

A Journey from Supramolecular Chemistry to Nanoscale Networks

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Abstract: The use of the coordination properties of metal centres to organise organic ligands in space is a concept that dates back to the seminal work of Alfred Werner that was recognised by the award of the first Nobel Prize for Chemistry in inorganic chemistry 100 years ago. Metal ions may be used to control the assembly of one-, two- or three-dimensional structures by matching the coordination number and geometry with the number and arrangement of donor atoms within ligands. These so-called coordination polymers have recently emerged from the category of unwanted insoluble side-products to materials of high scientific interest and economic potential. This short article presents the simple design principles that lie behind the synthesis of materials possessing useful properties and, often stunningly attractive structural motifs.

Keywords: Coordination polymers · Functional materials · Ligand design

Introduction

Extended coordination structures, also known as coordination networks, coordination polymers, metal organic frameworks or MOFs, have had a chequered history. They have emerged from the obscurity of unwanted, poorly soluble and even more poorly characterised materials obtained from the reaction of metal salts with multidentate ligands to species with technological importance and extreme scientific interest.^[1,2]

In this short article we present a brief introduction to the engineering of extended coordination structures through molecular design followed by an overview of our own activities in the development of functional one-, two- and three-dimensional materials.

signed multidentate ligands that could bridge two or more metal centres. This area of chemistry uses the simple precepts of metallocsupramolecular chemistry to pair the donor properties of metal-binding domains with the acceptor properties of metal centres.^[5] By matching the number and spatial arrangement of the donors in the metal-binding domains with the coordination number and favoured coordination geometry of the metal centres, the formation of discrete mononuclear or polynuclear complexes or one-, two- or three-dimensional coordination networks can be both predicted and controlled (Fig. 1).

The exponential growth in studies of coordination networks in the past 20 years has been predicated upon the availability of routine crystallographic methods for the structural characterisation of large structures together with the genesis of the

tools of nanosciences for the characterisation of both crystalline and non-crystalline materials at the micron, nanometre or molecular level. However, the basic strategy of elaborating molecular concepts to extended structures is almost as old as coordination chemistry itself, with a 1915 publication by Paul Pfeiffer 'Die Kristalle als Molekülverbindungen' (The crystal as a molecular compound) having a suspiciously modern ring to it.^[6] Another crucial piece of the background lies in Gautam Desiraju's 1996 volume 'The Crystal as a Supramolecular Entity'^[7] which sets the intellectual and experimental framework in which the interplay of strong- (coordination), mid- (classical hydrogen bonding, ionic) and weak-strength interactions (π -stacking, weak-hydrogen bonding) combine to determine the overall crystal topography and topology.

Coordination Networks

The modern era of coordination networks is best dated back to a series of paradigm shifting papers by Richard Robson^[3–5] in which he deliberately de-

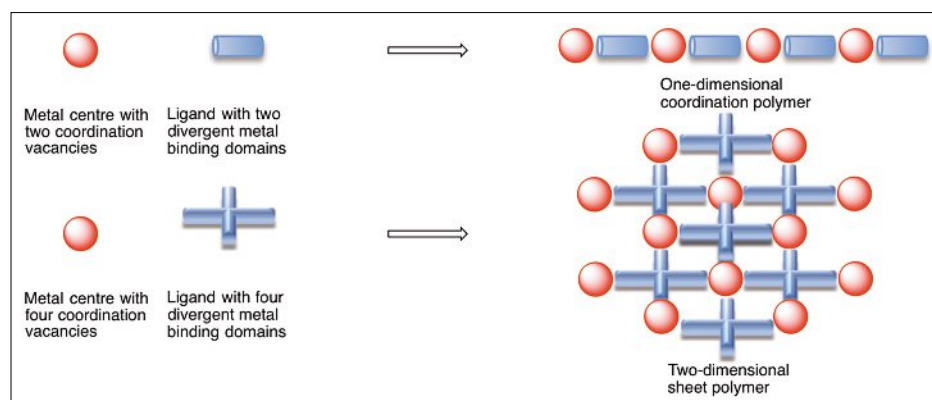


Fig. 1. Controlling dimensionality in a coordination polymer through ligand design and matching to donor requirements of a metal ion. In these cases a bidentate ligand is combined with a metal centre containing two coordination vacancies to give a one-dimensional material and a tetradentate ligand is combined with a metal centre containing four coordination vacancies to give a two-dimensional material.

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From Supramolecular Chemist to Control Freak – One-dimensional Systems

The ligand requirements for the assembly of one-dimensional systems are conceptually simple – namely, a species with two metal-binding domains that do not bind to a single metal centre. Many of our studies in this area have addressed the question of preparing heterometallic systems in which metals are arranged with long-range order in predefined sites. Our approach is based upon the use of two or more metal-binding domains which bind in a specific manner to two different metals, based upon coordination geometry, coordination number or preferred donor atom. The approach will be exemplified by concentrating upon ligands in which one of the metal-binding domains is a 2,2':6',2''-terpyridine (tpy) which we often incorporate into a six-coordinate $\{M(\text{tpy})_2\}$ motif. Ligand **1** can be regarded as an extension of the archetypical bridging ligand 4,4'-bipyridine by the replacement of one of the pyridine metal-binding domains by a tridentate 2,2':6',2''-terpyridine domain (Fig. 2). The N...N distances in 4,4'-bipyridine (7.134 Å)^[8] and between the central tpy ring and the pendant pyridyl in **1** (7.116 Å)^[9] are very similar. Complexes with non-labile metal centres such as $[\text{Cr}(\mathbf{1})_2]^{3+}$ and $[\text{Ru}(\mathbf{1})_2]^{2+}$ are direct analogues of 4,4'-bipyridine and the pendant pyridine donors can bind to a second metal centre. Prototype coordination arrays are obtained with the 'simplest' metal ion, the proton, and complexes $[\text{M}(\mathbf{1})(\text{H}\mathbf{1})]^{3+}$ form one-dimensional, topologically linear, polymers (Fig. 3a,b).^[10] With iron(II) in mildly acidic conditions, the one-dimensional system $[\text{Fe}(\mathbf{1})(\text{H}\mathbf{1})]^{3+}$ spontaneously assembles; a first example of the potential of the algorithm in coding for a perfect and infinite alternation of metal sites (in this case metal and proton sites) in a one-dimensional system.^[11] The analogy between **1** and 4,4'-bipyridine is maintained in these systems with similar N–H...N distances in, for example, $[\text{Ru}(\mathbf{1})(\text{H}\mathbf{1})]^{3+}$ (2.620 Å)^[10] and 4,4'-bipyridinium bromide hydrate (2.680 Å).^[12] These systems are of some interest as information storage systems and we have demonstrated that the emission and absorption properties of $[\text{Ru}(\mathbf{1})_2]^{2+}$ and its various protonated forms define various prototypical molecular logical operations.^[13] We recently drew attention to the analogy between the complexes $[\text{M}(\mathbf{1})_2]^{n+}$ and 4,4'-bipyridine as an aspect of a wider *expanded ligands* concept recognising the ubiquitous nature of the motif.^[14]

Of course, the proton is not generally recognised as a metal centre, but reaction of $[\text{Ru}(\mathbf{1})_2]^{2+}$ with silver(I) salts leads to the heterometallic one-dimensional co-

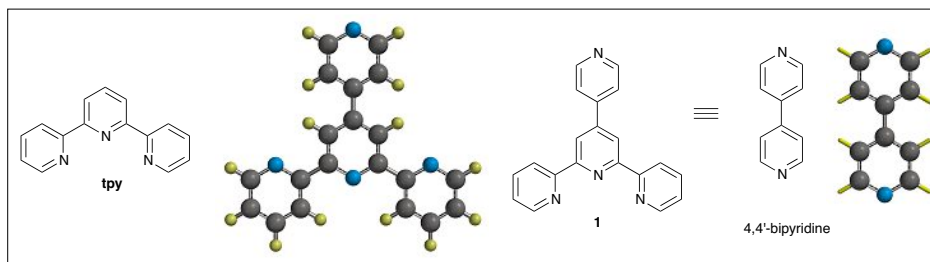


Fig. 2. By attaching a pendant 4-pyridyl substituent to the tpy metal-binding domain ligand **1**, which is a direct analog to 4,4'-bipyridine, is obtained. The metrical parameters in the 4,4'-domain of **1** closely resemble those of 4,4'-bipyridine itself.^[8,9]

ordination polymer $[(\mathbf{1})\text{Ru}(\mathbf{1})\text{Ag}(\text{NO}_3)] [\text{NO}_3]_2$, with a perfect alternation of ruthenium and silver centres and with adjacent Ru...Ag, and Ru...Ru (Ag...Ag) distances of 11.168 and 22.134 Å respectively (Fig. 3c). An analogous structure is obtained with $[\text{Fe}(\mathbf{1})_2]^{2+}$ cores and copper(II) nitrate in which the $\{\text{Ag}(\text{NO}_3)(\text{MeCN})\}$ units are replaced by seven-coordinate $\{\text{Cu}(\text{NO}_3)_2(\text{H}_2\text{O})\}$ units with adjacent Fe...Cu, Fe...Fe (Cu...Cu) distances of 10.889 and 21.696 Å respectively (Fig. 3d).^[15,16] Analogous homonuclear systems with $[\text{Ni}(\mathbf{1})_2]^{2+}$ or $[\text{Co}(\mathbf{1})_2]^{2+}$ cores connected by $\{\text{Co}(\text{dionate})_2\}$ ^[17] units have been reported.

In addition to assembling heteronuclear one-dimensional systems in which a six-coordinate metal is coordinated to two 2,2':6',2''-terpyridine metal-binding domains and a second metal (of whatever coordination number) is bound to two pyridyl nitrogen donors from different $[\text{M}(\mathbf{1})_2]^{n+}$,

we also considered that it should be possible to form homonuclear one-dimensional systems in which metal centres with at least four available coordination sites were coordinated to the 2,2':6',2''-terpyridine metal-binding domain of one ligand and the 4-pyridyl nitrogen of a second ligand. A square-planar arrangement of the four nitrogen donors is the most likely and we invested a significant amount of energy in an ultimately unsuccessful search for examples of this bonding mode in platinum(II) and palladium(IV) complexes of **1**.^[18] However, the reaction of **1** with copper(II) chloride initially yields the mononuclear five-coordinate complex $[\text{Cu}(\mathbf{1})\text{Cl}_2]$ which forms a one-dimensional polymer with six-coordinate copper(II) centres with an equatorial N_4 (tpy + py) donor set and two axial chloride ligands and a Cu...Cu distance 10.967 Å (Fig. 4a).^[19] A similar one-dimensional polymer with axi-

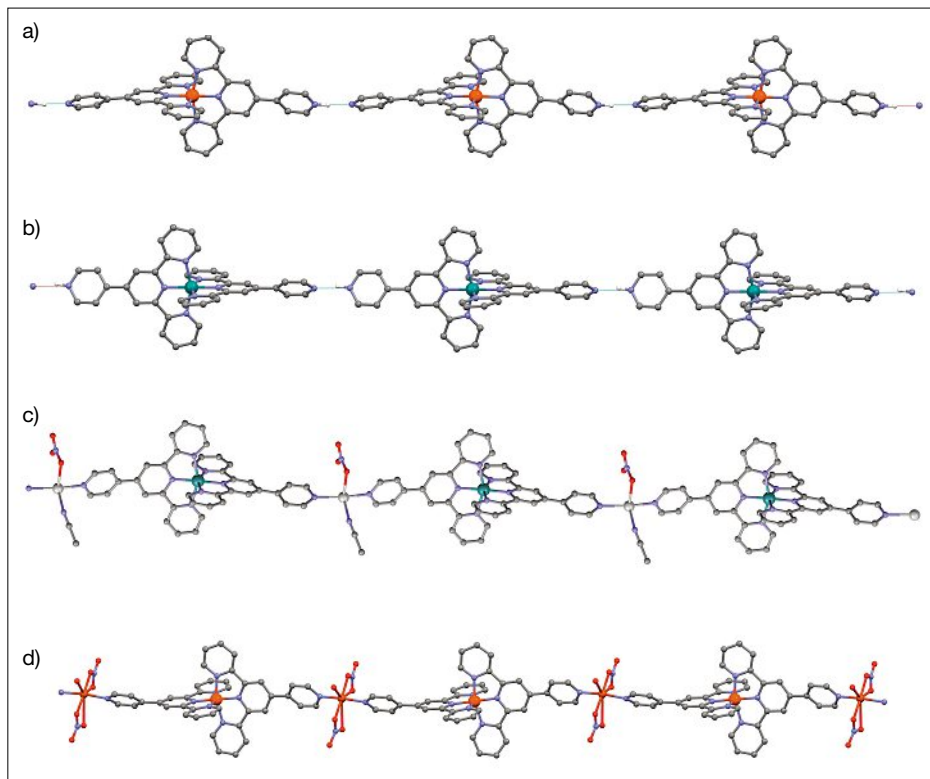


Fig. 3. One-dimensional coordination polymers formed by the connection of $[\text{M}(\mathbf{1})_2]^{2+}$ units with a) protons (M = Fe),^[11] b) protons (M = Ru),^[10] c) $\{\text{Ag}(\text{NO}_3)(\text{MeCN})\}$ units (M = Ru),^[15] and d) $\{\text{Cu}(\text{NO}_3)_2(\text{H}_2\text{O})\}$ units (M = Fe).^[16]

al *O*-donor nitrate ligands is obtained from the reaction of **1** with copper(II) nitrate (Fig. 4b).^[19] The same structure type has been demonstrated independently in the analogous zinc(II) nitrate complex of **1**.^[20] An interesting example of the importance of the ancillary ligands is seen in a comparison of the complexes $[\{\text{CoCl}_2(\mathbf{1})\}_n]^{[21]}$ and $[\{\text{Co}(\text{NCS})_2(\mathbf{1})\}_n]^{[22]}$ which are topologically and topographically linear (Fig. 4c) and $[\{\text{Co}(\text{SO}_4)(\mathbf{1})\}_n]^{[22]}$ in which the bidentate sulfato ligand imposes a 90° bend in the topologically linear system to give a topographically zig-zag arrangement (Fig. 4d). Interestingly, the zig-zag arrangement is also observed in $[\{\text{Mn}(\text{NO}_3)_2(\mathbf{1})\}_n]$ in which one bidentate and one monodentate nitrate ligand generate a facial O_3 donor set whereas $[\{\text{MnCl}_2(\mathbf{1})\}_n]$ is topologically and topographically linear.^[23]

Another elegant way in which the topographical properties of the coordination polymer can be influenced is through the engineering of the angle subtended between the metal-binding vectors (Fig. 5). In **1** the subtended angle is 180°, but in the isomeric ligand **2** it is 120°. Naturally, the dihedral angle between the pendant pyridine and the tpy domain will play a critical role in defining the fine details of the structure. Perhaps the simplest manifestation is in the complex $[\{\text{Ag}(\mathbf{2})\}_n][\text{NO}_3]_n$ in which near planar four-coordinate silver ions are coordinated to one tpy and one pyridine metal-binding domain from each of two **2** ligands.^[23] The Ag...Ag distance is 10.462 Å and the angle between the metal-binding domains of 122.7° is close to the expectation value (Fig. 5a). The presence of ancillary ligands does not perturb the algorithm and in the complex $[\{\text{CuI}(\mathbf{2})\}_n][\text{Cu}_2\text{I}_4]_{0.5n}$ trigonal bipyramidal five-coordinate copper(II) centres are bonded to a tpy and a pyridine metal-binding domain from two ligands as well as an iodide. In this case, the 124.05° internal angle within the trigonal bipyramid is partially compensated by the 59.8 torsional angle between the pendant pyridine and the tpy to give a relatively shallow pitch zig-zag structure (Fig. 5b).^[24] Complexes of **2** can also act as expanded ligands and in $[\{\text{Ni}(\mathbf{2})_2\text{Cd}(\text{NCS})_4\}_n]$ the $\{\text{Ni}(\mathbf{2})_2\}$ acts as an expanded 3,3'-bipyridine and coordinates to two $\{\text{Cd}(\text{NCS})_4\}$ units. Each cadmium is six-coordinate and in addition to the four NCS ligands is coordinated to two *trans*- $\{\text{Ni}(\mathbf{2})_2\}$ ligands (Fig. 5c). Once again, a perfect alternation of Ni and Cd sites is achieved with adjacent Ni...Cd, and Ni...Ni (Cd...Cd) distances of 9.814 and 19.698 Å respectively.^[25]

From One Dimension to Two

Simple ligand design allows the elaboration of **1**, designed to yield one-dimen-

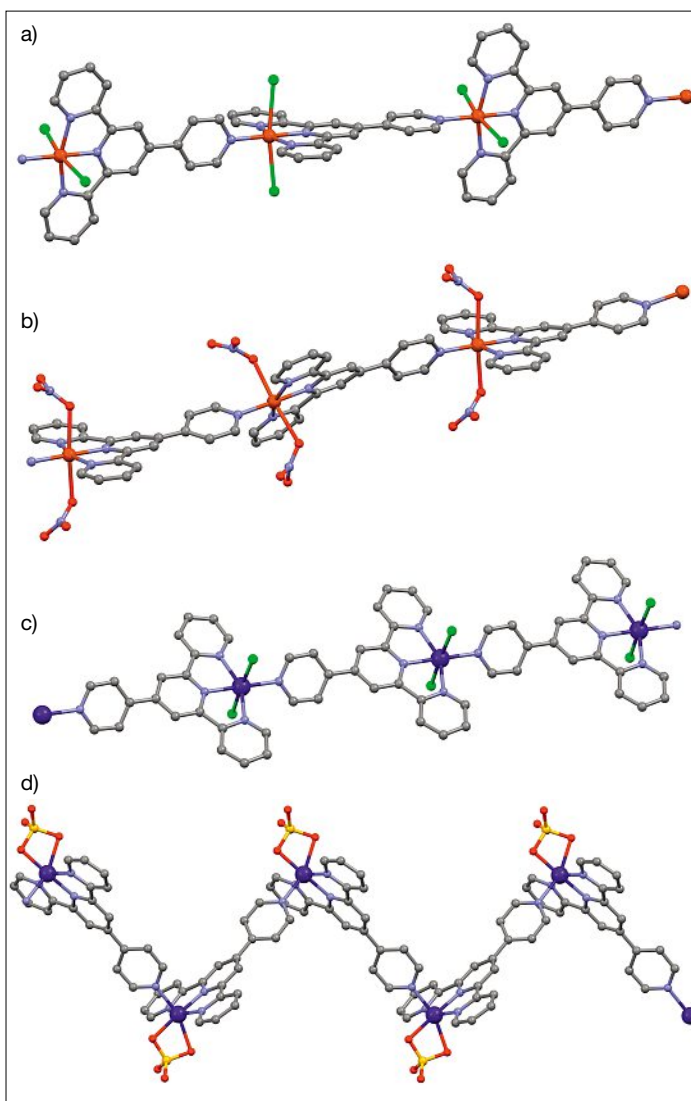


Fig. 4. a) A homonuclear 1D polymer resulting from the interaction of **1** with copper(II) chloride in which each metal is coordinated to a tridentate domain from one ligand and the pendant pyridyl of a second ligand. The remaining coordination sites of the six-coordinate copper(II) are occupied by two chloride ligands; b) the analogous structure with monodentate nitrate ligands;^[19] c) the topologically and topographically linear complex with CoCl_2 ^[21] and d) the corresponding sulfato complex in which the bidentate sulfato ligand occupies two adjacent coordination sites at each cobalt centre giving rise to a zig-zag structure.

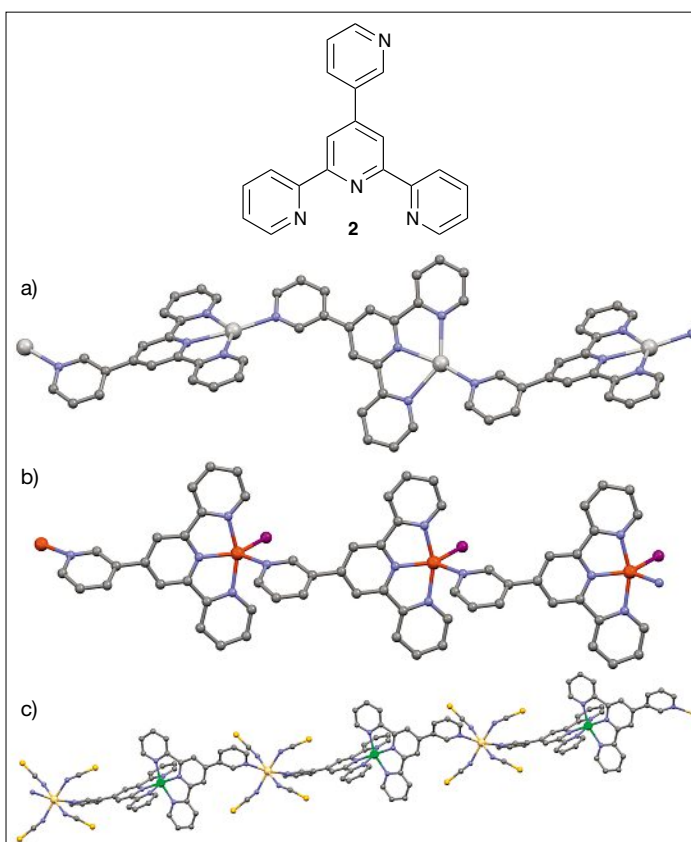


Fig. 5. In the ligand **2**, the pyridine and tpy metal-binding domains subtend an angle of $\approx 120^\circ$ and a zig-zag 1D polymer results in a) $[\{\text{Ag}(\mathbf{2})\}_n][\text{NO}_3]_n$ ^[23] b) $[\{\text{CuI}(\mathbf{2})\}_n][\text{Cu}_2\text{I}_4]_{0.5n}$ ^[24] as well as the expanded ligand complex c) $[\{\text{Ni}(\mathbf{2})_2\text{Cd}(\text{NCS})_4\}_n]$ ^[25]

sional polymers into **3**, which has two divergent donors in the pendant 5-pyrimidinyl substituent and can yield two-dimensional network structures. This has been realised by the reaction of $[\text{Ru}(\mathbf{3})_2]^{2+}$ with CuCl_2 which leads to the two-dimensional sheet-like complex $\{[\text{Ru}(\mathbf{3})_2][\text{CuCl}_2(\text{OH})_2][\text{CuCl}_3\text{Cl}]\}$ (Fig. 6).^[26] Once again, the positioning of the ruthenium(II) and the copper(II) centres in the network is precise and error-free and allows the investigation of the electronic interactions between the metal centres to be probed through the magnetic properties of the material. The copper(II) centres bridged by pyrimidinyl groups are separated by 5.825/5.839 Å with the Cu...Cu contacts over the $[\text{Ru}(\mathbf{3})_2]^{2+}$ unit being 18.283 and 19.250 Å. Magnetic susceptibility measurements indicate a dominant antiferromagnetic interaction with $g = 2.09(1)$ and $2J/k_B = -6.8(1)$ K using the Feyerherm model.^[27]

The conceptual model embodied in the ligand design of **1** is predicated upon only the 2,2':6,2''-terpyridine and the pyridine metal-binding domains. This allows the engineering of a wide range of secondary architectures into the bridging ligands which can be used to incorporate additional functionality or to provide subtle structure ameliorating influences. This development is seen in ligand **4**, which is an analogue of **1** in which the metal-binding domains are no longer directly linked, but rather spaced, in this case by an $-\text{NHN}=\text{CH}-$ bridge. In the iron(II) complex $[\text{Fe}(\mathbf{4})(\text{H4})]^{3+}$, the expected one-dimensional coordination polymer is observed (Fig. 7a).^[28] In the related ligand **5**, which only differs in the attachment to the pendant pyridyl ring at the 3- or the 4-position, the hydrazone spacer units orient the pendant 4-pyridyl substituents in $[\text{Fe}(\mathbf{5})_2]^{2+}$ in a crescent shape, such that tetranuclear $\{\text{M}(\mathbf{5})\text{Fe}(\mathbf{5})\text{M}\}$ units are formed. If the second metal centre M has additional coordination sites, a polymeric looped structure is obtained, as observed in $\{[\text{Fe}(\text{NCS})_2(\text{Ru}(\mathbf{5})_2)]_n\}^{4n+}$ (Fig. 7b), a system which exhibits not only the subtle and exquisite control that the molecular chemist can exert over the positioning of the metal ions but also the inherent beauty of coordination arrays.^[28]

We conclude by returning to ligand **2** and illustrate how the additional rotational freedom between the pendant pyridine and the tpy domain leads to additional structural complexity. The $\text{Cd}(\text{NCS})_2$ complex with **2** also exhibits a looped structure (Fig. 8a). The metallic core of the structure is a $\{(\text{SCN})\text{Cd}(\mu\text{-NCS})_2\text{Cd}(\mu\text{-NCS})_2\text{Cd}(\text{NCS})\}$ unit (coloured pink in Fig. 8a) in which the central six-coordinate cadmium is bonded to two 3-pyridyl domains of two **2** ligands (coloured green in Fig. 8a) and the two terminal cadmium centres are also six-coordinate and bonded

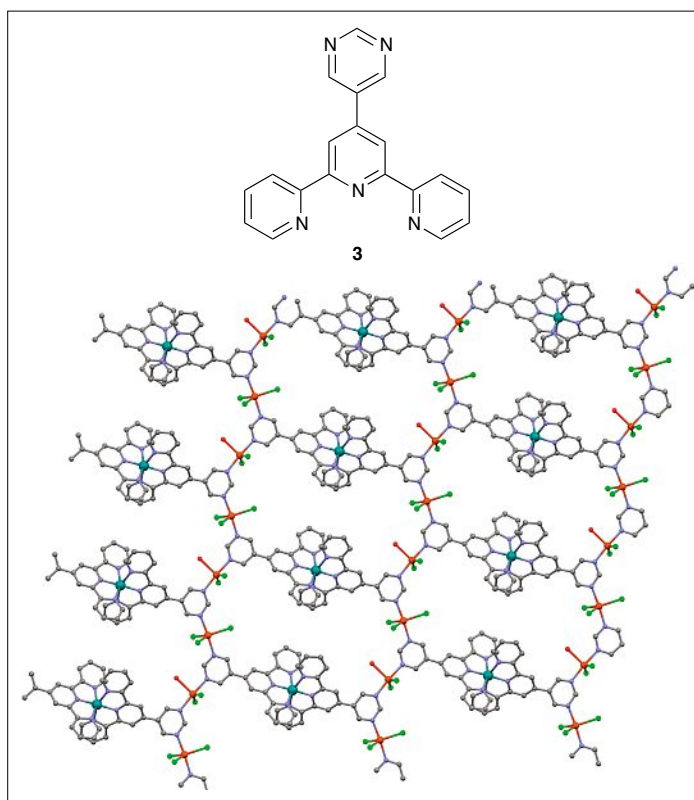


Fig. 6. Structure of ligand **3**, and the two-dimensional polymer resulting from the interaction of $[\text{Ru}(\mathbf{3})_2]^{2+}$ with copper(II) chloride.^[26]

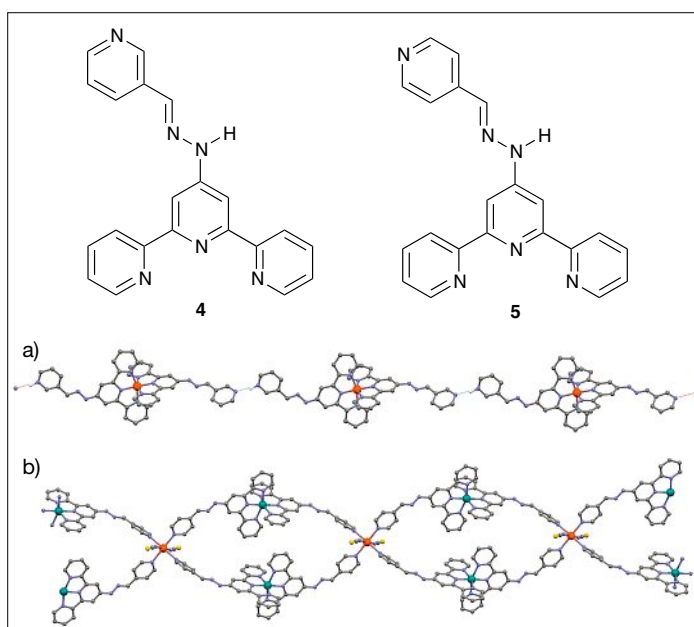


Fig. 7. Increasing the complexity of the ligands allows novel structural motifs to be developed. a) Whereas **4** gives a 1D polymer $[\text{Fe}(\mathbf{4})(\text{H4})]^{3+}$ ^[28] the topology of ligand **5** leads to b) the looped heterometallic system $\{[\text{Fe}(\text{NCS})_2(\text{Ru}(\mathbf{5})_2)]_n\}^{4n+}$.^[22]

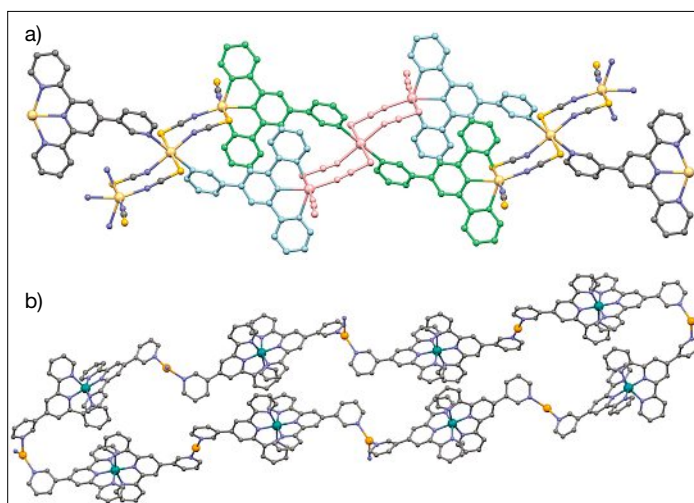


Fig. 8. Ligand **2** generates significantly more complex structures than **1** as a result of the three-dimensional consequences of rotation about the single bond linking the pendant pyridine and the tpy metal-binding domains. A looped structure with tricadmium cluster cores is obtained with cadmium(II) thiocyanate^[29] whilst with $[\text{Ru}(\mathbf{2})_2]^{2+}$ a $\{6,3\}$ planar net is obtained with silver(I).^[30]

to two bridging thiocyanate ligands, one terminal thiocyanate and the tpy domain of a **2** ligand (coloured blue in Fig. 8a).^[29] The reaction of $[\text{Ru}(\mathbf{2})_2]^{2+}$ with silver(I) salts is expected to result in a simple one-dimensional coordination polymer analogous to that obtained with **1**. In practice, a much more complex structure is obtained with a two-dimensional {6,3} net containing both linear two-coordinate and trigonal three-coordinate silver centres.^[30] The 'simple' unit in the {6,3} net comprises eight $\{\text{Ru}(\mathbf{2})_2\}$ expanded ligands linked by two two-coordinate silver centres (pale green) and the six three-connected silver nodes (pink) as presented in Fig. 8b.

Conclusions

This short review article has concerned itself with the design of ligands for the molecular engineering of structured and ordered multimetallic systems of defined dimensionality. This is an active and still emerging field and it is a pleasure and honour to be involved in the infancy of this area. The frustration of softly coded self-assembly algorithms is always alleviated by the beauty of the unexpected structure.

As always, I have the duty and honour to thank all of the talented co-workers in the Constable-Housecroft group for their hard work which makes our small contributions to understanding in this fascinating area possible.

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