule transition of PNIPAM chains in solution. Achieving an influence on the preferred

transition metal and oxidation state of a polymer bound ligand system, could thus be potentially of great interest in the development of metallo-supramolecular polymer systems.

Changing the preferred coordination geometry of metallo-supramolecular polymers, could be achieved through utilizing a redox responsive metal complex system as the linkage between homopolymers. For example, the relationship between the redox potential and the coordination geometry in copper chemistry

has been well studied and thus could be suitable for this purpose.^[81,82] For instance, Cu(II) tends to prefer six-coordinate geometries while Cu(I) predominantly exhibits four-coordinate geometries. Switching between these two oxidation states electrochemically in solution, could facilitate a change in the characteristics of the “active sites” of the metallo-polymer, and hence could have a large influence on the polymer architecture and hence self-assembled structure.

Furthermore, a redox responsive system enables stimuli induced external control over the self-assembled system, which is an important feature for controlled release and sensing applications. Towards this end, the development of asymmetrically linked metallo-supramolecular polymers, i.e. those with different ligand functionality either side of the metal center, are particularly important, since the incorporation of different and incompatible ligand functionalized polymers in complex metal bound geometries requires an orthogonal approach. Due to its inherent orthogonal nature, an asymmetric supramolecular approach may provide access to complex building blocks for this purpose and that are difficult to achieve in symmetrical or conventionally synthesized (covalently bonded) systems.^[32]

Asymmetrically linked metallo-supramolecular polymers also enable even further tuning and utilization of both ligand's binding modes, strengths, and properties, beyond that of symmetrically linked metallo-supramolecular polymers. The resulting asymmetric architectures retain the reversible character and novel properties of the supramolecular interactions, as with symmetrical systems, yet also allow for more selectivity over metal–ligand bond cleavage at either side/s of the metal center and hence enable selective removal of one or more of the system's components. Furthermore, selective metal–ligand bond cleavage (even over other non-covalent interactions)^[33] may be as a result of a change in external stimuli such as temperature or pH,^[45] thus allowing a greater magnitude of

external control over the entire polymer architecture or self-assembled nanostructure.

There are examples of asymmetrically linked metallo-linked block copolymers in the literature and are primarily based on coordination to palladium(II). In 2005,^[83] utilized a well-established unsymmetrical binding motif which consists of an SCS 'pincer' ligand and a pyridine ligand bound to a square planar palladium(II) metal center.^[84–88] This was used as a linking unit at the junction between two different homopolymers which were synthesized via a ROMP mechanism.^[83] O'Reilly and coworkers^[45,48] have also synthesized SCS 'pincer' ligand bound homo- and copolymers from SCS 'pincer' functionalized controlled radical polymerization (CRP) initiators which bind to palladium(II). Furthermore, they have synthesized the complementary ligand functionalized initiator and subsequently polymers, bearing the weaker binding pyridine moiety. They were able to demonstrate that when the 'pincer' ligand polymers were complexed with palladium(II) and bore a labile acetonitrile ligand, this pendant ligand could be readily displaced by the pyridine ligand moiety when bound to a polymer chain end, producing an asymmetric metallo-supramolecular diblock copolymer.

This strategy relied upon the quantitative ligand displacement chemistry for SCS 'pincer' complexes developed by Kickham and Loeb.^[89] Very recently, Weck and coworkers^[34] have utilized this ligand displacement strategy in conjunction with H-bonding interactions to produce novel ABC supramolecular triblock copolymers which could hold great promise as a building block in creating advanced self-assembled architectures with orthogonal supramolecular recognition and reversibility (Figure 5).

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Metallo-Supramolecular Block Copolymer Micelles

The groups of Schubert, Gohy, and coworkers^[39,43,90] have shown that, as for covalent analogues, amphiphilic AB metallo-block copolymers can self-assemble, to give various metal containing

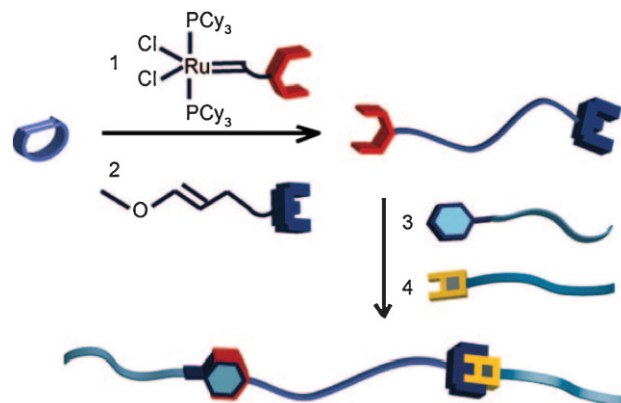


Figure 5. Schematic representation of the synthesis of a hetero-telechelic polymer from functionalized initiators and chain terminators and their self-assembly to form a supramolecular triblock copolymer.^[34]

micellar architectures in solution. Their first report in this area detailed the self-assembly of a *bis*-terpyridine Ru(II) linked PS-*b*-PEO block copolymer (PS₂₀-[Ru]-PEO₇₀) into spherical micelles, induced via the addition of a non-solvent for one of the blocks (Figure 6). The resultant aggregates were studied by dynamic light scattering (DLS), atomic force microscopy (AFM), and transmission electron microscopy (TEM).^[39] They found that the diameter of the micelles by DLS was 65 ± 4 nm and they had a spherical morphology by TEM analysis. They found that no contrast agent was needed for TEM, since the ruthenium complexes at the core-shell interface provided enough contrast to be visible on the TEM grids, also providing evidence for retention of the metal complexes on the interior of the micelles.

In further studies, they found that these micelles behave in a similar way to their covalent counterparts (a covalently linked PS₂₀-*b*-PEO₇₀ block copolymer); however, they also noted some unusual differences.^[40] For example, they observed that the addition of salt affects their hydrodynamic diameter (*D_h*) as monitored by DLS in aqueous solution due to the screening of repulsive ionic interactions of the metal complex counter ions. Furthermore, they found that the micelles had a tendency to aggregate to form larger,

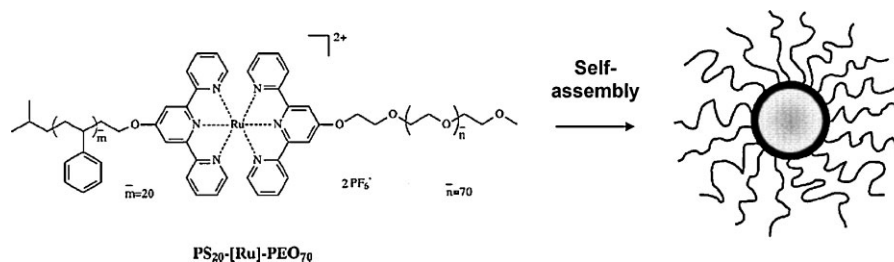


Figure 6. Schematic representation for the formation of micelles from the metallo-supramolecular AB diblock copolymer.^[39]

less uniform structures with $D_h = \text{ca. } 200 \text{ nm}$.^[91] However, they showed that the slow addition of water to a homogenous N,N' -dimethylformamide (DMF) solution of the copolymer, resulted in well-defined micelles (with one population by DLS with $D_h = \text{ca. } 65 \text{ nm}$) which showed no further aggregation.^[90]

Further investigations into their micellization behavior utilized a library of block copolymers of the type: $\text{PS}_x\text{-[Ru]-PEO}_y$ with varying block lengths (x and y). They found that, unlike the classical theory for covalent amphiphilic copolymers, the micelle size did not scale linearly with respect to the degree of polymerization (DP) of the PS core block. However, upon addition of a charge screening salt, they were able to show that the D_h did scale linearly with respect to the DP of the PS core block.^[43]

Schubert, Gohy, and coworkers^[92] have also investigated the influence of the glass transition temperature T_g of the hydrophobic core block on the micelle morphology. Their initial study of a $\text{PS}_{20}\text{-[Ru]-PEO}_{70}$ copolymer used a high T_g core block, PS, thus producing kinetically frozen micelles with a regular shape by DLS and AFM. However, they synthesized a copolymer with a soft (low T_g) poly(ethylene-co-butylene), PEB core, and a PEO corona, $\text{PEB}_{20}\text{-[Ru]-PEO}_{70}$; this self-assembled into micelles with a mean D_h (DLS) = 58 nm, with two populations at 32 and 115 nm. They hypothesized that the PEB core micelles were prone to re-organization when exposed to external stimuli, given their low T_g . They varied factors such as temperature and polymer concentration, to explore the stability of these nanostructures in solution by DLS analysis. They found that overall, the mean sizes by DLS for the aggregates were not affected by changes in concentration or an increase in temperature. However, their CONTIN size distribution histograms did change, as they saw less aggregation (less of the larger size population) for both variations. Moreover, this effect was reversible for changes in temperature, since upon returning to room temperature, the larger aggregates were again observable by DLS analysis. They attributed this phenomenon to the existence of a dynamic equilibrium between micelles and aggregates of micelles, for the $\text{PEB}_{20}\text{-[Ru]-PEO}_{70}$ micelle solution.

Gohy et al.^[41] have also investigated the self-assembly behavior of more complex *bis*-terpyridine containing metallo-copolymers, besides A-[Ru]-B type copolymers. They synthesized an A-b-B-[Ru]-C type copolymer, $\text{PS}_{32}\text{-b-P2VP}_{13}\text{-[Ru]-PEO}_{70}$, consisting of a pH responsive poly(2-vinyl pyridine) (P2VP) middle B block. This copolymer formed spherical micelles in aqueous solution consisting of a PS core, a pH sensitive P2VP shell, and a PEO corona and

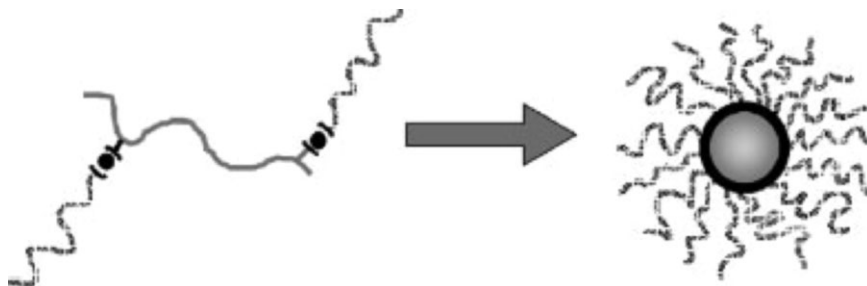


Figure 7. Schematic representation for the formation of micelles from the metallo-supramolecular ABA triblock copolymer.^[93]

also underwent predictable size changes in response to changes in the solution pH.

In 2003, Schubert and Gohy investigated the self-assembly behavior of an amphiphilic metallo-supramolecular graft copolymer in which PEG side chains were grafted from a poly(methyl methacrylate) (PMMA) backbone via a *bis*-terpyridine ruthenium (II) linkage (Figure 7). They varied the length of the PMMA chain while keeping the PEG chain length constant. The copolymers self-assembled into micelles giving a mean D_h by DLS of around 165 nm in aqueous solution, depending on the DP of the grafted chains. By TEM, the micelles appeared as white spheres surrounded by dark rings.

The dark rings were tentatively attributed to the presence of strongly electron adsorbing ruthenium ions of the metallo-supramolecular complexes found in higher concentrations at the interface of two polymer domains. The average size of these micelles by TEM were found to lie in the 15–20 nm range.^[93]

In 2004, along with Manners, Winnik, and coworkers,^[42] Schubert and Gohy synthesized an amphiphilic metallo-supramolecular diblock copolymer consisting of a hydrophobic poly(ferrocenylsilane) (PFS) block attached to a hydrophilic PEO block to give a PEO/PFS block ratio of 6:1. This polymer formed novel PFS cylindrical or rod-like micelles in water due to the crystallization of the PFS block. They showed by TEM and AFM, that they had a constant core diameter ($6 \pm 1 \text{ nm}$) but had a polydisperse length of around $438 \pm 12 \text{ nm}$ (Figure 8). Interestingly, the cylinders could be cleaved into smaller rods when exposed to ultrasound or when the temperature of the solution was increased, thus lending themselves toward advanced stimuli responsive applications. Furthermore, the PFS cores of these cylinders are well known for their ability to transport charge and also as precursors for ferromagnetic materials, thus making these nanostructures excellent candidates for nanotechnology applications.

Recently, Schubert and Gohy have further explored the self-assembly behavior of ruthenium(II) *bis*-terpyridine complex linked polymers with differing polymer architectures. In 2008, they reported the synthesis and

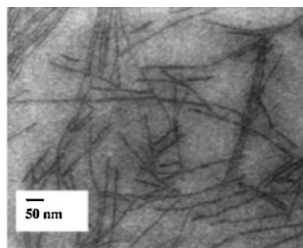
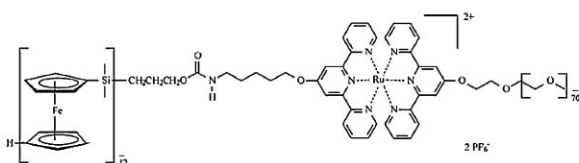


Figure 8. The amphiphilic metallo-supramolecular diblock copolymer PFS-[Ru]-PEO and the self-assembled diblock copolymer cylinders by TEM.^[42]

micellization of novel ABA coil-rod-coil type ruthenium(II) terpyridine triblock copolymers with PEG chains as the A blocks and various rigid rod ditopic terpyridine ligands as the conjugated B blocks. They observed by cryo-TEM and DLS that the triblocks self-assembled in water to give kinetically frozen spherical micelles that clustered into larger structures.^[94]

Schubert and Gohy also showed that a terpyridine end functionalized PS-*b*-poly(*tert*-butyl acrylate)-[diblock copolymer PS₄₇-*b*-P^tBA₅₅]-[formed micelles in ethanol with a PS core and a P^tBA corona with terpyridine ligands on their exterior.^[95] The authors exposed the micelles to various suitable *bis*-complexing metals such as; Fe(II), Ni(II), and Zn(II). When the concentration of the micelles was sufficiently low, the complexation resulted in intramolecular complexation and hence “looping” of the P^tBA corona chains and induced the formation of flower-like micelles, which was observable by a slight decrease in the *D_h* by DLS analysis.

Furthermore, a third terpyridine functionalized polymer block, PEO₁₂₅- [was added to a solution of partially mono-complexed Fe(II) PS₄₇-*b*-P^tBA₅₅]-[micelles in ethanol, thus forming a triblock copolymer (PS₄₇-*b*-P^tBA₅₅)-[Fe]-PEO₁₂₅ which self-assembled further to give larger micelles by DLS in ethanol, and upon dialysis into water, gave slightly smaller micelles. The reported structural changes, although significant, were limited in their applicability, owing to the small observable changes they involved. However, this report represents an excellent illustration of how metal complexation and the incorporation of polymer chains can be achieved post self-assembly. This concept could be an important feature in the increasingly broadening scope of metal complex utilization in self-assembled metallo-supramolecular block copolymer systems.^[96]

Post Self-Assembly Modification of Metallo-Supramolecular Block Copolymer Nanostructures

The formation of micelle structures from linear AB, ABA, and ABC type amphiphilic metallo-block copolymers is well-established and understood to an appreciable degree,

as a result of the pioneering work of Schubert and Gohy. The exploration of self-assembled linear metallo-block copolymers by their groups, and more recently, our research group, has targeted more complex morphologies in solution, in which a strategic element of their synthesis involves cleavage of the supramolecular binding unit after self-assembly has occurred.

This step takes advantage of the inherent reversibility of the non-covalent linkage between the polymers, whilst still retaining the functional ligand and possibly transition metal complex functionality after cleavage. Such self-assembled systems thus have selectively removable components, giving rise to novel and complex architectures with specifically placed metal-ligand functionality, which has many potential applications such as in transition metal supported catalysis. Moreover, this reversible and selective removal procedure may hold the key to unlocking many further potential applications for these and other metallo-polymer systems.

The utilization of this reversible strategy for a metal complex binding unit of a metallo-diblock nanostructure, was initially demonstrated by Schubert and Gohy via the opening of the *bis*-terpyridine Ru(II) linker of a self-assembled poly(ethylene-*co*-butylene)-[Ru]-PEO diblock copolymer.^[31,92] An aqueous micelle solution of the copolymer was exposed to a large excess of a competitive ligand for ruthenium (II) [hydroxyethylethylenediamine triacetic acid (HEEDTA)]. The HEEDTA acted as a chelating scavenger for Ru(II) and hence broke the *bis*-terpyridine complex via cleavage of the Ru(II)-terpyridine bonds. Dialysis to remove the detached coronal PEO polymer chains, gave spherical, nanosized particles, or so called “nano-objects,” (as visualized by AFM and observed by DLS analysis) which were surface coated with vacant terpyridine ligands (Figure 9). The availability for mono-complexation to other suitable transition metal ions was demonstrated via complexation of iron(II), giving a characteristic violet colored solution. This synthetic methodology could be utilized for the surface functionalization of various polymer architectures for use in many diverse applications including supported catalysis or selective transition metal scavengers.

Our group has recently extended the exploitation of this reversible linkage strategy at the core-shell interface of a block copolymer spherical micelle structure. In our initial investigations, we used a *bis*-terpyridine Ru(II) symmetrically linked amphiphilic block copolymer similar to those reported previously.^[46] Firstly, two terpyridine end functionalized polymers were synthesized: a hydrophobic PS₁₂₀-[block and a hydrophilic poly(acrylic acid)

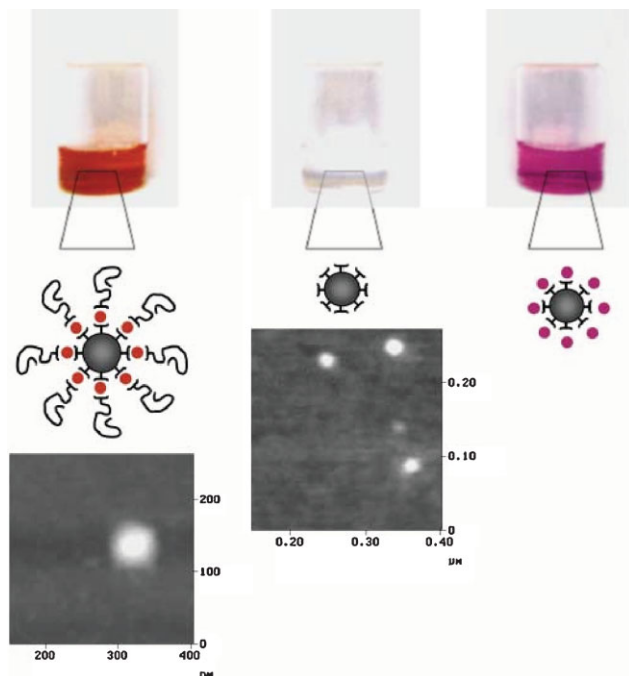


Figure 9. Formation of vacant terpyridine coated “nano-objects” from *bis*-terpyridine ruthenium(II) complex linked amphiphilic metallo-supramolecular block copolymers and subsequent complexation with iron(II).^[92]

PAA₁₃₅-[block, in a controlled manner, utilizing a terpyridine functionalized nitroxide mediated radical polymerization (NMRP) initiator. These two polymers were then linked together via a ruthenium(II) complex using chemistries previously established by Schubert and coworkers.^[36,97]

This amphiphilic diblock self-assembled via the slow addition of water to a homogenous DMF solution of the copolymer, followed by dialysis, forming uniform micelles, which were observable by DLS ($D_h = 79 \pm 3$ nm) and TEM ($D_{avg} = 45 \pm 4$ nm). Furthermore, in a departure from conventional metallo-supramolecular polymer micelles, these non-covalently connected micelles^[18,98] were then covalently cross-linked in their PAA shell domain (ca. 20% PAA cross-linking) to give non-covalently connected nanoparticles using cross-linking chemistry developed by Wooley and coworkers.^[12,15] This gave more robust, smaller nanoparticles, as evidenced by DLS in solution ($D_h = 71 \pm 2$ nm) and TEM in the dried state ($D_{avg} = 42 \pm 3$ nm), which is consistent with their covalent PAA-*b*-PS cross-linked nanoparticle analogues.^[12] Once stabilized, the nanoparticles were subjected to an excess of HEEDTA to selectively break the supramolecular linkage at the core-shell interface. As in the case for Schubert and Gohy's

report for the synthesis of “nano-objects,” the HEEDTA acts a chelating scavenger and breaks up the *bis*-terpyridine complex via cleavage of the Ru(II) terpyridine bonds. Upon dialysis into THF/water mixtures, to remove the detached PS core, this revealed well defined, functionalized, core hollowed hydrophilic nanostructures or “nanocages” (Figure 10) whose size by DLS had increased dramatically to 130 ± 8 nm. This was not surprising, since core excavation removed the constraints which the rigid PS core had imparted on the nanocages. Furthermore, upon PS core hollowing, the nanocages were now completely hydrophilic and held together by their flexible, covalent, ca. 20% cross-linked shell layer.

The complete loss of the terpyridine bound Ru(II) metal centers was evidenced by a loss of the characteristic metal-to-ligand charge transfer (MLCT) band at 490 nm in the UV-Vis spectrum of the nanocages. The further availability of the terpyridine ligands after this de-complexation step was evidenced via backfilling with *mono*-complexing ruthenium(III) and iron(II) as evidenced by UV-Vis spectroscopy.

Interest in such hollow nanomaterials is primarily based on their ability to encapsulate and release small molecules, which enables their potential application in the drug delivery and nanocatalysis areas.^[99–101] These applications could be facilitated by the ability of the cross-linked PAA shell layer of these nanostructures to swell and contract upon varying pH, due to the pH dependant repulsive electrostatic interactions of the PAA polymer chains. Thus, it was proposed, and subsequently demonstrated, that the nanocage structure showed pH-sensitive size dependence in analogy to naturally occurring viruses, showing a marked increase in their D_h , with increasing pH. However, the parent nanoparticles showed a much less dramatic pH-size dependence, suggesting that the nanocages have novel pH tuneable permeability which may not be achievable with other conventional core-shell self-assembled systems.

This synthetic approach was further extended in 2008 for the synthesis of functional hollow nanocages by utilizing an asymmetrically linked metallo-supramolecular diblock copolymer as a building block.^[45] Moughton and O'Reilly et al.^[45] synthesized an S-C-S ‘pincer’-palladium(II)–

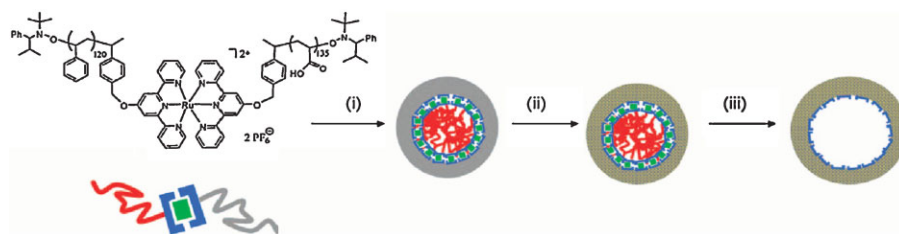


Figure 10. (i) Self-assembly of *bis*-terpyridine Ru(II) linked diblock to give micelles, (ii) cross-linking to give nanoparticles, and (iii) breaking of the *bis*-terpyridine-Ru(II) bonds and PS core hollowing in THF/water, to give terpyridine functionalized hollow nanocages.^[46]

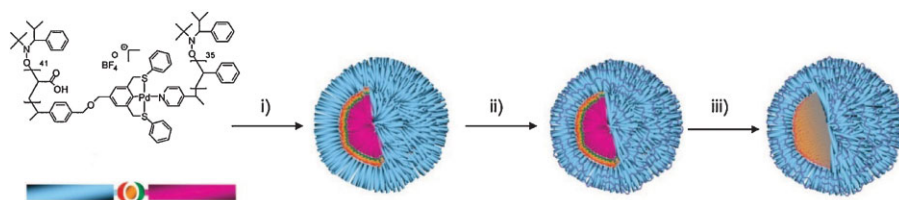


Figure 11. (i) Self-assembly of asymmetrically linked diblocks to give micelles, (ii) cross-linking to give nanoparticles, and (iii) core hollowing at lowered pH to form hollow and hydrophilic, SCS “pincer” Pd(II) complex functionalized nanocages.^[45]

pyridine linked amphiphilic diblock ($\text{PAA}_{41}\text{-[Pd]-PS}_{35}$ (where the notation [Pd] represents the asymmetric linkage between the two homopolymers) via ligand functionalized NMRP initiator techniques. Upon self-assembly into well-defined micelles and cross-linking to give nanoparticles using previously established chemistries, selective bond cleavage of the pyridine-palladium(II) bond was achieved via protonation of the pyridine moiety at low pH. The solution was then dialyzed into a THF/water mixture to remove the detached (protonated) pyridine functionalized PS core. After dialysis into water producing core SCS ‘pincer’-palladium(II) complex functionalized hydrophilic nanocages (Figure 11).

The authors followed the evolution of the nanocages from their parent nanoparticles via the observation of their increasingly hollow cores in the dry, flattened state by AFM (Figure 12). Further evidence for complete PS core removal of the nanoparticles to form completely hydrophilic nanocages was provided by sequestration studies of a water insoluble hydrophobic dye molecule. The results showed that the parent nanoparticles could uptake and sequester the dye molecules in their hydrophobic PS interior, yet the nanocages showed little uptake (above that of pure water), accounting for their lack of internal hydrophobicity and hence strongly suggests that core excavation was indeed successful.

The authors proposed that these functional nanocages may have interesting hydrophilic sequestration and supported catalysis applications, given the catalytically active nature of the incorporated SCS ‘pincer’-palladium(II) chloro complex.^[102–104] With a synthetic route toward metal complex functionalized nanocages established, the exploration of its utility in making more complex nanocage

derivatives was desirable toward the further exploration and understanding of their synthesis and properties.

To this end, the idea of retaining hydrophobicity after the core removal step was an attractive target, thus potentially creating a nanocage with a hydrophobic cavity. This would potentially allow for an increased ability for the nano-

cages to sequester molecules in their hollow interior cavity (as for covalently synthesized core hollowed nanocages), yet still allow for hydrophobic molecule sequestration. For example, in 2006, Wooley and coworkers^[105] showed that the re-incorporation of hydrophobic moieties (dye labeled lipid molecules) into the cavity of a hydrophilic hollow cross-linked PAA nanocage, increased their uptake of a dye molecule by 35% over that of the nanocage’s parent nanoparticle. Thus, it has been proposed that an increase in the interior free volume of a nanostructure, such as that observed in a nanocage, enables for the increase in loading of sequestered molecules in the cavity.

The mild, selective, and facile nature of the core removal step of the asymmetric SCS ‘pincer’ nanocage strategy, was particularly advantageous toward this new hydrophobic nanocage target. Furthermore, the ability of this strategy to enable the retention of fully complexed SCS Pd(II) complexes was desirable for their later use in supported catalysis applications of hydrophobic substrates in water.^[106] Given such features, the asymmetric SCS Pd(II) pyridine complex linked strategy was adopted by O’Reilly and coworkers^[48] and modified upon the addition of a third, covalently linked hydrophobic block located between the hydrophilic PAA and hydrophobic PS blocks (Figure 13). Thus, in theory, upon self-assembly into triblock micelles, cross-linking to give nanoparticles and subsequent selective PS core removal, the targeted core hollowed, hydrophobic nanocages incorporating a new PMA internal shell layer could be accessed.

An asymmetric SCS Pd(II) pyridine complex linked triblock terpolymer was synthesized with the structure: poly(acrylic acid)-*b*-poly(methyl acrylate)-[Pd]-PS or $\text{PAA}_{90}\text{-PMA}_{45}\text{-[Pd]-PS}_{35}$, upon polymerization with functional CRP initiator species.^[48] This strategy relies upon the established complexation chemistries of the previous system, but utilizes reversible addition fragmentation chain transfer (RAFT) polymerization to synthesize a covalently linked amphiphilic diblock ($\text{PAA}_{90}\text{-PMA}_{45}\text{-[Pd]}$) which, when complexed to a second block bearing a pyridine functionality,

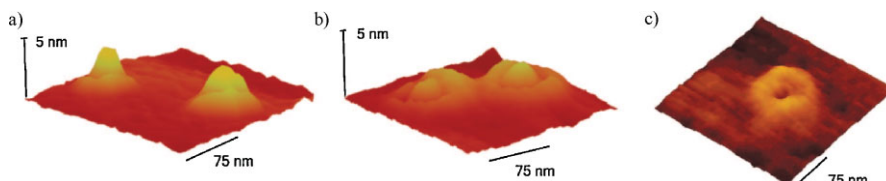


Figure 12. (a, b) AFM images of SCS “pincer” Pd(II) nanoparticles and (c) evolution into core hollowed SCS “pincer” Pd(II) nanocages.^[45]

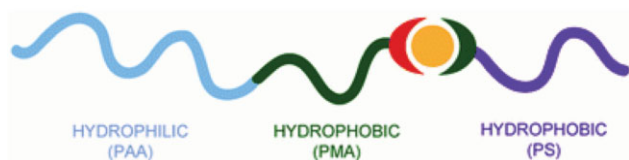


Figure 13. Schematic representation of the asymmetrically linked metallo-supramolecular triblock terpolymer, utilized for the synthesis of hydrophobic nanocages.^[48]

PS₃₅- creates the unsymmetrical supramolecular metallo-triblock terpolymer. The PAA₉₀-PMA₄₅-[copolymer was reacted to remove the thiocarbonyl end group to prevent it from binding to the palladium metal center. The end capped copolymer was then Pd(II) complexed and combined with a PS₃₅-block giving the triblock, PAA₉₀-PMA₄₅-[Pd]-PS₃₅ as evidenced by ¹H- and ¹³C NMR spectroscopies. The triblock terpolymer was self-assembled into triblock micelles in which the PS and PMA insoluble blocks were presumed to be multi-compartmentalized, based on their incompatibility, as observed for covalently linked PAA-*b*-PMA-*b*-PS micelles.^[107,108]

The micelles were then covalently cross-linked (ca. 25%) in their PAA shell domain to give triblock nanoparticles (Figure 14). Core removal of the nanoparticles at a lowered pH = 5, produced internally excavated, PAA-*b*-PMA-[Pd nanocages bearing SCS 'pincer' Pd(II) complexes and hydrophobic PMA domains, which were proposed to be highly suitable for hydrophobic sequestration and nanoreactor/nanocatalysis applications. Moreover, the enclosed nanosized cavity of these functional hydrophobic nanocages may provide a unique environment for catalysis which may potentially increase yields and decrease reaction times.^[9]

Block copolymers consisting of incompatible segments are known to self-assemble into ordered cylindrical micro-domained nanostructures in the solid state via the micro-phase separation of each homopolymer, upon evaporation of a good solvent from a copolymer solution on a substrate. Research in recent years has utilized this separation behavior

to create nanoporous thin films derived from conventionally synthesized, covalently linked diblock copolymers.

It is proposed that such nanoporous materials hold great potential for applications as separation membranes, dielectrics, catalysts, and templates for lithography.^[109–111] To date, routes utilizing diblock copolymer assembly methods require relatively harsh conditions for prolonged periods of time to create the nanopores, i.e., to degrade or destroy the covalently bound inner core domain of the nanopores, which could inherently disrupt or destroy any imparted functionality on the nanopore walls which may render this technique potentially limited for functional nanoporous films.^[112]

To increase the versatility of this method, it would be interesting to develop a system based on a diblock copolymer that has a reversible linkage at the homopolymer intersection, thus enabling faster and milder pore hollowing, and crucially for the ability to impart functionality on the interior walls. Recent efforts toward this goal include using reversible covalent bonds (via UV-Vis bond cleavage) at the intersection, to enable mild and selective cleavage of the cylinders to create the nanopores, and potentially allow for further functionalization by post modification of the remaining reactive handles.^[113,114]

Toward the goal of wall-functionalized nanopores for applications in selective membranes and catalysis, Gohy and Schubert have pioneered the field of metallo-supramolecular copolymer thin films in the solid state. They showed that a thin film of a PS₃₇₅-[Ru]-PEO₂₂₅ diblock formed cylindrical micro-domains of PEO, oriented normally to the substrate, surrounded by a continuous PS phase, when spin-coated from a good solvent for both blocks (non-selective) (Figure 15). The thin film was then exposed to oxidative conditions to oxidize the Ru(II) ions to Ru(III), and as a result, transformed the *bis*-complexes into *mono*-complexes, thus opening the linkage between the PS and PEO blocks releasing the PEO cylinder blocks to create terpyridine Ru(II) complex lined nanopores. The formation of functionalized nanopores was evidenced by AFM, SFM, X-ray photon spectroscopy (XPS), and X-ray reflectivity.

In 2008, a further study by Gohy and Schubert on the thin film formation of a similar copolymer, PS₃₀₀-[Ru]-PEO₂₂₅, set out to determine the influence of the metal-ligand complex on the self-assembly behavior and how it deviates from covalently linked PS-*b*-PEO blocks. Among their findings, they reported that the average center-to-center distance of the cylindrical micro-domains,

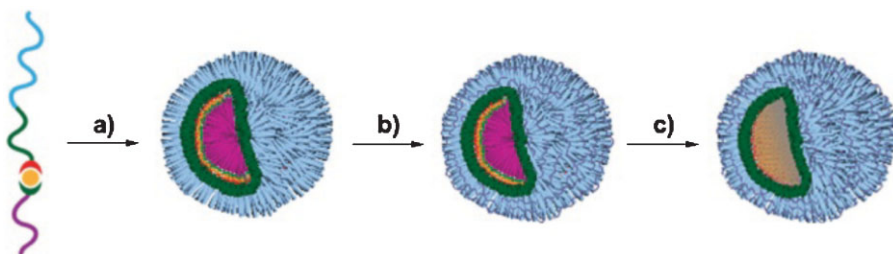


Figure 14. Schematic representation of the formation of nanocages via (a) self-assembly of asymmetrically linked metallo-supramolecular triblock copolymer to give micelles, (b) cross-linking to give nanoparticles, and (c) core hollowing at lowered pH to form hydrophobic, SCS "pincer" Pd(II) complex functionalized nanocages incorporating a new hydrophobic PMA layer.^[48]

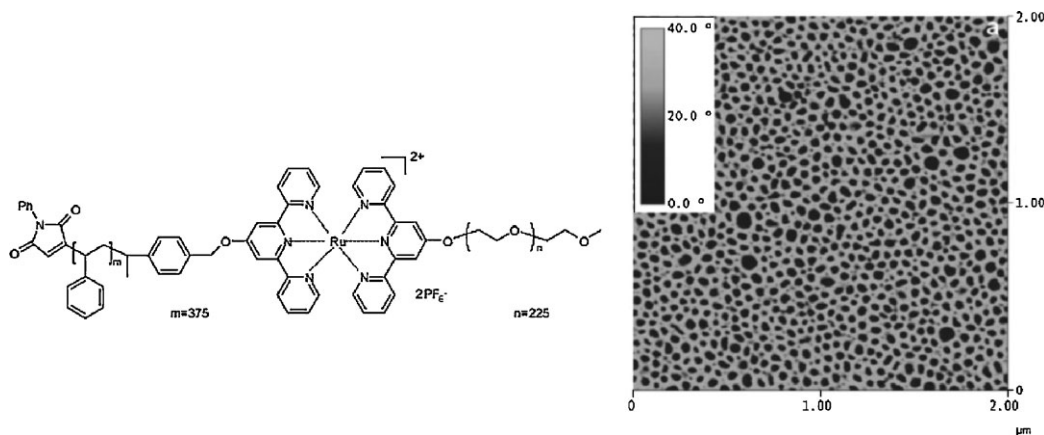


Figure 15. Schematic representation of the $\text{PS}_{375}\text{-[Ru]-PEO}_{225}$ diblock used and an AFM phase image showing the formation of cylindrical micro-domains of PEO in PS.^[115]

$k_{\text{C-C}}$, was 39 nm which is very different from that observed for a covalent PS-*b*-PEO block copolymer. Furthermore, the orientation of the cylinders for covalent diblocks is heavily dependent upon the conditions used for film preparation, i.e., polarity of the starting solvent used and relative humidity when forming the film. However, they found that the $\text{PS}_{300}\text{-[Ru]-PEO}_{225}$ diblocks formed cylindrical micro-domains oriented normal to the surface, independent of the preparation conditions.^[116]

They assigned these notable differences as a result of the presence of the metal complex at the interface between the two homopolymers. Furthermore, they postulated that these polymers behave as an ABC triblock copolymer where the metal-ligand complex and the associated counter-ions act as a strongly incompatible middle block which has a strong affinity for the silicon substrate used and that this also enhances the incompatibility of the PS and PEO blocks. They also showed that the first procedure

for film formation could be refined to produce better defined nanoporous films by exposing the film to THF vapors (solvent annealing) after spin coating, which improved the lateral ordering of the cylindrical micro-domains (Figure 16).

This methodology provides a route to extremely novel nanoporous films with well-defined interior terpyridine complex functionality. However, the conditions used to open the *bis*-complex were relatively harsh (a strong oxidizing agent, Ce(IV), at pH = 1), which may limit the possible applications of this system. To increase the versatility of this method, it would be interesting to develop a system based on a less stable supramolecular linkage, which would allow for the use of milder conditions for the core removal step to create the nanopores, yet still allow for retention of interior functionality. The use of another metal or an asymmetric metal complex as a linkage could be a particularly advantageous step toward this goal.^[116]

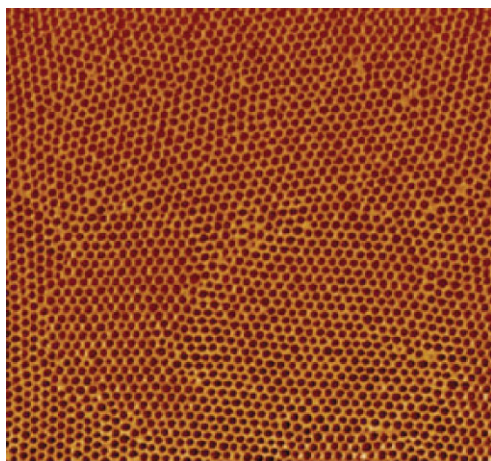


Figure 16. SFM phase image of a film of $\text{PS}_{300}\text{-[Ru]-PEO}_{225}$ spin coated from a THF solution and annealed for 24 h in THF vapor. The image size is $2 \times 2 \mu\text{m}^2$.^[116]

Stimuli Responsive Metallo-Supramolecular Block Copolymer Nanostructures

In a significant step toward the further advancement of self-assembled metallo-supramolecular polymers, Harruna and coworkers^[78,79] synthesized bipyridine and terpyridine linked PNIPAM and PS functionalized stars using RAFT polymerization. They also showed by AFM that the amphiphilic stars form uniform and thermoresponsive micelles in water. This thermoresponsive nature could potentially be utilized in polymer supported catalyst applications, since the polymer could be selectively removed and separated from aqueous solutions, and hence recovered and recycled afterwards for use in further reactions. Furthermore, once self-assembled, this thermoresponsive nature could be used to enable a change in morphology by shifting the hydrophobic to hydrophilic

ratio of the blocks. However, LCST data for the metallo-supramolecular polymers was not reported.

Schubert and coworkers have subsequently produced reports based upon PNIPAM containing metallo-supramolecular polymers. *Bis*-terpyridine Fe(II) and Zn(II) complex linked PNIPAM diblock copolymers were synthesized via RAFT techniques. It is known that LCST transitions can be influenced by several variables, such as electrolyte concentration, functional groups on the polymer chain ends, incorporation of comonomers, or molecular weight. The authors compared the LCST behavior of the uncomplexed ligand PNIPAM chains and their metal complexed diblocks.

Firstly, the authors showed by turbidity measurements, that all of the aqueous solutions of the polymers synthesized, exhibited LCST behavior as indicated by the clouding of the solutions upon heating. They found that an initially prepared PNIPAM with no chain end functionality had an LCST of 32.2 °C, while the terpyridine functionalized PNIPAM derived from this block showed a lower LCST of 26.1 °C due to the hydrophobicity of the chain end chelating unit. When *bis* complexed with Fe(II), the resulting copolymer showed a LCST of 31.6 °C with a PF₆[−] counter ion; however, when this was changed to CH₃COO[−], the LCST raised to 34.7 °C and when changed to Cl[−], the LCST changed to 35.2 °C. This increasing LCST trend was attributed to an increase in the relative hydrophilicity of the counter ion going from PF₆[−] to Cl[−]. When *bis* complexed to Zn(II), the copolymers showed a similar trend for counter ion influence on LCST behavior when in solution. Upon decomplexation via the addition of HEEDTA to selectively scavenge the Fe(II) or Zn(II) ions, the diblocks then showed similar LCST behavior as the starting terpyridine functionalized homopolymers, which hold great promise for the development of fully tuneable thermo-responsive metallo-supramolecular systems.^[117]

Further promising advances toward the future applications of metallo-polymers with thermoresponsive polymers include a recent report by Schubert and coworkers,^[44] who showed the self-assembly of a novel metallo-supramolecular triblock terpolymer; PS-*block*-poly(*para*-trifluoro-

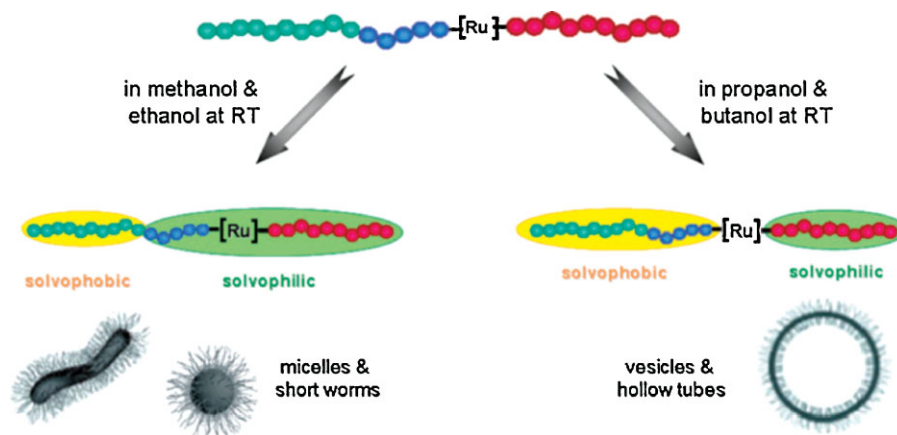


Figure 17. The formation of various morphologies from the self-assembly of metallo-supramolecular triblock copolymers in various solvents.^[44]

methylstyrene)-[Ru]-PEG, PS₇₆-*b*-PTFMS₄₂-[Ru]-PEG₇₀ linked by a *bis*-terpyridine ruthenium (II) complex. The amphiphilic metallo-supramolecular triblock copolymer self-assembled into various morphologies which were dependent upon the polarity of the solvent. This was attributed to a result of a change in the solubility of the PTFMS block in various solvents, which changes the solvophobic to solvophilic ratio and hence packing parameter, changing the interfacial curvature and thus favored morphology in solution. For example, the same triblock terpolymer formed spherical micelles in methanol, micelles, and worm-like micelles in ethanol but vesicles and hollow tubes in 2-propanol and 1-butanol respectively (Figure 17).

Interestingly, a solution of the triblock terpolymer in 2-propanol was shown to undergo a thermo-reversible morphology transition from vesicles to micelles. This is due to the upper critical solution temperature (UCST) of the PTFMS block in less polar solvents giving rise to an increased interfacial curvature of the amphiphile and hence a change in its preferred self-assembled morphology in solution (Figure 18).^[44]

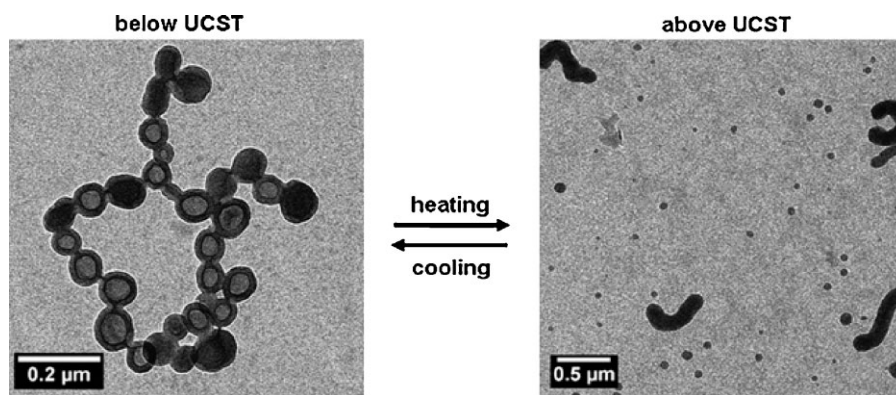


Figure 18. Representative TEM images showing the thermo-reversible transition from vesicles to micelles above and below the UCST for PTFMS.^[44]

The ability for self-assembled metallo-supramolecular polymers to change not only morphology, but size and sequestration properties, could enable them to be used for advanced encapsulation and release of both hydrophilic and hydrophobic molecules which would be attractive for not only their use as nanoreactors, but in wider reaching applications such as drug and/or gene delivery.

Conclusion

In recent years the self-assembly of metallo-supramolecular block copolymers has made significant progress toward achieving the synthesis of novel and functional nanostructures through versatile and facile strategies for many desirable applications. However, to achieve a higher level of complexity and hence make significant advancements in this field, chemists must start to utilize the whole breadth of well-studied transition metal coordination chemistry in the pursuit of this goal. Moreover, the specifically designed incorporation of uniquely tuneable coordination environments into metallo-supramolecular block copolymers and specifically their self-assembled nanostructures in solution, could facilitate morphological, structural, and chemical changes in response to external stimuli, offering access to novel application areas, such as nanocatalysis and drug delivery.

Furthermore, the combination of a selective ligand removal approach with multiple, orthogonal, asymmetric, non-covalent interactions and/or the incorporation of stimuli responsive polymers, may hold great promise in enabling the construction of highly tuneable polymer architectures, with a view for the creation of advanced self-assembled supramolecular structures with potentially, as yet unforeseen, unique properties and applications.

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