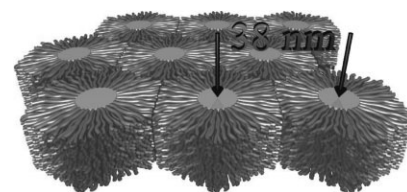


Metal–Ligand-Containing Polymers: Terpyridine as the Supramolecular Unit

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New and interesting properties can be obtained from macromolecular architectures functionalized with supramolecular moieties, particularly metal–ligand complexes. Self-assembly, based on the selective control of noncovalent interactions, guides the creation of hierarchically ordered materials providing access to novel structures and new properties. This field has expanded significantly in the last two decades, and one of the most ubiquitous functionalities is terpyridine. Despite its wide-spread use, much basic knowledge regarding the binding of terpyridine with metal ions remains unknown. Here, the binding constants of PEG-substituted terpyridine in relation to other literature reports are studied and a few examples of supramolecular materials from our laboratory are summarized.



Introduction

Many interactions are used to self-assemble molecules into supramolecular materials including hydrogen and metal bonds, π – π and donor–acceptor associations, electrostatics, hydrophilic–hydrophobic, and van der Waals forces.^[1] In contrast to the field of supramolecular chemistry, the use of polymeric macromolecules as basic elements in supramolecular materials has not received as much attention.^[2] However, supramolecular design allows more than just the building of complex architectures, it enables the simultaneous integration of increased functionality into the material.^[1] When appropriately designed, a supramolecular architecture will direct the organization of constituent molecules and express their functionality in the final material. Such materials are referred to as supramolecular materials since the supramolecular interaction is critical to their overall architecture, order, properties, and function.^[3] In fact, when a macromolecule plays a critical role in the overall assembly process this may be called supramolecular polymer science, which is clearly different from conven-

tional supramolecular chemistry, since the constituents are macromolecules as opposed to small molecules.

Many natural materials have unique and complex architectures that directly control their properties. Gaining a better understanding of the fundamental principles govern this assembly and their properties is one of the goals of supramolecular science.^[4] Moreover, supramolecular design allows an increased level of complexity and this is sure to generate new materials with tailored properties, which will be required over the next several decades as advance devices demand multifunctionality.^[2] Eventually, the essential features of many biological systems will be successfully mimicked by materials created through supramolecular design principles. In fact, the properties of these supramolecular systems will likely outperform natural systems because they are not limited to the building blocks of life but to the toolbox of organic and materials synthesis. As shown in Figure 1, several different architectures have been studied including the traditional diblock copolymer, but with one block containing a metal–ligand on every monomer (see Figure 1C), being one of the newest additions to the toolbox.

Although these approaches to new materials hold great promise; in many cases research progress is hindered because simple fundamental knowledge regarding the binding interactions remains unknown. Since terpyridine (terpy) is perhaps the most ubiquitous metal ligand used in

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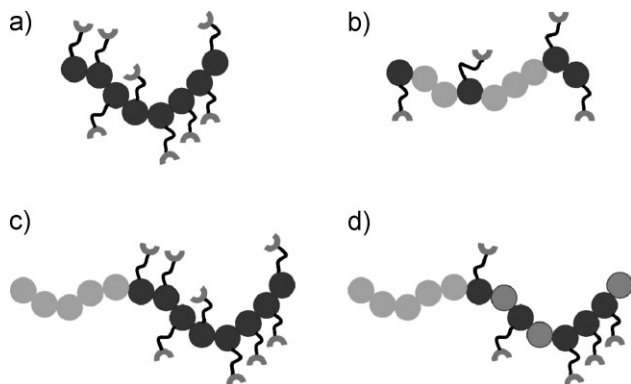


Figure 1. Schematic representation of different linear polymer architectures containing metal-ligand complexes at specific locations. (a) Homopolymer with metal-ligand on every monomer; (b) Random copolymer; (c) Diblock copolymer, and (d) Diblock copolymer, in which the metal-ligand block is a random copolymer of metal-ligand and nonmetal-ligand containing monomers.



Gregory N. Tew received a B.Sc. in Chemistry from North Carolina State University in 1995 and performed undergraduate research with Prof. D. A. Shultz. In 2000, he earned his Ph.D. from the University of Illinois-Urbana under Samuel Stupp after which he joined the Faculty at the Polymer Science and Engineering Department at the University of Massachusetts, Amherst. Before starting there, he spent one year in William DeGrado's laboratory at the University of Pennsylvania Medical School. Current research interests include bioinspired and biomimetic macromolecules, supramolecular polymer science, molecular self organization, and materials for regenerative medicine. This work has led to Young Investigator awards from the National Science Foundation (CAREER), the Office of Naval Research, the Army Research Office, 3M, and DuPont. The Army award was selected for the Presidential Early Career Award for Scientists and Engineers in 2002 and has funded the work from his laboratory related to metal-ligand polymers.



Raja Shunmugam received his bachelor degree in 1994, master degree in 1996 from V. O. C. College, Manonmaniam Sundaranar University. He received his Ph. D. from the Indian Institute of Technology Madras under Professor R. Dhamodharan. He then joined Professor Gregory N Tew's laboratory as a post doctoral research associate in 2003. In his graduation research, he mostly studied polymer modification chemistry, while his post doctoral research has focused more on the synthesis of novel polymers and materials chemistry. His research interest centers on an interdisciplinary approach using chemistry to study new materials and biological problems.

these systems (see Figure 2), the binding constants of a PEG-4'-substituted terpy in DMSO and water solutions were studied. These results are discussed in detail and in perspective with the relevant literature. This should provide a framework for future fundamental studies into the often-used terpyridine-based systems.

Results and Discussion

Terpyridine-Metal Binding Constants

Despite intense interest in terpy-based metal complexes over the years, limited data are available on the binding constants in various solvents. Although upon initial inspection the landscape looks relatively straightforward, the problem is quite complex due to the influences of counterions, solvents, reaction conditions, and kinetic concerns. It is well known that terpy can bind a wide range of metal ions in the periodic table including the transition metal series, lanthanides, and actinides.^[5] The transition metals that are more commonly studied include Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ru(II), Rh(III), Pd(II), Cd(II), Os(II), Ir(III), and Pt(II). The complexation reaction between terpy and different metal ions can be represented by an equilibrium reaction shown in Figure 3.^[6–8]

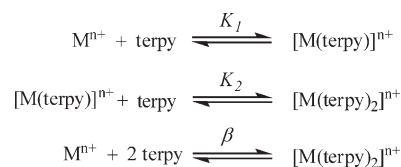
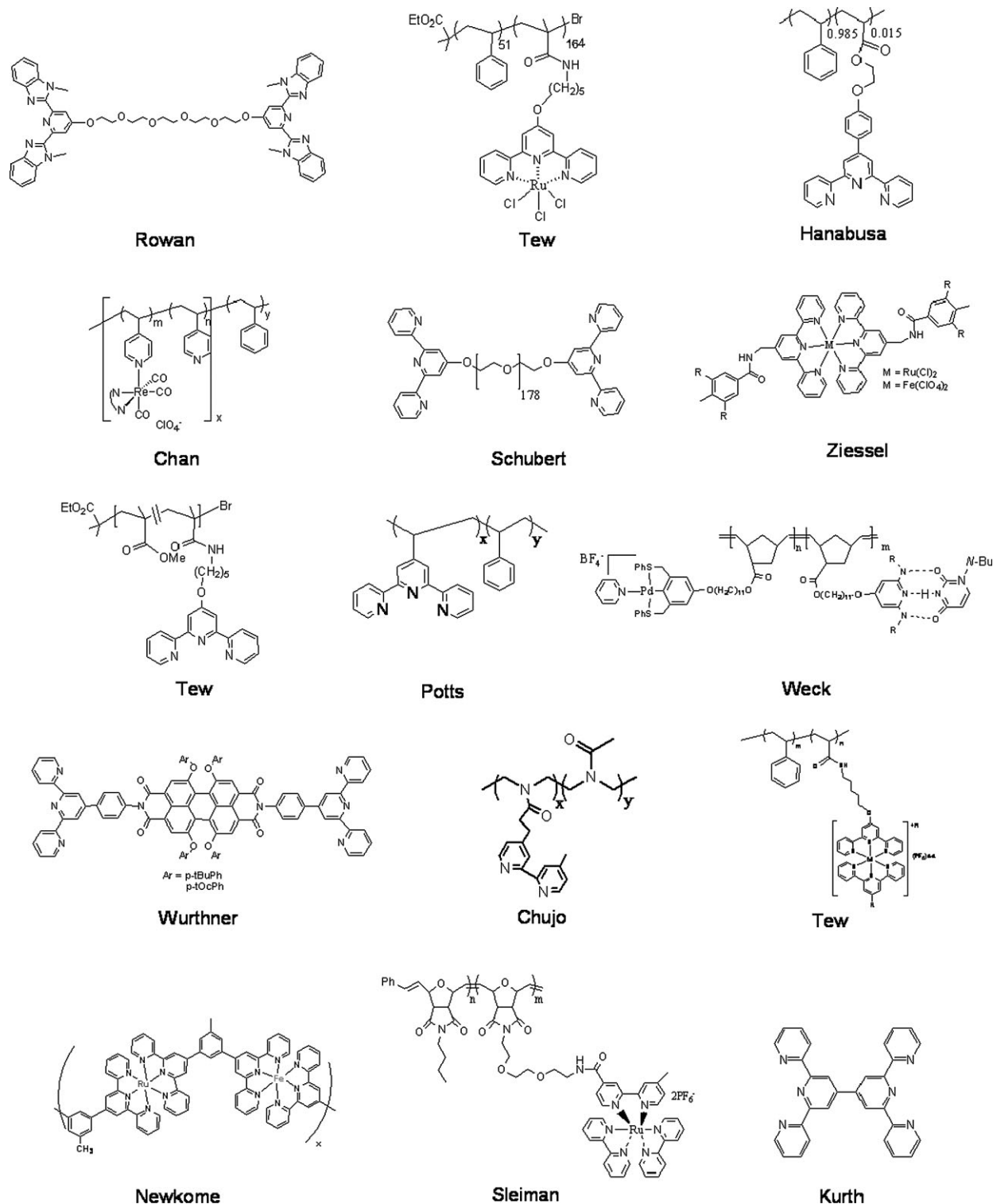


Figure 3. Complexation scheme between the metal ion and terpy to form the monoterpy and bisterpy complexes. M^{n+} = metal ion, K_1 , K_2 , and β are the thermodynamic equilibrium stability constants for $[M(\text{terpy})]^{n+}$ and $[M(\text{terpy})_2]^{n+}$ complexes. Since it is not always possible to determine K_1 and K_2 independently, β represents the total reaction ($\beta = K_1 K_2$).

Ideally, formation of the bis-complex $[M(\text{terpy})_2]^{n+}$ occurs in two steps, reaction of the metal ion with terpy to form the monocomplex $[M(\text{terpy})]^{n+}$ followed by reaction with a second free terpy to form the bis-complex. The extent of these reactions is determined by the stability constants K_1 and K_2 . Although there are not many studies in the literature specifically conducted to measure K_1 and K_2 for a wide range of metal ions and terpy, some values are collected in Table 1.^[9] This is one example of the difficulties researchers face; all of these binding constants are in water while most of the self-assembly studies are conducted in organic solvents. In addition, this simplified scheme indicates that it is relatively easy to form the monocomplex, $[M(\text{terpy})]^{n+}$; however, it is often observed that the bis complex is formed preferentially, as discussed below.



■ Figure 2. Various chemical structures containing terpyridine, or close derivatives.

More recently, Würthner reported lower limit stability constants for the reaction between terpy and five metal ions [four of them identical to Hogg and Wilkins,^[10] $M = \text{Fe(II)}$, Co(II) , Ni(II) , and Cu(II)] using a combination of UV–Vis,

NMR, and isothermal titration calorimetry (ITC) in acetonitrile (see Table 2).^[6] In their detailed studies, they examined the forward (metal ions into terpy) and reverse titration (terpy into metal ions) allowing more insight into

Table 1. Thermodynamic stability constants determined for a series of $M(\text{terpy})_2^{2+}$ complexes in water at 25 °C.^[9]

	$\log K_1/M^{-1}$	$\log \beta/M^{-2}$
	$M^{2+} \rightarrow [M(\text{terpy})]^{2+}$	$2\text{terpy} + M^{2+} \rightarrow [M(\text{terpy})_2]^{2+}$
Mn(II)	4.4	–
Fe(II)	7.1	20.9
Co(II)	8.4	18.3
Ni(II)	10.7	21.8
Zn(II)	6.0	–

the thermodynamic landscape. They examined only the perchlorate salts in acetonitrile so that their different methods could be compared internally. As a result of their studies, lower-limit values for K_1 , K_2 , and β were reported and are collected in Table 2. Using NMR, which was able to distinguish the mono- and biscomplexes of Zn(II), they showed that at metal ion/terpy ratios of 1:2, 1:1, and 2:1 there was 100, 60, and 25% bis complex, respectively. These studies raise the issue of kinetics, or complex lifetimes, which adds yet another layer of complexity to the landscape.

In work using terpy to sense metal ions in minute quantities, the discovery of a unique color change in the presence of Hg(II) prompted Tew and co-workers to investigate the binding constant for this metal ion along with Co(II) and Cu(II).^[11] Using the water-soluble molecule shown in Figure 4, ITC experiments were performed in the forward direction and the determined $\log K$ s were measured to be 6, 7, and 8, for Hg(II), Co(II), and Cu(II) respectively. The ability to reversibly form the mono Cu(II) complex was also observed in Tew and co-workers' ITC experiments.^[6,11] For comparison, $\log K$ was measured for Co(II) in neat water and did not change appreciably compared to the DMSO/water mixture, although changes were observed in the enthalpy and entropy values. This highlights one of the unique features of this terpy molecule, which is solubility in a host of different solvents and, as a

result, may allow access to stability constants for identical systems as a function of solvent.

One of the biggest concerns for accurately estimating stability constants by ITC with available equilibrium models is obtaining enough data points along the critical transition to allow good curve fitting. In some cases, there may not actually be any data points along the inflection point of the isotherm; however, as shown in Figure 4, it is possible to obtain a reasonable number of data points along the transition. The curves shown in Figure 4 were successfully fitted using several different parameters including a one-site ($\log K \approx 7$) or a two-site model ($\log K_A \approx 8$, $\log K_B \approx 8$). In addition, manually adding 5% error to the measured heat values, systematically or randomly, did little to influence the fitted curve and therefore the obtained K . Not surprising, the largest changes in K (around 1.5 logs) were observed when the values near the inflection point were changed. These data manipulation experiments illustrate that small errors on the measured heats at each injection do not result in significantly different observed binding constants. Hence, real differences in the binding behavior of terpy with metal ions should be observable using ITC. It is worth mentioning that the two-site model provides K values of very similar magnitude for Co(II), which presumably correspond to K_1 and K_2 ; however, we have chosen not to report them.

Another concern for any method is the potential for competitive equilibrium events (for example, formation of the monocomplex), but with ITC these events would not be observed, unlike, for example, NMR or UV–vis. However, using rate constants from Hogg and Wilkins^[10] and molar concentrations in the ITC experiments, the presence of Cobalt monocomplex at 0.5 metal/terpy is expected to be minimal. This agrees with Würthner's NMR experiments on Zn(II) which showed very little monocomplex until after the 0.5 metal ion/ligand ratio.

The complicated role of counterions, solvent, and even molecular structure can be highlighted here by comparing several different observations from the literature. Wilkins studied complexes in water, while Würthner studied them in acetonitrile; within one log their values of K_1 for Co(II)

Table 2. Lower limits for the binding constants determined for a series of $M(\text{terpy})_2(\text{ClO}_4)_2$ complexes in acetonitrile by ITC at 25.3–25.5 °C.

	$\log K_1/M^{-1}$	$\log K_2/M^{-1}$	$\log \beta/M^{-2}$
	$M^{2+} \rightarrow [M(\text{terpy})]^{2+}$	$M(\text{terpy})^{2+} \rightarrow [M(\text{terpy})_2]^{2+}$	$2\text{terpy} + M^{2+} \rightarrow [M(\text{terpy})_2]^{2+}$
Fe(II)	>8	>8	>16
Co(II)	>8	>8	>16
Ni(II)	>8	>8	>16
Zn(II)	>8	>8	>16
Cu(II)	>8	≈6	>16

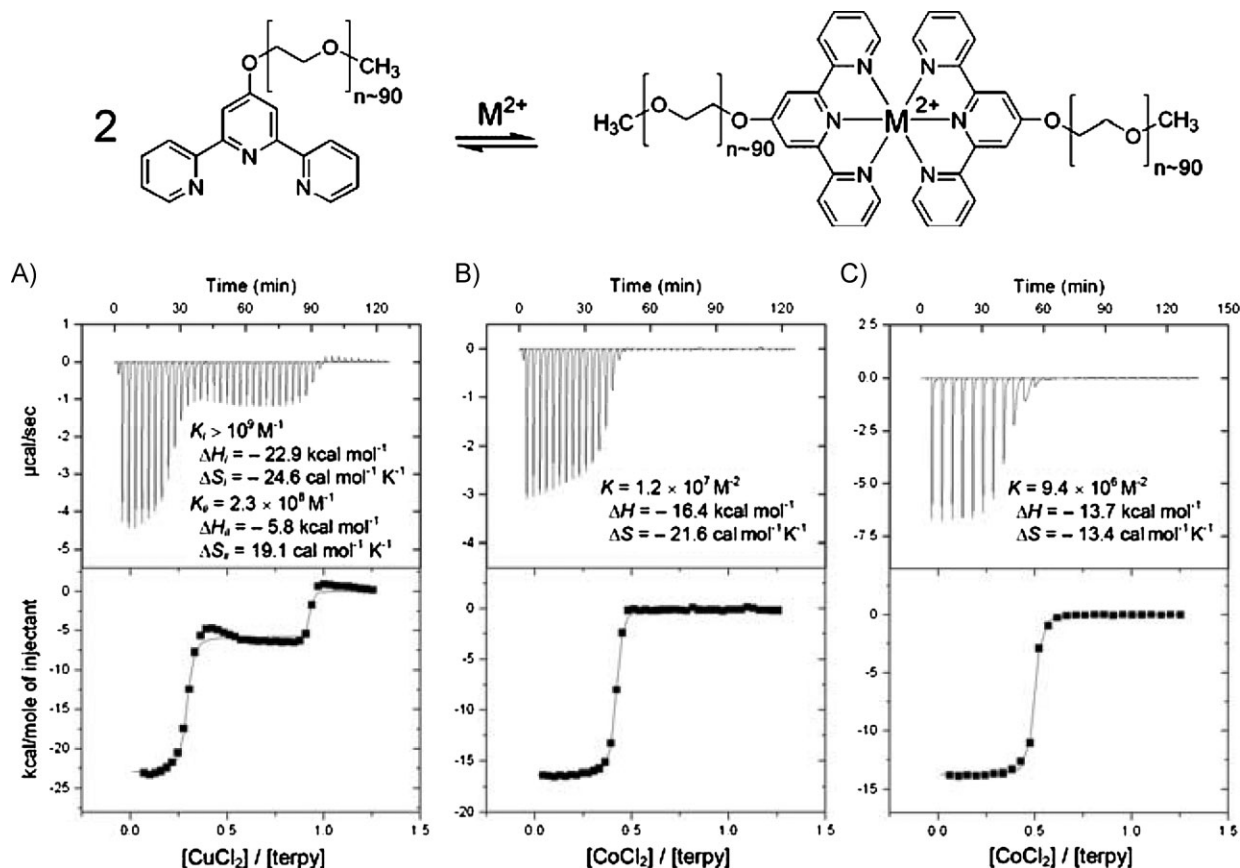


Figure 4. Chemical reaction showing the titration studied by ITC along with three different systems. (A) and (B) were performed in DMSO/water mixtures while (C) was performed in neat water. All values are based on one-site model.

and Fe(II) agree while Ni(II) is two logs higher and Zn(II) is two logs lower (Würthner reports lower limits so Ni(II) might have closer agreement). In identical experiments performed in the same laboratory, Würthner reported that zinc trifluoromethane sulfonate showed 10% bis complex at an excess metal-ion ratio (two metal ions for every one terpy) compared to the perchlorate, which gave 25%. Che and co-workers reported no reversibility with Zn(II) when using acetate or chloride counterions in DMSO, but reversible complexes with nitrate.^[12] Their structure was a 4'-oxo-alkyl substituted terpy compared to unsubstituted terpy used by Würthner. Similarly, Tew's ethylene oxide substituted terpy, which rendered it water soluble, also has a 4' donating atom, which would be expected to influence the electron density of the ligating nitrogen, especially with regard to the back-donation of electron density from the metal ion. Schubert and co-workers reported ITC-obtained K values of 10^8 for 4'-chloro-terpyridine (again 4'-substituted) in MeOH with cobalt (II) acetate.^[13]

When metal ion is titrated into terpy solutions, the expected product is the bis-metal complex. According to the Equations shown in Figure 3, this should yield β . However, the values of K from Schubert and Tew are on the order 10^8 , more similar to K_1 or K_2 . If the curves are extremely sharp, it

could follow that $K_2 = K_1 = K$ so that only one K is measured; on the other hand, if K_1 is rate-limiting it may be the observed K . Further, as mentioned above, the two-side model yields two K values on the order 10^8 so that the product would be on the order 10^{16} , similar to values reported for β . In any case, ITC provides insight into the thermodynamic landscape, which can be coupled with functionalized molecules to build a database of stability constants in various solvents. This will also allow the influence of solvent on enthalpy and entropy to be compared directly. These various solvents may also be used for kinetic studies which are of equal importance.

Although the bis-complex $[M(\text{terpy})_2]^{n+}$ is the final form obtained in solution (usually), the dynamic nature of these complexes were investigated by Hogg and Wilkins for the reaction of various $[M(\text{terpy})_2]^{n+}$ complexes with excess terpy in water and by Würthner in acetonitrile. Hogg and Wilkins showed that $[\text{Fe}(\text{terpy})_2]^{2+}$ and $[\text{Ni}(\text{terpy})_2]^{2+}$ are kinetically stable with half-lives of $t_{1/2} = 8400$ and 610 min, respectively, while $[\text{Co}(\text{terpy})_2]^{2+}$ is much more reversible with $t_{1/2} = 60$ min. Würthner reported that Zn(II) perchlorate is reversible by NMR. Schubert found that Cu(II), Co(II), and Cd(II) complexes were also labile in viscometry experiments with terpy-substituted poly(ethylene

oxide).^[14] The monocomplexes $[M(\text{terpy})\text{Br}_2]$ of Fe(II), Fe(III), Co(II), and Ni(II) have been reported but since they are expected to disassemble in solvent certain caution should be appreciated.^[15] In contrast, stable monoterpy complexes can routinely be made with Ru(III), Rh(III), Os(III), and Ir(III).^[14,16–27] The $[\text{Ru}(\text{terpy})_2^{2+}]$ complex is relatively easy to synthesize in either symmetric or asymmetric forms and its photophysical data are available in the literature making it one of the most popular choices. $[\text{Ir}(\text{terpy})_2^{2+}]$ is not as easy to synthesize as its ruthenium counterpart but due to its desirable emission properties and the potential use in many applications^[19–21,23,24,28–30] has received some attention in polymeric side chains.^[31–33]

Despite the limited binding constant data available for the environments in which supramolecular polymer chemistry studies have been conducted, a variety of interesting materials have been reported. The focus below shifts from fundamental binding constant studies to a discussion of synthetic methods used to generate macromolecules inspired by Figure 1 and then a brief highlight of various materials generated from these novel macromolecules.

Macromolecular Chemical Synthesis

It appears that the initial reports on macromolecules containing metal complexes, or at least terpy, can be traced back over more than 20 years ago with the initial reports by Potts and Usifer^[34] and Hanabusa et al.,^[27,28] in which they reported the conventional radical (co)polymerization of vinyl functionalized terpys. The initial polymers^[34] had molecular weight distributions (MWD) of 10 to 44 depending on the position of the vinyl bond. Copolymers with styrene had narrower MWDs but were still significantly broad; the reactivity ratios between styrene and 4'-viny1-2,2':6',2''-terpyridinyl were determined to be 0.47 and 1.12, respectively. They reported mono terpy complexes with Co and Zn but the materials were significantly insoluble, hindering characterization. Hanabusa, on the other hand, radically copolymerized terpy based acrylate monomers with styrene and methyl methacrylate (see Figure 1). The inherent viscosity of the copolymer solutions decreased with the complexation with Fe(II) suggesting polymer chain shrinkage. In recent years, Fraser and co-workers,^[35–40] Schubert and co-workers,^[8,41–51] Sleiman and co-workers,^[52–54] Calzai and Tew^[55], and Weck and co-workers,^[56–60] among others have become interested in more precise polymer architectures by employing controlled polymerization techniques (see Figure 4). Their focus has been on the noncovalent functionalization with metal complexes and hydrogen bonding to achieve multistep and orthogonal self-assembly. The majority of these approaches have polymerized metal complexes or grown polymers in the presence of metal complexes.

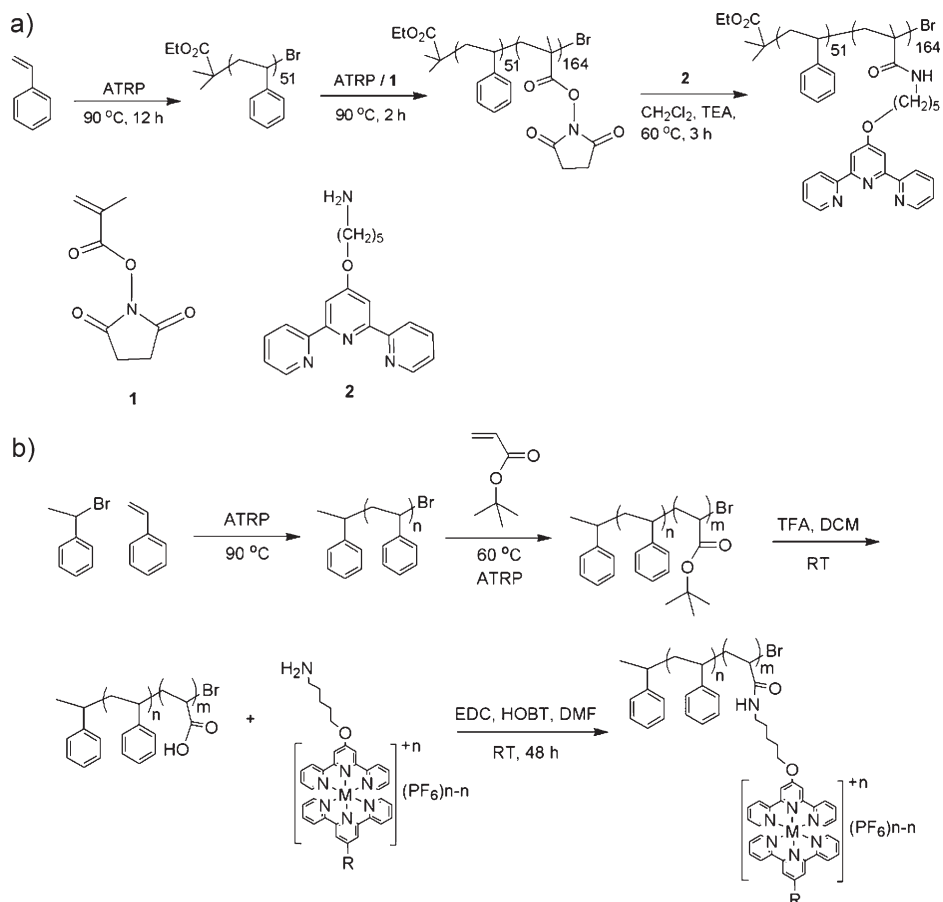
Interestingly, the direct polymerization and/or characterization of polymers containing terpy proved to be extremely difficult. Not surprisingly, methods such as ATRP are incompatible with such a large quantity of terpy during the reaction and even when the polymer can be made, for example by RAFT, characterizing the polymer with SEC can be impossible, or at least cost prohibitive. In order to establish a broad synthetic platform that would allow the synthesis of various monomers and architectures containing terpy anywhere along the backbone, Tew and co-workers reported several different strategies including the first direct polymerization of block-random copolymers and two indirect, or post-polymerization, strategies.^[61–64] Figure 5 outlines two indirect methods leading to well-characterized copolymers including block copolymers with dense metal–ligand functionality. One of the most attractive aspects of these indirect methods is their versatility toward metal–ligands other than terpy. It appears that as long as an amine can be placed into the metal–ligand, or complex, these indirect methods can be employed.

Self-Assembled Materials

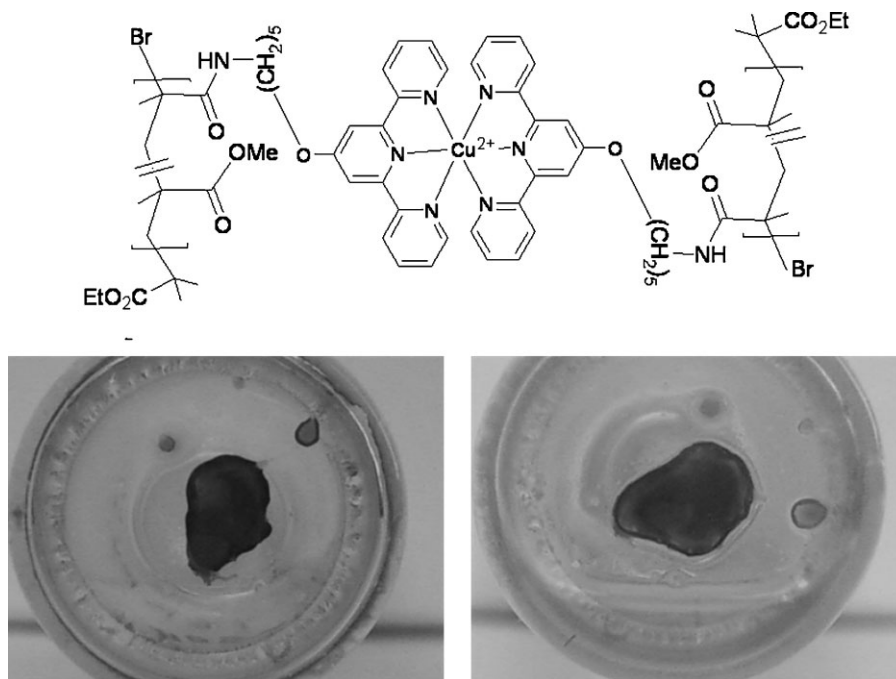
Gels

Supramolecular organogels have recently evolved as fascinating smart materials due to their potential applications as rheology modifiers, stimuli-responsive materials such as sensors and actuators and drug carriers. Despite this intense interest in gelators, it is rather surprising that organo- or hydrogels via metallophilic interactions are not very well explored in the literature even though metal coordination plays the major role in supramolecular chemistry. Chujo reported very early that bipyridyl-substituted poly(oxazoline)s complexed with Co(III) formed reversible intermolecular crosslinked networks that responded to both redox and thermal stimuli (see Figure 2). The system formed thermally reversible crosslinked networks with Fe(II). Similarly, Tew et al. reported that the intrinsic viscosity of solutions containing terpy-functionalized polymers increased as Cu(II) was added to the solution.^[64] Schubert and co-workers studied the impact of Fe(II) and Zn(II) on crosslinking and observed that Fe(II) increased the relative viscosity more than Zn(II) due to its higher binding constant.^[35,65–68]

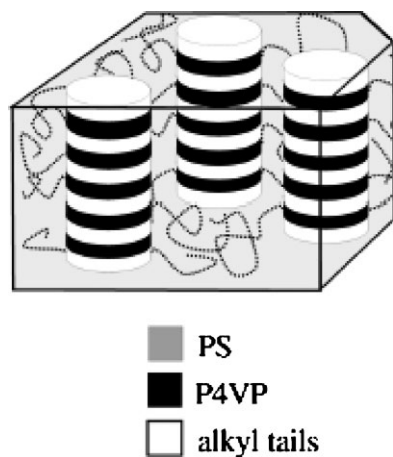
Instead of using macromolecules to form crosslinked networks, Rowan and co-workers elegantly manipulated this concept by using transition metal ions and lanthanides to form linear chains and create cross-linked junction points from a α,ω -assembler based on bis(2,6-bis(1'-methylbenzimidazolyl)-4-hydroxypyridine) functionalized with ethylene oxide (see Figure 8).^[69,70] Tew studied solutions containing higher concentrations of polymer, which led to crosslinked materials (see Figure 5). This figure shows that the blue solid is insoluble in any solvent, including



■ Figure 5. Schematic representation of two indirect methods that leads to well-characterized block-copolymers.



■ Figure 6. Picture of a highly crosslinked gel produced by adding Cu(II) ions to a more concentrated polymer solution. The addition of DMF, a good solvent for the apo- and metal-containing polymer, swells but does not dissolve the sample.

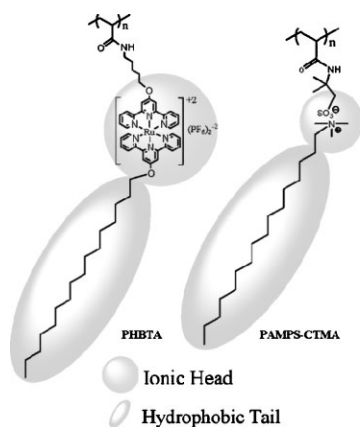


■ Figure 7. Schematic representation of lamellar within cylinders.

DMF, which usually dissolves both the apo-polymer (no metal ion) and metal-complexed polymer. This insolubility suggests the precipitate is highly crosslinked by the metal-ligand complexes.

Hierarchical Assembly

Learning how to program self-assembly into functional materials with organization over many different length-scales remains a very important scientific challenge. One such example within block copolymers has been the discovery of “structure-within-structure” morphologies (see Figure 7). On one hand, conventional AB diblock copolymers form highly organized microphase separated structures with the characteristic length scale providing the long spacing, which is usually within the 10–100-nm range. On the other hand, organization at a smaller length scale has been achieved using liquid-crystalline (LC) polymers, polyelectrolyte/surfactant complexes, or hydrogen bonded



■ Figure 8. (left) Chemical structure of PHBTA and poly(2-acrylamido-2-methyl-1-propanesulfonate) cetyltrimethylammonium salt), PAMPS-CTMA. Each structure is composed from an acrylamide backbone with side-chains containing a charge unit and long hydrophobic alkyl group. (right) Schematic representation of the hexagonal phase adopted by PHBTA.

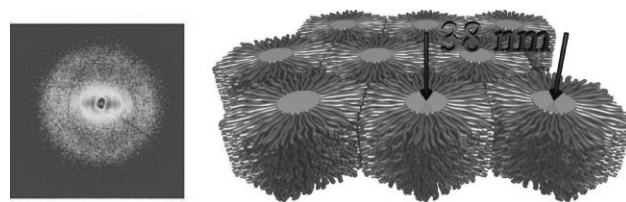
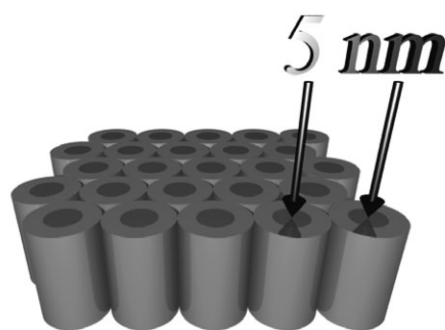


Figure 9. (left) Oriented SAXS pattern leading to characterization of the “cylinders in a sea of rods” morphology. (right) Schematic illustration of the hierarchically ordered “cylinders in a sea of rods.”

polymer/amphiphile complexes. These materials form organized nanostructures with a typical length scale of 2–6 nm. One such example is schematically shown in Figure 6 using polystyrene-block-poly(4-vinylpyridine), (PS-*b*-P4VP), hydrogen bonded to an amphiphile like nonadecylphenol.^[71–76] Using these principles, lamellar-within-lamellar, lamellar-within-cylindrical, cylindrical-within-lamellar, spherical-within-lamellar, and lamellar-within-spherical morphologies have been reported. These materials, which take advantage of the pyridine ring in the poly(vinyl pyridine) block, are not side-chain containing metal-complexes polymers per say but do utilize supra-molecular interactions that generate a variety of “order-within-order” morphologies.

Recently, Aamer and Tew proposed that metal-complex containing homopolymers behaved as rigid-rod-like molecules due to the increase in persistence length generated by the metal complex. The observed rigidity was proposed to originate from the charged nature of the metal-complex resulting in a “polyelectrolyte-surfactant-like” complex (see Figure 7). Control experiments supported the importance of the C₁₆ chain and the bisterpyRu(II) complex, which caused backbone stiffening. One of the key design criteria for this system was the ability to synthesis asymmetric metal complexes (Figure 8).



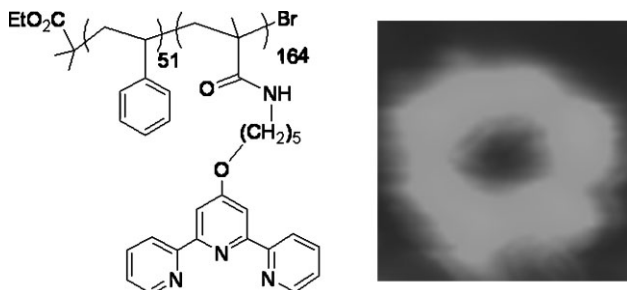


Figure 10. Chemical structure of block copolymer and its self-assembly in the presence of RuCl_3 , and its AFM image shows the formation of the aggregation upon metal chelation.

This work was then extended to diblock copolymer architectures, in which one block contains a dense array of metal-complexes, while the other block was based on styrene. This novel architecture led to hierarchical self-assembly of the p(S-b-HBTA) diblock into “cylinders in a sea of rods” morphology, which showed nanostructured order on two different length scales of 5.7 and 38 nm, as shown in Figure 9. The outer shell C_{16} chains of the homopolymer were crystalline in nature, which was retained even in the diblock and star copolymer architectures. This hierarchical “cylinders in a sea of rods” morphology is a direct result of the molecular design. Such a structure requires two critical elements to be included in the block architecture. Here, microphase separation into PS and PHBTA domains that pack into hexagonal cylinders (38 nm) and additionally the rodlike nature of the constituting elements within the PHBTA block (5.7 nm) (Figure 9).

The ability to organize single molecules into aggregates that then assemble into larger structures is another example of hierarchical organization. The block copolymer shown in Figure 10 was found to assemble into objects ca. 50 nm by light scattering upon the addition of RuCl_3 . When these objects were cast onto a low energy surface, like gold, they further assembled into circular structures which are always hollow in the middle with diameters of ca. 250 nm. The rich chemistry of the metal–ligand complex coupled to polymeric architectures will continue to generate interesting self-assembled materials (Figure 10).

Conclusion

Metal-containing polymers remain an important component of modern supramolecular polymer chemistry. The general availability of metal containing polymers will be critical to exploiting their “applications”. Fortunately, significant synthetic progress in the area of metal-containing polymers has established a robust platform for generating a great variety of materials. However, a greater

understanding of the basic metal–ligand binding chemistry remains essential for the development of future materials. In this report, a detailed discussion of the dynamic binding landscape is provided. Hopefully this will stimulate other binding studies with appropriate ligands, metals, and environmental conditions. As interdisciplinary science continues to grow stronger, metal containing polymers are likely to see increased growth and attention from chemists, physicists, engineers, and biologists.

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