

2,2':6',2''-Terpyridines: From chemical obscurity to common supramolecular motifs

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This *tutorial review* describes the use of 2,2':6',2''-terpyridine (tpy) metal-binding domains in supramolecular chemistry. The origins of tpy chemistry are described and the reasons for its current importance in supramolecular chemistry are explained. Examples of tpy compounds in a wide variety of supramolecular chemistry are presented. The content will be of interest to organic, inorganic, supramolecular and nanoscale chemists.

Introduction

This article is about the use of derivatives of the compound 2,2':6',2''-terpyridine (tpy, **1**, Fig. 1) in supramolecular chemistry. What is so special about this compound and what differentiates it from ligands such as 2,2'-bipyridine (bpy, **2**) and 1,10-phenanthroline (phen, **3**), which are encountered early on in any study of coordination chemistry? The recent explosion in tpy chemistry (Fig. 2) parallels the maturity of supramolecular (and particularly metallosupramolecular chemistry); a monograph on the chemistry of this ligand has recently been published.^{1a} This short article attempts to illustrate the variety of supramolecular chemistry possible with tpy metal-binding domains. The constraints of space have lead to an emphasis on our own contributions to the area.

Regardless of the precise definition of supramolecular (or supermolecular) chemistry, metallosupramolecular chemistry is concerned with the assembly of supramolecular structures through the interaction of metal ions with metal-binding domains (\equiv ligands). The specificity of the interactions are

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and development of 2,2':6',2''-terpyridine motifs into supramolecular chemistry.

defined by the preferred coordination number, geometry and donor-type of the metal ion, and the number, type and spatial arrangement of the donor atoms of the metal-binding domain. The tpy sub-structure is a typical metal-binding domain, presenting (usually) three near-coplanar nitrogen donor atoms to the metal ion. We will see the consequences of this shortly. However, before eating the pie, we must first catch the rabbit!

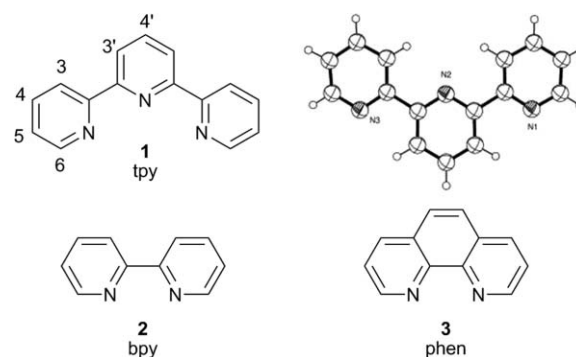


Fig. 1 Structures of the most commonly encountered oligopyridine ligands, tpy, bpy and phen, together with the solid state crystal structure of tpy^{1b} showing the *trans,trans*-conformation adopted in the solid state by most tpy derivatives. The numbering scheme for substituents in tpy derivatives is also shown.

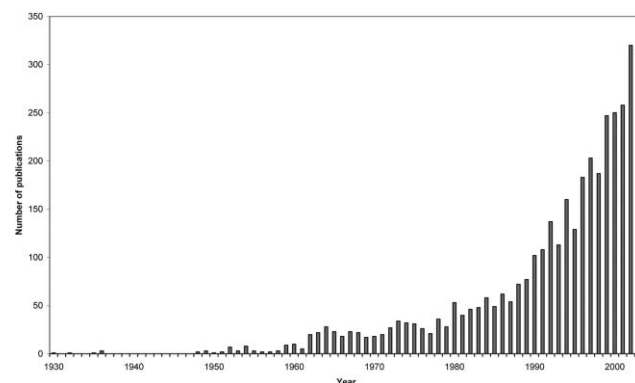


Fig. 2 Publications reporting tpy derivatives by year (Source: SciFinder2006, search date 30.8.2006).

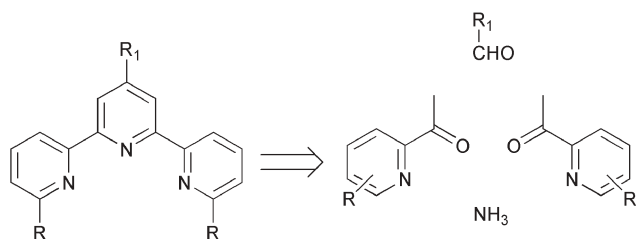
How can compounds containing tpy metal-binding domains be prepared?

Synthesis

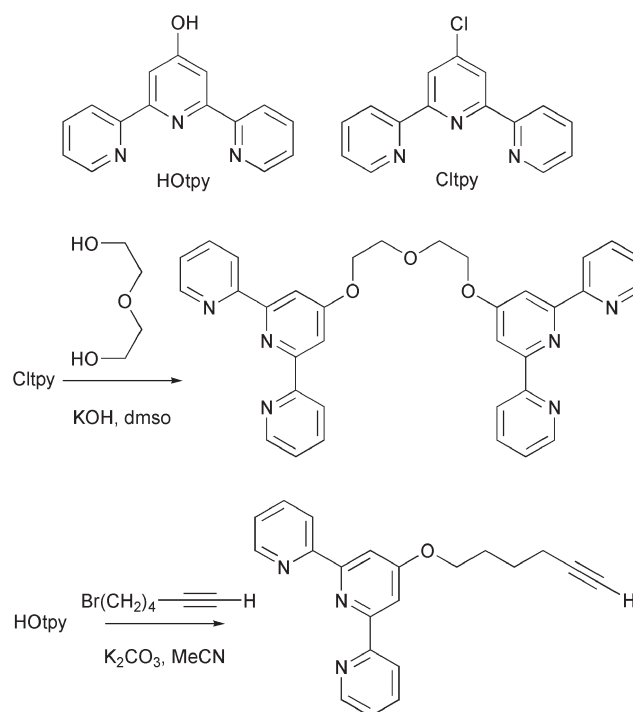
The first preparation of tpy was reported in 1932 and involved the oxidative condensation of pyridine by its reaction with iron(III) chloride,² a reaction that gives predominantly bpy. However, from the reaction of 8 kg of pyridine with 1.5 kg FeCl₃ at 50 atmospheres pressure and 340 °C, only 55 g of tpy was isolated. Although this reaction works (the present author is possibly the only person who has ever repeated it), it is far from safe, pleasant or convenient, and the work-up requires several weeks! Fortunately, a multitude of methods exist for the preparation of the tpy ring sub-structure and the introduction of substituents at specific sites, which may then undergo functional group interconversions to other desired functionalities.^{3–5,7}

Construction of the tpy core from three intact pyridine rings is initially an attractive prospect, and a variety of methods ranging from unselective Ullmann cross-couplings of 2-halopyridines with 2,6-dihalopyridines to Stille or Suzuki reactions of appropriate pyridines and 2,2'-bipyridines have proved popular at various times. All of these methods are dependent upon the availability of the appropriate 2- or 2,6-haloderivatives, and for all but the simplest compounds, these require preparation using 19th Century chemistry, very often through Tschitschibabin reactions (to introduce an amino substituent) followed by diazotization, hydrolysis and halogenation. Other reactive substituents on the pyridine do not usually survive these harsh reaction conditions and yields are often depressingly low. Synthetic approaches based on the synthesis of one, two or three new pyridine rings are usually favoured, and have been reviewed elsewhere.^{3–5,7} The commonest disconnections lead to 2-acetylpyridine equivalents to provide the terminal rings and an aldehyde or equivalent for C4 of the central ring (Scheme 1). This allows the introduction of substituents in the 4'-position of the tpy; however the need for an oxidation step limits the variability of the R₁ group.

Procedures introduced by Krohnke⁶ and Potts⁷ obviated the need for an oxidation step, and we introduced the key intermediates HOtpy and Cltpy as nucleophilic and electrophilic reagents, respectively, for functionalisation at the 4'-position.^{8a} From these two intermediates, a vast array of amino- and oxy-functionalised species have been prepared. Scheme 2 presents typical examples of the use of Cltpy and HOtpy for the preparation of ditopic ligands and a ligand with a pendant



Scheme 1 The commonest disconnection applied in 2,2':6',2''-terpyridine synthesis.



Scheme 2 The intermediates HOtpy and Cltpy and their use in the synthesis of tpy derivatives.^{8b}

alkyne functional group, which can subsequently be used for additional reactions (metallation, coupling *etc.*).

Coordination behaviour of tpy metal-binding domains

2,2':6',2''-Terpyridine commonly acts as a terdentate N₃ donor, although rare examples of the ligand acting as a bidentate N₂ or monodentate donor have been reported.⁹ In adopting the chelating N₃ bonding mode, it is necessary for the ligand to change conformation from the average *trans,trans* conformation observed in the free ligand (Fig. 1) to *cis,cis*, and this has consequences for the kinetics of coordination. In metallosupramolecular chemistry, the most commonly encountered motif is a {M(tpy)₂} unit, which ideally possesses D_{2d} symmetry (Fig. 3). Herein lie a duality of reasons for the use of tpy rather than bpy or phen metal-binding domains in

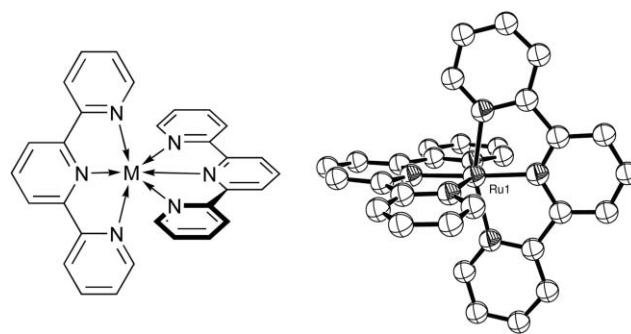


Fig. 3 Left: The idealised D_{2d} structure of a {M(tpy)₂} motif. Right: The solid state structure of the [Ru(tpy)₂]²⁺ cation in [Ru(tpy)₂][PF₆]₂.^{10b}

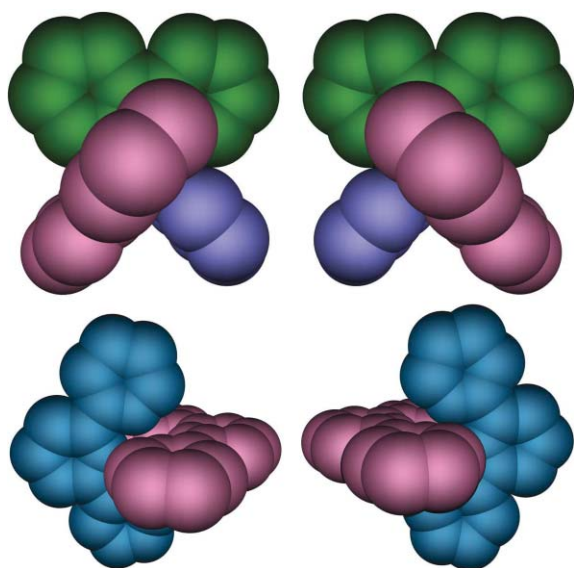


Fig. 4 Λ and Δ enantiomers of a $\{M(\text{bpy})_3\}$ complex (top) compared to an achiral $\{M(\text{tpy})_2\}$ species (bottom) with a symmetrical ligand.

metallo-supramolecular chemistry. Firstly, the presence of two chelate rings per ligand makes the $\{M(\text{tpy})_2\}$ motif more stable than the corresponding $\{M(\text{bpy})_3\}$ species; for example, $\log \beta_3$ for $[\text{Fe}(\text{bpy})_3]^{2+}$ is ≈ 17.8 whilst $\log \beta_2$ for $[\text{Fe}(\text{tpy})_2]^{2+}$ is $\approx 21^{10a}$, although the comparison should be treated with some caution as the parent β values have different dimensions.

The second important aspect relates to the stereogenic properties of $\{M(\text{bpy})_3\}$ and $\{M(\text{tpy})_2\}$ motifs. The former are chiral, giving Δ or Λ enantiomers, whereas $\{M(\text{tpy})_2\}$ motifs with tpy itself, or with symmetrically substituted tpy ligands, are achiral (Fig. 4).

The importance of this becomes apparent when we consider multi-nuclear species containing multiple $\{M(\text{bpy})_3\}$ or $\{M(\text{tpy})_2\}$ motifs; in the former case, there is likely to be a mixture of diastereoisomers with differing spatial arrangements of the metal centres and different physical and chemical properties, whereas in the latter case there will be a single species.

Naturally, the metal centre plays a critical role, both in determining the chemical and photophysical properties of the supramolecule, and also in controlling the kinetics of assembly and the overall lability or inertness of the complex. As a general rule, kinetically inert metal centres (d^3 or d^6) are used as preformed complex building blocks in metallo-supramolecular chemistry whilst labile metal ions (usually first row) are most often encountered in spontaneous self-assembly reactions, during which a new $\{M(\text{tpy})_2\}$ motif is generated.

Crystal engineering of $\{M(\text{tpy})_2\}$ motifs

The $\{M(\text{tpy})_2\}$ motif is very well structurally characterised, and there are 210 entries in the CSD (CSD version 5.27 update, August 2006)¹¹ that confirm its cruciform appearance with two orthogonal near-planar tpy ligands. The bite distance between the central and terminal nitrogen atoms is in the range 2.55–2.6 Å, and the bite angle $\angle_{\text{N}_{\text{term}}\text{M}-\text{N}_{\text{central}}}$ is in the range 75–80° for transition metal ions. The dimensions $\text{H4}'\cdots\text{H4}'$, between the two ligands, and $\text{H5}\cdots\text{H5}'$, within a single ligand, are

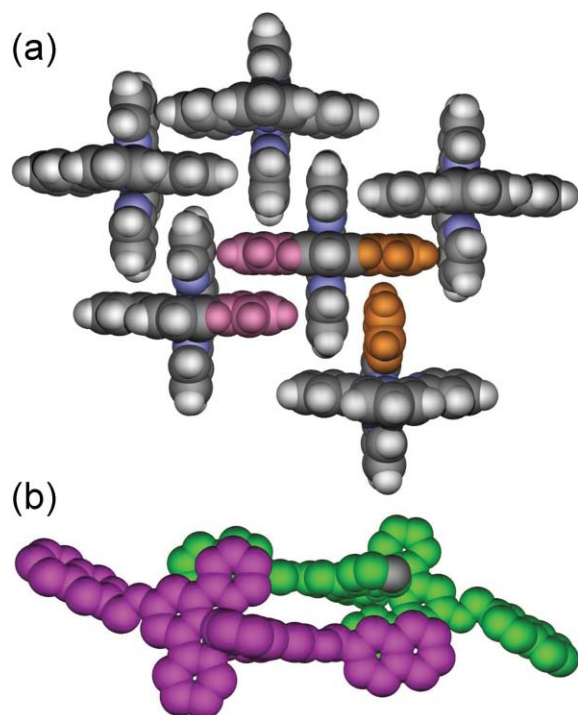


Fig. 5 (a) Part of a sheet of $[\text{Co}(\text{tpy})_2]^{2+}$ cations in $[\text{Co}(\text{tpy})_2]\text{I}_2 \cdot 2\text{H}_2\text{O}$ showing the face-to-face (pink) and edge-to-face (orange) interactions leading to the “tpy embrace”,^{15b} and (b) naphthyl–tpy interactions in a complex of a naphthyl-functionalised ligand.^{15a}

remarkably similar (11–12 Å) and lead to interesting crystal packing effects.

Dance has identified a “tpy embrace” motif present in solid state structures of $\{M(\text{tpy})_2\}$ complexes.¹² This is a combination of edge-to-face and face-to-face interactions of the aromatic rings, and with simple anions results in the formation of two-dimensional sheets of cations (Fig. 5a). In the absence of anions, the cation \cdots cation interaction in the two dimensional array is estimated to be $\sim 29 \text{ kJ mol}^{-1}$. These initial observations have been extended to illustrate the influence of the anion or lattice solvent¹³ and substituents^{14,15a} on the crystal packing. Aryl substituents^{15a} introduce new possibilities for aromatic–aromatic interactions, and a wide variety of packing motifs are emerging (Fig. 5b).

Mononuclear complexes, diads and triads

Moving from crystal engineering to more mainstream supramolecular chemistry, one of the simplest ways of using a single $\{M(\text{tpy})_2\}$ motif is as a molecular scaffold, to which substituents that can interact with the metal centre or with each other are attached. The use of 4'-substituted ligands is particularly advantageous as it maintains a linear vector between the substituents. Information (most often energy or electron transfer) can pass directly between the two substituents in ligand–ligand interactions, or from the ligand to the metal or from the metal to the ligand; the latter two processes combining to give stepwise transfer in a triad (Fig. 6).

Much of the interest in this area has been stimulated by attempts to improve the photophysical properties of

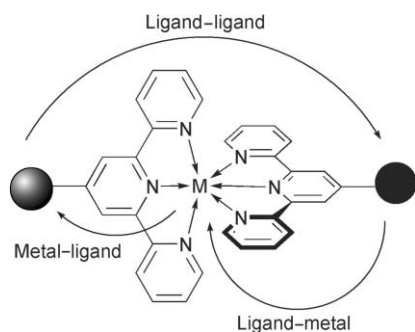
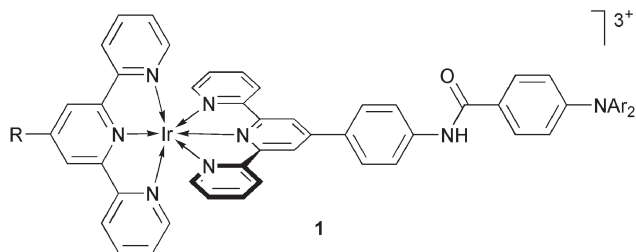


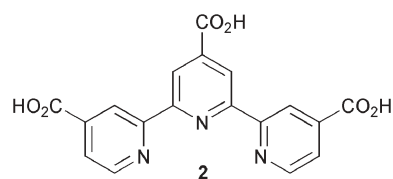
Fig. 6 Schematic representation of a mononuclear diad or triad, where the various ways in which information can be transferred in the molecule are indicated.

$\{\text{Ru}^{\text{II}}(\text{tpy})_2\}$ species (in particular, increasing the triplet excited state lifetime) for incorporation into artificial photosynthetic systems.¹⁶ In contrast to $\{\text{Ru}^{\text{II}}(\text{bpy})_3\}$ complexes, which have long-lived excited states in fluid solution at ambient temperature (typically longer than 200 ns), $[\text{Ru}(\text{tpy})_2]^{2+}$ salts have lifetimes significantly less than 1 ns.¹⁷ In contrast, $[\text{Os}(\text{tpy})_2]^{2+}$ motifs have triplet excited states that are lower in energy and longer lived, setting the scene for energy transfer from $\{\text{Ru}^{\text{II}}(\text{tpy})_2\}$ to $\{\text{Os}^{\text{II}}(\text{tpy})_2\}$ motifs, monitored by the characteristic $\{\text{Os}^{\text{II}}(\text{tpy})_2\}$ emission. Much effort has been devoted to the design and synthesis of diads and triads of the donor–acceptor or donor–acceptor–donor type, with a wide variety of electron donors being attached to $\{\text{M}(\text{tpy})_2\}$ scaffolds.

A typical example of a recent diad is seen in iridium(III) complex **1** ($\text{R} = 3,5\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3$, $\text{Ar} = 4\text{-methoxyphenyl}$).¹⁸ The triarylamine substituent is easily oxidised, and upon irradiation, an electron transfer reaction occurs to give a charge-separated state (formally $\text{Ir}^{\text{II}}\cdots\text{N}^+$), which has a lifetime of 70 ps—subsequent charge recombination leading to the ground state iridium(III) complex. This is just one example of a vast range of polynuclear systems designed for investigating the intimate details of energy and electron transport in compounds relevant to imitating photosynthetic light capture processes.



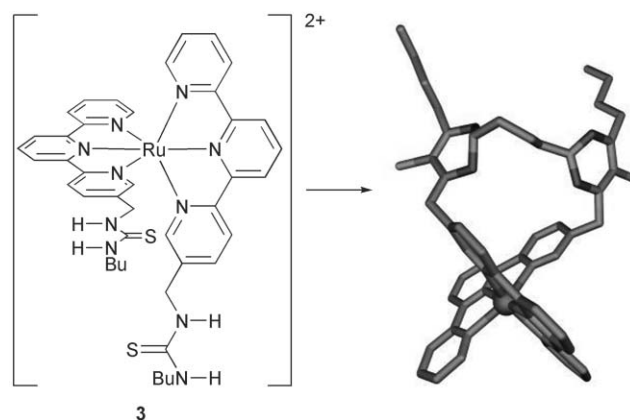
Another area of intense activity is related to the design of light absorbing complexes for incorporation into nanostructured interfacial photovoltaic devices (e.g. Graetzel cells). One of the most successful types of device is based upon nanostructured TiO_2 functionalised with $\{\text{Ru}^{\text{II}}(\mathbf{2})(\text{NCS})_3\}$ (**3**). The cell is completed by a second redox couple, such as I_2/I^- , which returns ground state ruthenium(III) to ground state ruthenium(II). The function of the carboxylate substituents is to bind to the surface of the metal oxide nanoparticles.¹⁹ The complex is dark green (colloquially known as the “black dye”) and absorbs across much of the visible region of the electromagnetic spectrum.



Square planar complexes, typified by species such as $[\text{Au}(\text{tpy})\text{Cl}]^{2+}$ and $[\text{Pt}(\text{tpy})\text{Cl}]^+$, are also of considerable interest. The planar structure of them has led to their investigation as metallointercalators that are able to insert between the base pairs of nucleic acids. The two compounds (and their derivatives with functionalised tpy ligands) bind DNA and are of continuing interest as potential therapeutics. Interestingly enough, it is suggested that the two compounds interact differently with DNA, presumably as a result of the charge difference between them, as their molecular shapes and volumes are nearly identical.²⁰

Finally, we note that the use of tpy metal-binding motifs in supramolecular chemistry is not limited to non-labile metal centres. The use of labile metal centres has the advantage that self-assembly of complexes is rapid, but the potential disadvantage that ligand exchange is also rapid. This latter phenomenon has recently been exploited, and the combination of strong but labile metal–ligand bonds used for the construction of dynamic and virtual dynamic combinatorial libraries of metal complexes.^{21–23} For example, treatment of a labile six-coordinate metal ion with a mixture of tpy ligands A, B and C can give a library with six components: $\{\text{MA}_2\}$, $\{\text{MB}_2\}$, $\{\text{MC}_2\}$, $\{\text{MAB}\}$, $\{\text{MAC}\}$ and $\{\text{MBC}\}$.

This approach has been used for the optimisation of receptors for dicarboxylates (Scheme 3).²¹ The coordination of two thiourea-functionalised tpy ligands to ruthenium(II) generates the bis(thiourea) species **3**, which acts as a receptor for dicarboxylates. The dynamic properties of the library can be exploited, allowing the amplification of a desired receptor. Consider a library composed from two equivalents each of ligands A, B and C, and one equivalent of M. The six species are in dynamic equilibrium with the free ligands. Assuming that only species, $\{\text{MA}_2\}$, can bind substrate X to give a species $\{\text{MA}_2\}:\text{X}$, by Le Chatelier’s principle, the equilibrium will be displaced towards $\{\text{MA}_2\}$ in the library; this being the

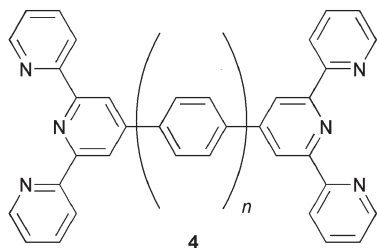


Scheme 3 Binding of glutarate to a bis(thiourea) receptor on a $\{\text{Ru}(\text{tpy})_2\}$ scaffold **3**.²¹

process of amplification. Amplification of the dynamic libraries of tpy complexes by reacting them with species able to interact with one component specifically has met with moderate success.²⁰ We have demonstrated that performing ¹H NMR spectroscopy on dynamic libraries of paramagnetic cobalt(II) complexes is a powerful technique for investigating both the kinetics of equilibration and speciation.²²

Discrete rigid rods, rigid, and flexible metallopolymers

The well-defined spatial characteristics of the {M(tpy)₂} unit led to one of its earliest applications in supramolecular chemistry. The rigid bridging ligands of generic structure **4** are advantageous in that their dinuclear complexes have a precisely defined intermetallic distance, allowing systematic studies of the rates of energy or electron transfer between metal centres in model systems of artificial photosynthesis. In particular, studies of compounds with {Os(tpy)₂} and {Ru(tpy)₂} motifs yielded profound insights into the mechanisms of energy transfer in such systems.^{16,24}



The use of ligands **4** with labile metal ions leads to rigid rod (linear) metallopolymers. These metallopolymers are polycationic, and a particularly interesting use of these species is in the formation multi-layered devices, with amphiphiles or polyanions as counterions. Detailed structural studies of the multi-layers of iron(II) metallopolymers have given information about the local environment within the {Fe(tpy)₂} unit as well as information about the periodicity and packing of the cationic and anionic components.²⁵

On moving from rigid rod ligands such as **4** to ditopic ligands with two tpy metal-binding domains linked by more flexible spacers, the situation becomes more complex. In particular, it is possible to form metallopolymers or metallomacrocycles (Fig. 7). High molecular weight metallopolymers with novel properties are formed,^{5,26} although there is increasing evidence that the systems are dynamic and that,

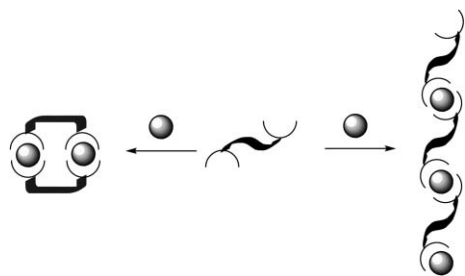


Fig. 7 The formation of metallomacrocycles (left, in this case a dinuclear [2 + 2] species) or metallopolymers (right) from the interaction of flexible ditopic ligands with metal ions (grey spheres).

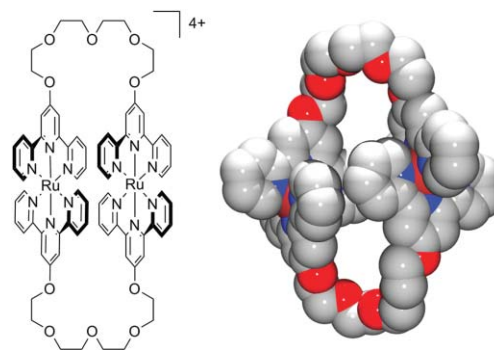


Fig. 8 The reaction of RuCl₃·3H₂O under reductive conditions with the ditopic ligand with an O(CH₂CH₂O)₄ spacer gives the diruthena-macrocyclic in 35% yield.²⁷

over time, the ratio of metallopolymer to metallomacrocyclic varies, with the formation of increasing amounts of metallomacrocycles under thermodynamic conditions. Under equilibration conditions, iron(II) and ruthenium(II) metallomacrocycles are obtained in good yield from bis(tpy) ligands with O(CH₂CH₂O)_n spacers. A typical example is the dinuclear ruthenium metallomacrocyclic shown in Fig. 8, which is isolated in 35% yield from the reaction of the ligand with RuCl₃·3H₂O under reductive conditions.²⁷

Metallopolymers

We have noted above the ambiguity associated with the use of flexible spacers in ditopic ligands. It is well-established by Fujita, Stang and others that pre-organised multi-topic ligands may be used for the construction of a wide variety of polygonal and polyhedral systems. By using pre-organised but non-linear ditopic bis(tpy) ligands, it is possible to prepare metallomacrocycles with designed dimensionality and nuclearity. One of the most elegant examples of this strategy utilises ligands in which tpy metal-binding domains are attached through the 4'-position to the 1- and 3-positions of a benzene spacer. In any complex, the M–N_{central} vectors of the two tpy domains will make an angle of 120° with respect to each other. This is exactly the internal angle of a planar hexagon, and the reaction of ligand **5** (with a hydroxymethyl substituent to increase solubility) with iron(II) chloride gives the hexanuclear metallomacrocyclic in 81% yield.²⁸ We have shown that the less highly pre-organised ligand **6** gives a tetranuclear metallomacrocyclic upon reaction with iron(II), in which the conformation about the disulfide bond appears to be the critical feature.²⁹ In this case, although the Fe₄ core is approximately planar, the metallomacrocyclic framework is not. Even highly functionalised ditopic ligands such as **7** give metallomacrocycles upon reaction with iron(II), in this case a heterodimetallic diironplatinum species (Fig. 9).³⁰

Metallopolymers

As mentioned earlier, although {M(bpy)₃} and {M(tpy)₂} motifs have similar coordination environments, they differ significantly in their stereogenic properties. Specifically, supramolecules containing two or more chiral {M(bpy)₃}

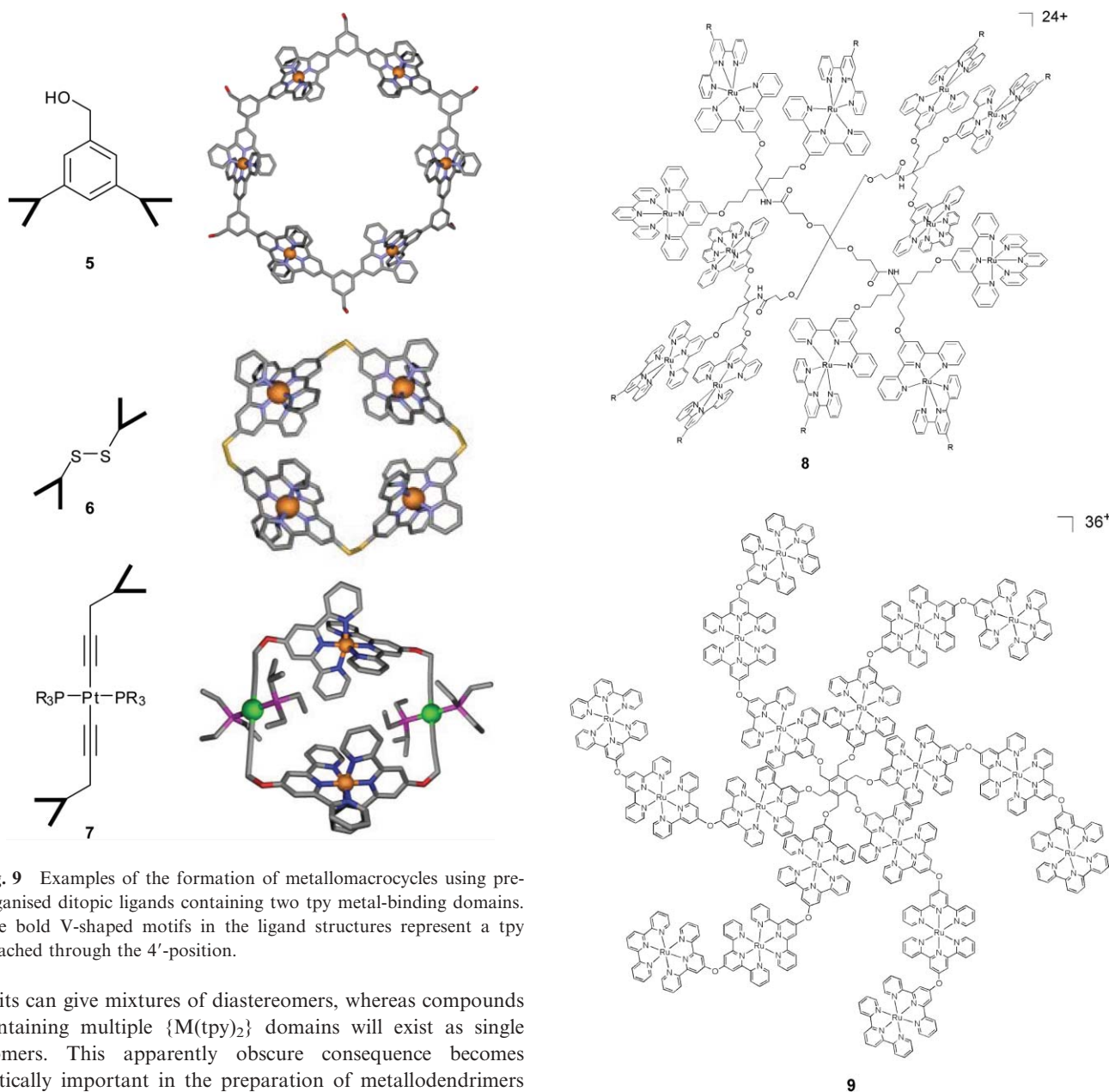


Fig. 9 Examples of the formation of metallamacrocycles using pre-organised ditopic ligands containing two tpy metal-binding domains. The bold V-shaped motifs in the ligand structures represent a tpy attached through the 4'-position.

units can give mixtures of diastereomers, whereas compounds containing multiple $\{M(\text{tpy})_2\}$ domains will exist as single isomers. This apparently obscure consequence becomes critically important in the preparation of metallodendrimers containing multiple metal centres.

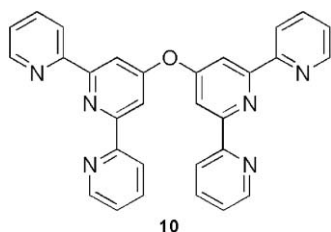
The first examples of metallodendrimers incorporating tpy metal-binding domains were reported in 1993, and included the dodecaruthenium species **8** with a pentaerythritol core and a $\text{H}_2\text{NC}(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_3$ branching unit, prepared by a divergent approach, in which the final step of the reaction was the decoration of a dendrimer with twelve surface non-coordinated $[\text{Ru}(\text{tpy})\text{Cl}_3]$ -derived tpy units.³¹ The high charges on these species often lead to difficulties in their isolation, and in order to obtain tractable compounds it is usually necessary to incorporate additional hydrophobic or hydrophilic decoration at the surface. One of the highest nuclearity systems we have prepared is the octadecylruthenadendrimer **9**, with a charge of 36+.³² A wide variety of metallodendrimers based on tpy domains are now known, many of which have been prepared as putative “antenna molecules” for the collection of light at surface photoactive sites, and subsequent energy and/or electron transfer to internal reaction centres.³²

Metal-directed reactivity—kinetically inert building blocks

One of the methodologies that has been crucial in allowing the synthesis of high nuclearity metallodendrimers utilises the “organic” reactions of coordinated ligands in kinetically inert complexes (most often low-spin d^6 complexes of ruthenium(II) or osmium(II)).³³ This approach has the advantage that both divergent and convergent strategies utilising small preformed complexes are possible, and that ligands not capable of an independent existence might be used.

Typically, the metal complex building blocks are used in electrophilic or nucleophilic reactions, although it is also well-established that carbon–carbon bond forming reactions, such as Suzuki or Stille couplings, are possible with metal complexes. For example, the octadecylruthenium compound **9**

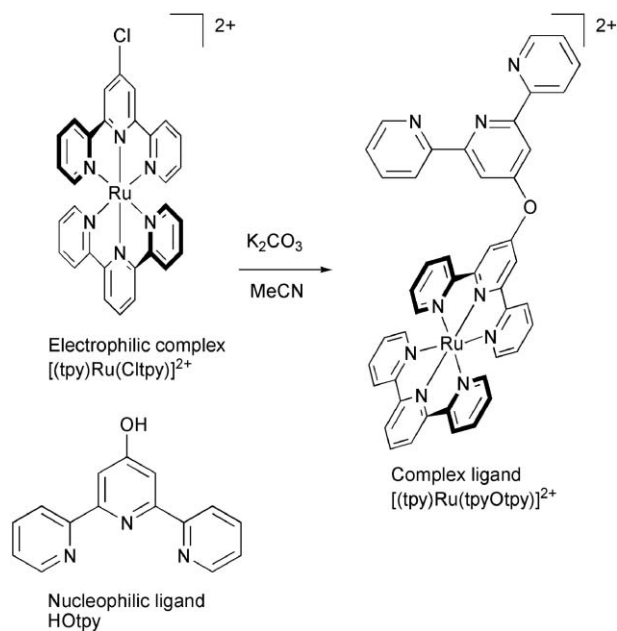
is prepared by a convergent synthesis, in which the final step is the reaction of the trinuclear nucleophilic complex $[(\text{tpy})\text{Ru}(\text{tpyOtpy})\text{Ru}(\text{tpyOtpy})\text{Ru}(\text{tpyOH})]^{6+}$ ($\text{tpyOtpy} = \mathbf{10}$) with hexakis(bromomethyl)benzene under mildly basic conditions. Note that the desired complex of the core ligand $\text{C}_6(\text{CH}_2\text{Otpy})_6$ is generated in this final reaction step without the need to isolate the free ligand itself. In this reaction, the metal ion does not activate the HOtpy ligand; indeed, the 6+ charge on the complex should render the coordinated HOtpy less nucleophilic than the free ligand.



More interesting is the case of the electrophilic ligand Cltpy. In this case, coordination to a cationic metal centre increases the positive charge on the ligand and consequently increases its electrophilicity.³⁴ This is used to advantage in various steps of the synthesis of the trinuclear building block required to make **9** (Scheme 4).

And into the nanoworld and beyond

As noted earlier, the $\{\text{M}(\text{tpy})_2\}$ motif has dimensions in the order of 1.12 nm, both across a single ligand and across the metal centre. By definition, any supramolecules based upon these units will be nanodimensioned. Recently, we and others have become interested in the use of tpy compounds for the assembly of monolayers with micrometric or millimetric long



Scheme 4 Use of a metal complex containing a ligand with enhanced electrophilicity. The coordinated Cltpy reacts with free HOtpy to give a new complex with a free tpy metal-binding domain.

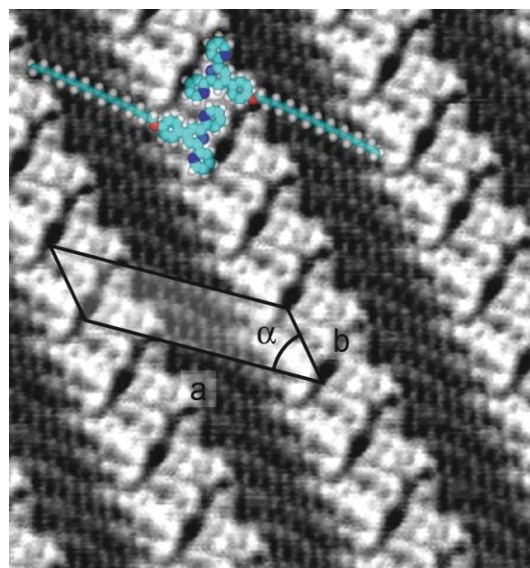
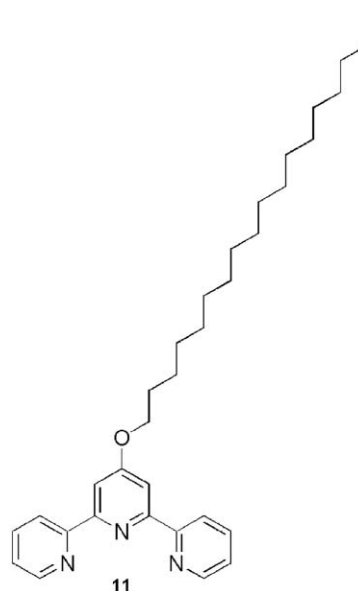


Fig. 10 STM image of a monolayer of **11** on a highly ordered pyrolytic graphite surface.³⁵ The image shows a unit cell, defined by the two cell lengths a and b , and the internal angle α .

range, two-dimensional order. It seems appropriate to bring this review to a conclusion with an indication of possible future applications of the tpy motif and a spectacular visualisation of molecular structure through scanning tunnelling microscopy (STM) rather crystallographic techniques. Fig. 10 shows the molecularly-resolved STM image of a solution of 4'-(4-octadecyloxyphenyl)-2,2':6',2''-terpyridine (**11**) in 1-phenyloctane at a highly ordered pyrolytic graphite surface; a monolayer is formed and the conformation of the molecule can be clearly seen.³⁵ An interesting feature of this study is the recognition that molecules such as **11** are prochiral—when a face is defined by absorption onto the graphite surface; the octadecyl chain can lie to the left or right hand side. Separate domains are observed on the surface with opposite chiralities.



Concluding remarks

This short review has taken a journey through some modern aspects of tpy chemistry. I hope that it has served to whet the appetite of the reader and stimulate further reading into the extensive chemistry of these species. Above all, I hope that I have convinced some that metallocsupramolecular chemistry is fun!

Acknowledgements

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