

Emily Kate Harris (Autor) Polymer or Macrocycle? Cobalt Complexes of Ditopic 2,2':6',2"- Terpyridine Ligands with Flexible Spacers



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1 Introduction

1.1 Supramolecular chemistry and self-assembly

The term "supramolecular chemistry" incorporates the Latin prefix *supra*- meaning "above" or "beyond" and is therefore commonly defined as "chemistry beyond the molecule".¹ However, over the short history of this discipline, the term has come to have several other definitions including "the chemistry of intermolecular interactions or the non-covalent bond", "the formation of elaborate structures using coordination chemistry", or "the controlled organisation of multiple chemical components".²

While chemists have traditionally focused on the synthesis of molecules based on the irreversible formation of strong covalent bonds, supramolecular chemists are interested in the (usually) weak, reversible interactions between molecules. These intermolecular interactions include ion–ion, ion–dipole (including metal–ligand coordination bonds) and dipole–dipole interactions, hydrogen bonding, cation– π , anion– π and π – π interactions.¹ A summary some of these interactions is given in Table 1.1.^{1, 3}

Interaction	Energy	Stability	Lability	Example
	/ kJ mol ⁻¹			
Covalent Carbon	150 - 500	high	low	C–X
Ion–Ion	100 - 350	high	high	NaCl
Metal-Ligand	100 - 350	high	high	1 st row M–L
		high	medium	2 nd row M–L
		high	low	3 rd row M–L
Ion-Dipole (other)	50 - 200	high	high	crown ethers
Dipole-Dipole	5 - 50	low	high	carbonyls
Hydrogen Bond	4 - 60	medium	high	Х–Н…Ү
π-π	5 - 20	low	high	benzene

Table 1.1 Comparison of covalent and intermolecular interactions.^{1,3}

One of the core concepts in supramolecular chemistry is that of "self-assembly", or the spontaneous and reversible association of several molecular components into more complex supramolecular entities.¹ Reversibility of the assembly process is necessary to allow the system to "self-repair", or correct any defects in the initial assembly of the structure, ideally leading to the formation of a single thermodynamically stable product. By careful choice of the components and conditions used, the nature of the final product can often be predicted in advance, enabling the synthesis of supramolecular entities designed to have specific properties.

Much of the inspiration for supramolecular chemistry and self-assembly is drawn from biology, as nature has been self-assembling large, complex and functional structures based on weak interactions for billions of years. Examples of these include proteins, DNA and even viruses. An understanding of the processes that nature uses to build these structures could potentially provide an understanding of life at a level which is currently inconceivable. In the more immediate future, the application of even the most basic of these concepts could result in the development of new materials with remarkable properties.

Supramolecular assemblies based on directional interactions can be divided into two very broad categories; those forming polymeric species, and those forming discrete aggregates.¹ Considering specifically metallosupramolecular chemistry, or the assembly of supramolecular architectures based on metal–ligand interactions,⁴ ligands can be designed accordingly with metal-binding domains arranged in such a way that the formation of either polymers or discrete species is favoured. Alternatively, the metal ion can be protected such that it has only a limited number of coordination sites in a specific geometry available for coordination to the ligands.⁵ If the components are not designed in such a way as to promote the formation of a particular species, the outcome of the coordination is less certain, with the potential formation of polymers, discrete supramolecular species or mixtures of the two.^{6,7}

1.2 Metallosupramolecular polymerisation

The incorporation of metallosupramolecular building-blocks into polymeric systems has become an attractive area of research in polymer chemistry, leading to new materials which combine the properties of polymers with those of metal complexes (catalysis, light-emission, conduction etc.).^{8, 9} The properties of the resulting polymers can be tuned to suit individual circumstances by selection of the ligand, an appropriate metal cation and corresponding

counteranion. Differences in the thermodynamic and kinetic stability of the metal complexes within the polymeric system result in different degrees and reversibility of the polymerisation. Modification of the metal centre therefore affects the size of the resulting polymer, the response of the system towards changes in temperature, pH and addition of competing ligands or redox agents, and the physical properties of the material. Adjustment of the counterion alters the intermolecular interactions in the structure and, as a result, the solubility of the final polymer. Based on a single ligand, the synthesis of many different polymers with many distinct properties can therefore be envisaged. Considering in addition the wide variety of potential ligands, many thousands of new polymeric systems can be imagined. Even ligands with identical binding motifs can behave very differently on coordination to metal ions depending on the nature of the spacer linking the binding units.

1.3 Formation of discrete molecular species

Many examples of increasingly complex architectures have already been described in the literature, including molecular squares, cubes, boxes, racks, grids and ladders, cages or capsules, rosettes, catenanes, rotaxanes, helices, knots, and even a nanoscale version of the Borromean rings.¹ The number of possible structures for future self-assembled supramolecular architectures is probably only limited by the imagination of supramolecular chemists.

1.4 *Examples of metallosupramolecular polymerisation and macrocycle formation with ditopic bis(2,2':6',2''-terpyridine) ligands*

2,2':6',2"-Terpyridine-based (tpy) ligands have become attractive building-blocks for the formation of self-assembled species in metallosupramolecular chemistry.¹⁰ These ligands have several advantages over the related bidentate 2,2'-bipyridine (bpy) ligands. One of the most important of these is that, provided that symmetrically substituted ligands are used, the $\{M(tpy)_2\}$ motif is achiral, while the equivalent $\{M(bpy)_3\}$ species gives rise to Δ and Λ enantiomers. This, along with the increased complexity introduced by incorporating three ligands around each metal centre, becomes an important consideration for multinuclear species containing these metal-binding units.^{10, 11} Functionalisation of the 2,2':6',2"-terpyridine unit at the 4'-position preserves the symmetry of the ligand and there are many examples of ditopic bis(2,2':6',2"-terpyridine) ligands linked by a spacer through the 4'-

position. Some of these are described below. Careful design of a rigid spacer can lead to the preferential formation of metallosupramolecular polymers or discrete macrocyclic species. Alternatively, a flexible spacer can be incorporated into the ligand, making the outcome of the coordination to metal ions significantly more uncertain.

1.4.1 Metallosupramolecular polymerisation with rigid ditopic bis(2,2':6',2"terpyridine) ligands

Coordination of ditopic bis(2,2':6',2"-terpyridine) ligands containing rigid linear spacers to octahedral transition metal ions can be expected to give linear coordination polymers as shown in Scheme 1.1. Conjugated systems are particularly attractive due to their interesting electrochemical and photophysical properties. Several studies of the synthesis and properties of di- and trinuclear complexes containing this type of ligand have been carried out.¹¹⁻²¹



Scheme 1.1 Schematic representation of a metallosupramolecular polymer incorporating a ditopic bis(4'-substituted-2,2':6',2"-terpyridine) ligand.

One class of ligands used for the construction of rod-like metallosupramolecular polymers is the set of ditopic bis(4'-substituted-2,2':6',2"-terpyridine) ligands linked by phenylene spacer units. Some of these ligands are shown in Scheme 1.2,²²⁻³³ and have been used to synthesise metallosupramolecular polymers incorporating ruthenium(II),^{25, 26, 28, 29, 33} iron(II)^{22, 24, 27, 30, 31, 33} and cobalt(II)^{32, 33} metal ions. In addition, a ruthenium(II)-containing oligomer formed from seven monomer units has been assembled in a stepwise approach.²³

Introduction



Scheme 1.2 Ditopic bis(2,2':6',2"-terpyridine) ligands with rigid phenylene-based spacers.²²⁻³³

Formation of metallosupramolecular polymers was suggested by the broadening of the ¹H NMR spectrum,^{22, 25, 26} and confirmed with viscosity measurements^{25, 26} or analytical ultracentrifugation,²² and the synthesis of polymers consisting of at least 25 repeat units has been proposed.^{22, 25, 26, 29} As well as confirming the high molecular weights, viscosity measurements also demonstrated the rod-like structures of the polymers.^{25, 26} The properties and colours of the polymers were found to be easily adjusted by variation of the metal ion or by the introduction of substituents on the terminal pyridine rings of the ligand.³¹⁻³³

Other polymeric systems containing bis(2,2':6',2"-terpyridine) ligands with rigid spacers include ruthenium(II)-containing polyimides (for an example see Scheme 1.3 (top)),

synthesised using a polymerisation reaction between a bis(4'-(4-amino)phenyl-2,2':6',2"-terpyridine)ruthenium(II) complex and several dianhydride monomers,³⁴ and zinc(II)-containing polymers of ditopic bis(2,2':6',2"-terpyridine) ligands with perylene bisimide spacers with up to 35 repeat units (Scheme 1.3 (bottom)).³⁵ A library of other conjugated ditopic bis(2,2':6',2"-terpyridine) ligands with rigid ethene- or ethyne-based spacers and their zinc(II)-containing metallosupramolecular polymers was also recently synthesised,³⁶ illustrating the versatility of this polymerisation approach.



Scheme 1.3 Ruthenium(II)-containing polyimide with a ditopic bis(2,2':6',2"-terpyridine) ligand (top) and zinc(II)-containing polymer with a ditopic bis(2,2':6',2"-terpyridine) ligand with a perylene bisimide spacer (bottom).

1.4.2 Metallosupramolecular polymerisation with flexible ditopic bis(2,2':6',2"-terpyridine) ligands

If, instead of well-defined rigid spacers, a long flexible spacer is used to link the two 2,2':6',2"-terpyridine units, the outcome of the coordination is much less predictable. As well as synthesis of the desired polymer, formation of discrete metallomacrocycles is also possible. The use of ditopic ligands composed of covalent polymers end-functionalised with 2,2':6',2"-

terpyridine units as ligands was in response to the limitations of the existing coordination polymers based on ligands with short rigid spacers described above. These systems are usually sparingly soluble in water and common organic solvents, or require multi-step syntheses in order to incorporate solubilising side-chains. Additionally, the molecular weights of the resulting polymers are limited by the low molecular weights of the ligands.

The coordination chemistry of many divalent transition metal ions with ditopic ligands containing two 2,2':6',2"-terpyridine units linked by a poly(ethylene glycol) spacer has been studied in detail by Schubert.³⁷⁻⁴⁶ In addition, several different counteranions and a model system incorporating a ligand with a shorter chain di(ethylene glycol) spacer have been considered. A summary of the systems studied is shown in Scheme 1.4. The combination of the water-soluble poly(ethylene glycol) with a well-studied bis(2,2':6',2"-terpyridine) complex was anticipated to give water-soluble coordination polymers with interesting properties.



m = 2, 180 M = Fe, Cd, Cu, Co, Ni, Ru, Zn X = Cl, Br, OAc, BF₄, PF₆

Scheme 1.4 Metallosupramolecular polymers synthesised from bis(terpyridyl)di(ethylene glycol) and bis(terpyridyl)poly(ethylene glycol) ligands.³⁷⁻⁴⁶

The conditions required to synthesise the metallosupramolecular polymers vary depending on the metal ion chosen, but the process is identical to complexation reactions of other 2,2':6',2"-terpyridine ligands with metal ions. An automated parallel synthesis approach has also been developed, although this was found to give species with lower molecular weights.⁴² Formation of the bis(2,2':6',2"-terpyridine)metal complex was confirmed by ¹H NMR measurements and UV/vis titrations, with a maximum extinction coefficient found at a 1L:1M ratio,^{38, 39} and using a chloride counterion gave water-soluble complexes. Evidence for the

formation of extended metallopolymers was obtained using several techniques described below; however the formation of cyclic structures cannot be excluded.

The macroscopic properties of the materials resulting from the complexation of the ligand with all the metal ions used suggested the formation of extended coordination polymers. While the ligand itself was a powdery solid, the complexes had film-forming properties typical of polymers.³⁷⁻⁴¹ Films formed from the short chain di(ethylene glycol)-based ligand were brittle; this was attributed to the high charge density of the resulting polymers.³⁸ while complexes of the poly(ethylene glycol)-based ligand formed flexible films.⁴⁰ The signals in the ¹H NMR spectra of the complexes tended to be broadened, also suggesting the formation of extended coordination polymers.^{39, 41} MALDI-TOF mass spectrometry was expected to provide a useful insight into the molecular weights of the resulting polymers. However, for complexes of the di(ethylene glycol)-based ligand, only peaks corresponding to the free ligand and a $[MLX]^+$ species were observed.^{38, 39} As the ¹H NMR spectra showed that no free 2,2':6',2"-terpyridine units remained in solution after the complexation step,³⁹⁻⁴² the metalligand bonds were assumed to rupture under the conditions used. Analysis of the polymers formed from the longer chain ligands was more successful using MALDI-TOF mass spectrometry, with signals corresponding to oligomers with up to seven repeating units.^{39, 41} As the length of the polymers predicted by this characterisation technique did not agree with the (longer) lengths determined from other methods (see below), the absence of fragments with higher molecular weight was explained by insufficient desorption or decomplexation under the conditions used.

Viscosity measurements were carried out on all of the synthesised polymers in solution in order to estimate the proportion of high molecular weight species in the product mixtures.^{39-41,}

⁴³ The relative viscosity is related to the molecular weight of the polymers and the presence of small cyclic species will thus lead to a solution with a lower viscosity.⁴¹ In all cases, the maximum relative viscosity was obtained at 1L:1M ratios and addition of an excess of metal ions resulted in a decrease in the relative viscosity.^{39, 41} The maximum relative viscosity and the behaviour of the viscosity of the polymer solutions on addition of an excess of metal ions was found to be dependent on the nature of the metal salt used for the complexation. The maximum relative viscosity of polymer solutions of different metal ions increases in the order cadmium(II) < copper(II) < cobalt(II) < nickel(II) < iron(II).^{39, 41} This order corresponds qualitatively to the thermodynamic stability of the bis(2,2':6',2"-terpyridine) complexes.⁴⁷ The behaviour of the polymer solutions on addition of an excess of metal ions was related to the kinetic stability of complexes of the metal ions.^{39, 41} For kinetically very labile complexes such as the bis(2,2':6',2"-terpyridine)cobalt(II) and -copper(II) complexes,⁴⁸ the relative viscosity dropped sharply on addition of an excess of metal ions, whereas for complexes more stable towards ligand exchange such as those of iron(II) and nickel(II),⁴⁸ a more gradual decrease in the relative viscosity was observed.^{39, 41} Changing the anion also had an effect on the value of the maximum relative viscosity of bis(terpyridyl)poly(ethylene glycol)iron(II) polymer solutions.⁴²

The effect of the reaction conditions on the relative viscosity of the resultant polymer solution has also been studied.^{40, 41, 43} The synthetic procedure can be modified in three ways to give solutions with higher relative viscosities. Firstly, carrying out the reaction at higher concentrations results in higher relative viscosities as intermolecular complexation is favoured under these conditions (when considering a system under kinetic control).^{40, 41, 43} Secondly, an improved mode of metal salt addition, in which two equivalents of the metal salt are initially added to one equivalent of the ligand followed by addition of a second equivalent of the ligand, has also been found to increase the relative viscosity of the resulting polymer solutions.^{41, 43} Using an initial excess of metal salt is expected to result in the formation of mono(2,2':6',2"-terpyridine)metal complexes at both ends of the ligand, thus preventing the formation of [1+1] metallomacrocycles.^{41,43} Finally, the use of chloroform-ethanol (19:1) in place of ethanol as the solvent for the complexation reaction also leads to solutions with higher relative viscosities.⁴⁰ The 2,2':6',2"-terpyridine moieties are more soluble in chloroform and it is believed that they are therefore more accessible for complexation in this solvent mixture, resulting in a higher degree of polymerisation.³⁹⁻⁴¹ By size exclusion chromatographic studies (see below), it has also been established that the reaction time is important in determining the degree of polymerisation in ruthenium(II)-containing systems.⁴⁵ The highest molecular weights were observed after a reaction time of 12 hours and it was suggested that low molecular weight species are formed first, and then couple to give higher molecular weight polymers. At longer reaction times, the molecular weight decreases slightly. A possible explanation for this is that the complexation is an equilibrium process and the proportion of thermodynamically favoured rings increases with time.⁴⁵

Size exclusion chromatography (SEC) (or gel permeation chromatography (GPC)) is frequently used for the determination of the molecular weights of polymers, but presents

several problems for reversible systems, due to breaking of the metal-ligand bonds and reequilibration of the product mixture.⁴⁴ In addition, standards for calibration are not usually available for metallosupramolecular polymers. A GPC method was developed for the analysis of bis(terpyridyl)poly(ethylene glycol)ruthenium(II) tetrafluoroborate а metallosupramolecular polymer and the number averaged molecular weight was found to be 138000 g mol⁻¹ with a polydispersity index of 1.55.⁴⁴ This value is in good agreement with the average molecular masses determined by analytical ultracentrifugation $(143000 \text{ g mol}^{-1})^{44}$ and from viscosity measurements (123000 g mol⁻¹),⁴⁰ and these molecular weights correspond to polymers with 14 to 16 repeat units. The presence of other macromolecular species, potentially metallomacrocycles, is also suggested by the GPC data. While analytical ultracentrifugation⁴⁹ gives absolute molecular weights, removing the need for calibration standards, both the experimental procedure and the interpretation of the results are timeconsuming, making this method unsuitable as a standard characterisation technique.

Studies of the effects of oxidation³⁹ and addition of a competing ligand (HEDTA)^{38, 39} have confirmed the reversibility of the polymerisation. The bis(2,2':6',2"-terpyridine)iron(II) units in the iron(II) polymer of the bis(terpyridyl)di(ethylene glycol) ligand have been found to be stable up to 210 °C,^{38, 39} but cooling to room temperature after heating above this temperature results in a reversible formation of the complexes after 12 hours. The thermal properties and morphology of the linear coordination polymers have also been studied.^{40, 41, 46}

The concept behind these homopolymeric systems was extended and a similar simple synthetic strategy was developed for the formation of metallosupramolecular block copolymers, the covalent analogues of which can be difficult to synthesise using conventional polymerisation techniques.⁵⁰⁻⁵³ The synthesis of metallosupramolecular AB diblock copolymers (see Scheme 1.5) using ruthenium(II) as the metal centre,⁵³⁻⁵⁷ and those proposed more recently with cobalt(III) and nickel(II),⁵⁸ was extended to form metallosupramolecular ABA triblock copolymers based on similar ligands to the homopolymeric systems described above.⁵⁰⁻⁵³ Some of these metallosupramolecular ABA triblock copolymers are shown in Scheme 1.6, showing the versatility of the method.