

Ditopic and Tetratopic 4,2':6',4''-Terpyridines as Structural Motifs in 2D- and 3D-Coordination Assemblies

Catherine E. Housecroft* and Edwin C. Constable

Abstract: We overview the coordination chemistry of ditopic and tetratopic ligands with 4,2':6',4''-terpyridine metal-binding domains and illustrate the adaptability of these divergent ligands as building blocks in 2D- and 3D-coordination networks. The ditopic ligands we discuss are limited to roles as linkers in coordination assemblies, while the tetratopic ligands have the potential to be 4-connecting nodes. Both di- and tetratopic ligands are equipped with functionalities, typically alkyloxy chains, the nature of which has a profound effect upon the coordination assembly. Combinations of 4-connecting ligand nodes with metal-linkers lead to both 2D- and 3D-networks, while combinations of 4-connecting metal and ligand nodes give 3D-architectures. We also demonstrate constraint of the coordination assembly to 2-dimensions by depositing ditopic 4,2':6',4''-terpyridine ligands onto Au(111) or Cu(111) platforms with Cu adatoms in the former case; highly ordered ladder assemblies result which are independent of solvent molecules or anions.

Keywords: Coordination network · Coordination polymer · Ditopic ligand · Terpyridine · Tetratopic ligand



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1. Introduction

The coordination chemistry of 2,2':6',2''-terpyridine (tpy, Scheme 1), the 'big brother' of the archetypical chelating ligand, 2,2'-bipyridine, has held a special place in the heart of one of us

since the 1980s.^[1,2] As Scheme 1 shows, tpy undergoes a conformational change from the *trans,trans*-form encountered in the free ligand upon coordination to a metal ion and terdentate coordination results in the formation of two five-membered chelate rings. The driving force of the formation of the chelate rings typically leads to tpy being *monotopic*, with the three tpy nitrogen atoms binding only one metal ion. Coordination polymers can be formed from the interaction of ligands with multiple metal-binding domains with two or more metal centres.^[3,4] While mononuclear metal coordination compounds of tpy and its derivatives abound,^[1,2] entry into the world of coordination polymers usually requires functionalization of the tpy domain (most easily in the 4'-position) by a second metal-binding domain such as a carboxylic acid or pyridinyl unit to generate an {M(tpy)₂}-centred 'expanded ligand'.^[5] Although symmetry-breaking of the tpy metal-binding domain to give N₂+N₁ donors sets is known,^[6] 2,2':6',2''-terpyridine is usually classed as a convergent terdentate ligand. Ligands with divergent sets of donor atoms are most appropriate for use as building blocks in infinite coordination assemblies of various dimensionalities, and over the last decade, we have exploited the divergent donor sets in two isomers of tpy. Of the 48 possible isomeric terpyridines, 4,2':6',4''-terpyridine (4,2':6',4''-tpy) and 3,2':6',3''-terpyridine (3,2':6',3''-tpy) and their 4'-functionalized derivatives are readily accessible using either Wang and Hanan's one-pot synthetic approach^[7] or the Kröhnke methodology.^[8] We have applied these strategies to prepare a suite of ligands for use as motifs in 1D-, 2D- and 3D-coordination assemblies.^[9–11] Scheme 1 illustrates that rotation about the inter-ring C–C bonds in 4,2':6',4''-tpy has no influence on the vectorial directionality of the outer nitrogen donors. Interestingly, there are no examples in which the central pyridine ring coordinates and 4,2':6',4''-tpy is, therefore, a *ditopic* N+N ligand, binding two metal centres. In contrast, conformational changes associated with rotation about the interannular C–C bonds in 3,2':6',3''-tpy lead to different vectorial orientations of the two N–M vectors of the ditopic ligand, three of which are illustrated in Scheme 1. By connecting two 4,2':6',4''-tpy or 3,2':6',3''-tpy domains, we can also access tetratopic ligands as depicted in Scheme 2. (We note at this point that this usage of mono-, di-, tri- or tetratopic is preferable to an earlier

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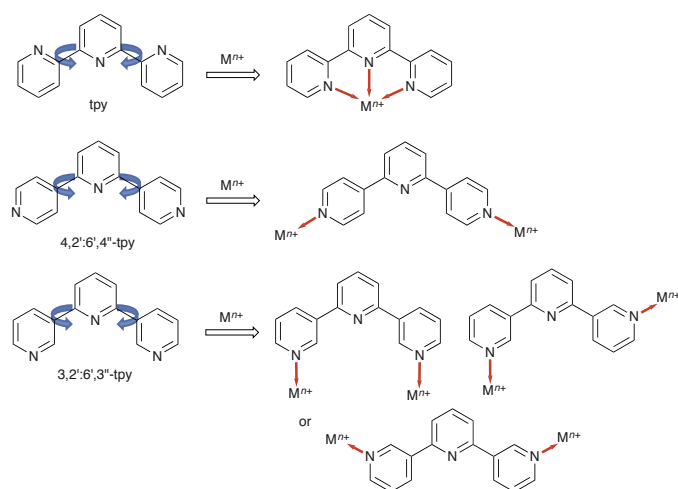
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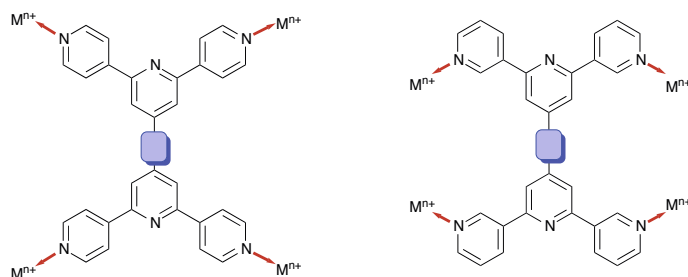
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Scheme 1. Conformational changes (bond rotation, blue arrows) in 2,2':6',2''-terpyridine (tpy), 4,2':6',4''-terpyridine (4,2':6',4''-tpy) and 3,2':6',3''-terpyridine (3,2':6',3''-tpy) leading to monodentate (for tpy) and ditopic (for 4,2':6',4''-tpy and 3,2':6',3''-tpy) ligands.



Scheme 2. Bis(4,2':6',4''-tpy) and bis(3,2':6',3''-tpy) as tetrapotic ligands. The nature of the spacer (in blue) is highly influential in directing the coordination assembly.

use of these prefixes to mean one, two, three or four tpy domains.) Naturally, there is scope for further expansion and one of our current goals is to realize hexatopic ligands.

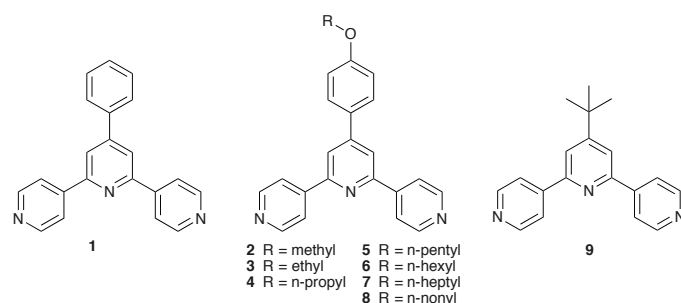
In this short overview, we focus on the assembly of 2D- and 3D-coordination assemblies using di- and tetrapotic ligands with 4,2':6',4''-tpy metal-binding domains, and we show how the nature of any 4'-substituents in the ditopic ligands or the spacer in the tetrapotic ligands influences the outcome of the metal coordination assembly process. Such architectures are typically discussed in topological terms, often speaking of 'metal nodes' and 'organic linkers'.^[4] As the discussion will subsequently reveal, a noteworthy feature of the terpyridine ligands shown in Scheme 2 is their ability to be defined as nodes (or often virtual nodes when the topological focus cannot be atomistically identified). Conversely, use of a metal salt such as a zinc(II) halide results in a 2-connecting metal centre and reduces the role of the metal to that of a linker. Thus, prudent choice of metal and ligand provides a flexible toolbox of nodes and linkers. We note that all coordination assemblies discussed below, except those in Section 4, were obtained under ambient conditions with crystal growth by layering.

2. Ditopic 4,2':6',4''-tpys and 4-Connecting Metal Nodes

In coordination assemblies, 4,2':6',4''-terpyridine is restricted to a role as a linker unless functionalized with additional donor(s). Consequently, reactions of simple 4,2':6',4''-tpys with ZnX_2 (in which the two halide X anions remain coordinated to the zinc) inevitably yield 1D-polymers and/or metallomacrocycles.^[9,12,13] If the dimensionality of the assembly is to be increased, for example to a 2D-sheet, the metal centre must have more than two vacant coordination sites. Two suitable choices of metal salt are $Co(NCS)_2$

and $Cd(NO_3)_2$. Both $Co(II)$ and $Cd(II)$ are likely to adopt a six-coordinate geometry, although $Cd(II)$ (d^{10}) is rather more flexible in its coordination number than $Co(II)$. In the case of $Co(NCS)_2$, the thiocyanato ligands typically coordinate, leaving four additional coordination sites available. In the case of $Cd(NO_3)_2$, the outcome is less-well defined, both in terms of the coordination number of the metal and of the monodentate or bidentate bonding of the nitrate. Reactions of $Co(NCS)_2$ and $Cd(NO_3)_2$ with ligands **1–7** and **9** shown in Scheme 3 lead to 2D-nets, but with some intriguing differences arising from the peripheral functionality. A combination of ligand **1** (Scheme 3) with $Cd(NO_3)_2 \cdot 4H_2O$ produced our first example of a 2D-assembly involving a 4,2':6',4''-tpy.^[14] In $\{[Cd(NO_3)_2(1)]MeOHCHCl_3\}_n$, each $Cd(II)$ centre is six-coordinate with two monodentate nitrate ligands in a *trans*-arrangement. The $Cd(II)$ centre, thus, acts as a 4-connecting node, with each Cd bound to four N donors from four different **1** ligands, and a (4,4) net is assembled. The 4'-phenyl substituents also engage in face-to-face π -stacking which locks adjacent sheets together (Fig. 1a). Figs 1b and 1c show only the Cd atoms to illustrate the (4,4) net and the planarity of the array of metal atoms that defines the net.

When $Cd(NO_3)_2 \cdot 4H_2O$ is combined with ligands **4**, **5**, **6** or **7** (in a 1 : 3 metal : ligand molar ratio), the nature of the peripheral alkoxy group has a significant impact on the assembly.^[15] The solid-state structure of $\{[Cd_2(NO_3)_4(4)_3] \cdot 3CHCl_3\}_n$ consists of a (6,3) net with each Cd atom acting as a 3-connecting node (Fig. 2a); the metal atoms in each net are essentially coplanar (Fig. 2b). The 4'-(4-*n*-propoxyphenyl) substituent in **4** protrudes above or below each net with the *n*-propoxy group neatly accommodated in a pocket in the next sheet. Adjacent sheets are also locked through face-to-face π -stacking of phenyl and tpy domains. This combination of efficient packing motifs also allows the formation of an analogous structure with an *n*-butoxy chain,^[15] but not with longer chains. A combination of $Cd(NO_3)_2 \cdot 4H_2O$ and **5**, **6** or **7** results in the formation of (4,4) nets. $\{[Cd_2(NO_3)_4(5)_4] \cdot 3CHCl_3\}_n$ and $\{[Cd_2(NO_3)_4(6)_4]CHCl_3 \cdot MeOH\}_n$ are structurally analogous with 4-connecting Cd-nodes which also bind *trans*-nitrate ligands.



Scheme 3. Structures of ditopic ligands **1–9**.

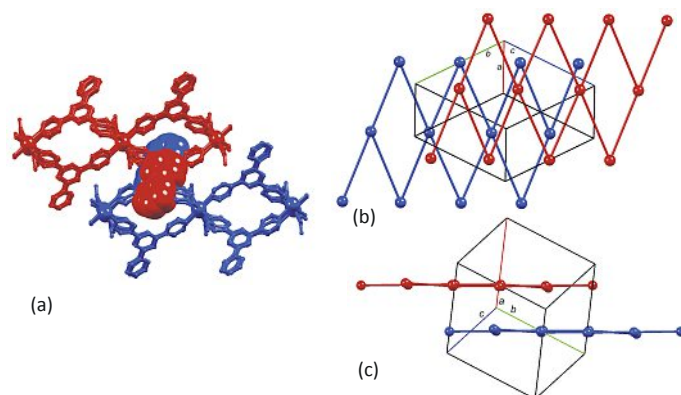


Fig. 1. $\{[Cd(NO_3)_2(1)]MeOHCHCl_3\}_n$: (a) Part of two 2D-sheets showing adjacent Cd centres linked by ligands **1**, (b) and (c) two views of parts of two {4,4} nets.

4-Connecting Cd-nodes are also found $[\{Cd(NO_3)_2(7)_2\}2MeOH]_n$, but here the two coordinated nitrate ligands per Cd atom are mutually *cis*. Even so, an essentially planar (4,4) net (defined by the Cd atoms) assembles as shown in Fig. 3a. In the three 2D-networks incorporating **5**, **6** and **7**, the (4,4) nets are eclipsed (Fig. 3b) and the *n*-pentyl, *n*-hexyl and *n*-heptyl chains from one net extend through the cavities in the next net providing an efficiently locked assembly.^[15]

A preference for (4,4) nets is also observed in reactions of $Co(NCS)_2$ with the ditopic 4,2':6',4''-terpyridines **2**, **3**, **4** and **9**, and persists when the 4'-substituent is a ferrocenyl unit.^[16–18] However, with *n*-hexyloxy or *n*-nonyloxy chains (ligands **6** and **8**, Scheme 3), we observed the unexpected assembly of 3D-networks (metal-organic frameworks, MOFs).^[19] Crystals of $[Co_2(NCS)_4(6)_4]_n$ were found to belong to either the tetragonal space group $P4_12_12$ or $P4_32_12$, and since these are an enantiomorphic pair, the network in $[Co_2(NCS)_4(6)_4]_n$ is chiral. Each Co centre is octahedral with *trans*-NCS ligands and four *N*-donors from four different

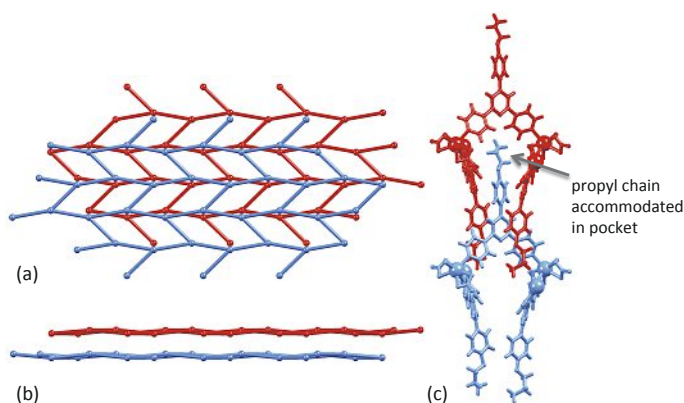


Fig. 2. $[\{Cd_2(NO_3)_4(4)_3\}3CHCl_3]_n$: (a) Top and (b) side views of the (6,3) nets with the Cd atoms as 3-connecting nodes. (c) The 4'-(4-*n*-propyloxyphenyl) substituents protrude above and below each sheet with the *n*-propyl unit accommodated in a pocket in the adjacent sheet.

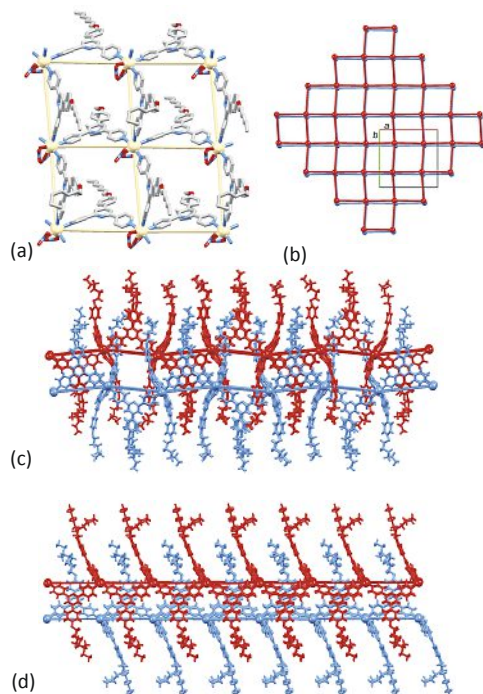


Fig. 3. (a) In $[\{Cd(NO_3)_2(7)_2\}2MeOH]_n$, a planar (4,4) net assembles even though the local geometry at each Cd atom is *cis*- $\{Cd(NO_3)_2(N_{4,2':6',4''-tpy})_4\}$. (b) Eclipsed nets in $[\{Cd_2(NO_3)_4(6)_4\}CHCl_3\cdot MeOH]_n$. Alkylloxy chains from one net extend through the cavities in the next net shown for (c) $[\{Cd_2(NO_3)_4(6)_4\}CHCl_3\cdot MeOH]_n$, and (d) $[\{Cd(NO_3)_2(7)_2\}2MeOH]_n$.

6 ligands in the equatorial sites. However, one needs to think beyond the local geometry of the $\{CoN_4\}$ node to appreciate the subtleties of the 3D-network in $[Co_2(NCS)_4(6)_4]_n$. Just as we saw in Fig. 3a that the local geometry of the *cis*- $\{Cd(NO_3)_2(N_{4,2':6',4''-tpy})_4\}$ unit does not preclude Cd acting as a planar 4-connecting node, we emphasize that the local geometry of the *trans*- $\{Co(NCS)_2(N_{4,2':6',4''-tpy})_4\}$ unit combined with a ditopic ligand (a simple linker) does not necessarily lead to a planar 4-connecting node and a (4,4) net. Whereas it does in $[\{Co(NCS)_2(3)_2\}4CHCl_3]_n$ (with ethoxy substituents, Fig. 4),^[16] it results instead in pseudo-tetrahedral Co nodes in $[Co_2(NCS)_4(6)_4]_n$ and $[Co_2(NCS)_4(8)_4]_n$ and to a 3D-network comprising interconnected 6^6 cages (Fig. 5). The latter is an example of the relatively uncommon *neb* net.^[20] The assembly of this chiral net from achiral nodes and linkers in our case is noteworthy. The switch from 2D-nets to the 3D *neb* net appears to be related to the presence of long alkyloxy chains which can thread through the cavities in the 3D network.

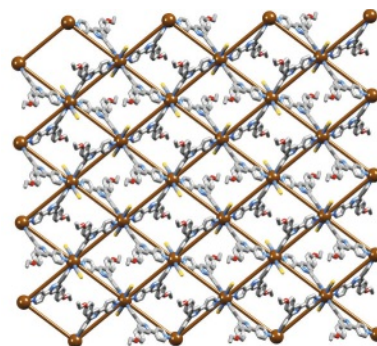


Fig. 4. Part of the (4,4) net in $[\{Co(NCS)_2(3)_2\}4CHCl_3]_n$ with the structure overlaid on the net. Each ligand **3** links a pair of 4-connecting Co nodes.

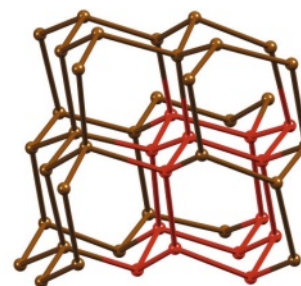


Fig. 5. Part of the 3D-network in $[Co_2(NCS)_4(6)_4]_n$ and $[Co_2(NCS)_4(8)_4]_n$ comprising interconnected 6^6 cages. One 6^6 cage is shown in red.

3. Tetratopic 4,2':6',4''-tpys with Metal Linkers and 4-Connecting Metal Nodes

Scheme 4 shows a family of tetratopic ligands **10–16** consisting of two linked 4,2':6',4''-tpy metal-binding domains. Initially, the substituents in the phenylene spacer were introduced to increase the solubility of the ligand. However, it became apparent that the length and steric properties of the chain were also extremely influential in directing the coordination assembly. Our first examples of coordination networks with tetratopic 4,2':6',4''-tpys were obtained with **10** and **14**. When combined with zinc(II) halides, **10** (methoxy substituents) and **14** (*n*-octyloxy substituents) produced 2D nets and 2D→2D parallel interpenetrating sheets, respectively (Fig. 6).^[21,22] Each 2D net is a uninodal (4,4) assembly with ligands **10** or **14** acting as 4-connecting nodes. As Fig. 6a shows, the *n*-octyloxy chains in coordinated **14** adopt extended conformations and are directed through the middle of the interpenetrated nets, while Fig. 6c illustrates that the shorter methoxy substituents in **10** are oriented above and below the sheet. The reproducibility

of these results with different halides^[22] and the observation of interpenetration when ligands **13** (*n*-hexyloxy substituents) and **15** (*n*-decyloxy substituents) react with zinc(II) halides^[23] provide a clear indication that long chains are a pre-requisite for the stabilization of the 2D→2D parallel interpenetrating assembly.

In the assemblies in Fig. 6, the zinc(II) ions are merely linkers. However, a change to $\text{Co}(\text{NCS})_2$ with ligands of type **10–15** combines (potentially) 4-connecting metal and 4-connecting ligand nodes. Reactions of $\text{Co}(\text{NCS})_2$ and **11** (*n*-propoxy substituents) or **12** (*n*-pentyloxy substituents) resulted in 3D-frameworks in which both metal and ligand function as planar 4-connecting nodes.^[18,24] The observed arrangement of half of the adjacent nodes being mutually perpendicular and half coplanar corresponds to the *cds* net.^[4,20] This is observed for both $[\{\text{Co}(\text{NCS})_2(\mathbf{11})\} \cdot 2\text{C}_6\text{H}_4\text{Cl}_2]_n$ ^[18] and $[\{\text{Co}(\text{NCS})_2(\mathbf{12})\} \cdot 0.8\text{C}_6\text{H}_4\text{Cl}_2]_n$ ^[24] and is depicted for $[\{\text{Co}(\text{NCS})_2(\mathbf{12})\} \cdot 0.8\text{C}_6\text{H}_4\text{Cl}_2]_n$ in Fig. 7. We have yet to investigate how robust this framework is with respect to further lengthening of the alkyloxy chains.

So far, we have focused on varying the length of the *n*-alkyloxy chains, for example in ligands **10–15**. However, introducing a terminal phenyl group proved to be extremely beneficial in terms

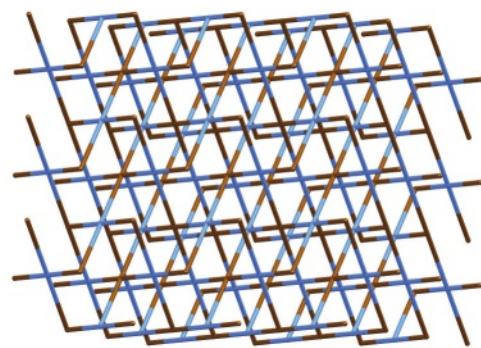
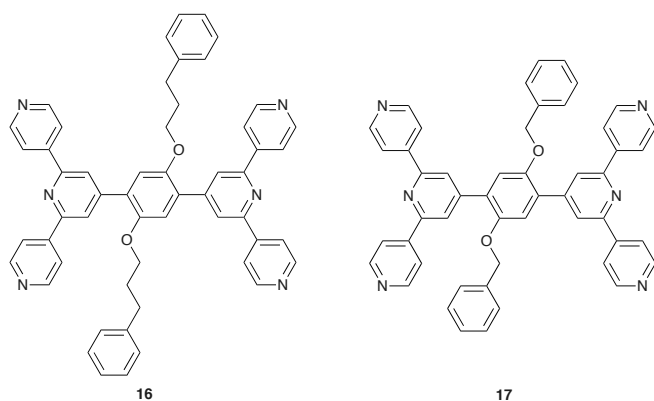
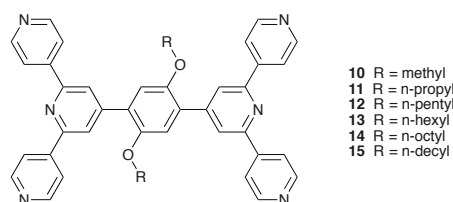


Fig. 7. Part of the *cds* net in $[\{\text{Co}(\text{NCS})_2(\mathbf{12})\} \cdot 0.8\text{C}_6\text{H}_4\text{Cl}_2]_n$ in which both Co and **12** are planar 4-connecting nodes (blue and brown). The centroid of the phenylene spacer in **12** defines the node.

of generating a porous 3D-network rather than a 2D-network. A combination of tetratopic ligand **16** (Scheme 4) with ZnBr_2 resulted in the formation of $[\{\text{Zn}_2\text{Br}_4(\mathbf{16})\} \cdot \text{H}_2\text{O}]_n$ comprising 2-fold interpenetrating *nbo* nets. Unlike the *cds* net (Fig. 7), an *nbo* net possesses all mutually perpendicular adjacent nodes.^[4,20] The MOF assembly in $[\{\text{Zn}_2\text{Br}_4(\mathbf{16})\} \cdot \text{H}_2\text{O}]_n$ is entirely directed by the ligand nodes, with the Zn centre purely being a linker. The feature that makes this network particularly exciting is the close association of the two interpenetrating *nbo* nets through face-to-face π -stacking involving the pendant phenyl rings (Fig. 8a) which leads to a solvent accessible void space of around 65% (Fig. 8b).^[23] While it is clear that the 3-phenylpropoxy chains are critical to the formation of the beautiful architecture illustrated in Fig. 8, the length of the chain remains a critical factor and we are far from being able to state ‘design rules’ to deliberately direct these assemblies. The divergence of well-defined assembly pathways and those resulting from serendipity is nicely exemplified by the unexpected formation of a mononuclear complex in which ligand **17** (carrying benzyl instead of the 3-phenylpropoxy substituents present in **16**, Scheme 4) coordinates in a monodentate fashion in the mononuclear complex $[\text{Co}(\text{NCS})_2(\text{MeOH})_2(\mathbf{17})_2]_n$.^[24] Although we were not able to verify that this single crystal structure was representative of the bulk sample, this last result underlines the difficulties in designing ligands, and in selecting specific combinations of ligands and metal salts, to achieve a predetermined structural assembly unless the nodes and linkers are inflexible in their connectivity patterns.^[25–27]

Before leaving tetratopic 4,2':6',4''-tpys, it is appropriate to add a further word about the spacer (Scheme 2). In addition to functionalized phenylene spacers, we have investigated the use of 1,1'-disubstituted ferrocenyl units. The rotational freedom of the ferrocenyl core in ligand **18** (Fig. 9) may be seen as advantageous as far as ligand flexibility in assembling a 3D-network is



Scheme 4. Structures of tetratopic ligands **10–17**.

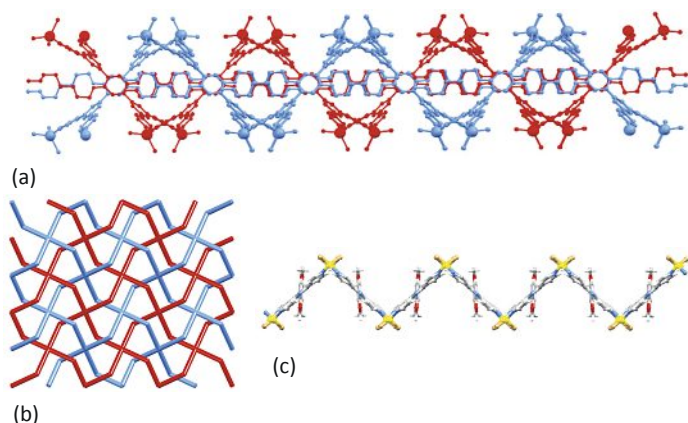


Fig. 6. (a) 2D→2D parallel interpenetration of nets (red and blue) in $[\{\text{Zn}_2\text{Cl}_4(\mathbf{14})\} \cdot 4\text{H}_2\text{O}]_n$ showing the *n*-octyloxy chains in extended conformations running through the middle of the sheets. (b) Representation of the 2D→2D parallel interpenetrated nets in $[\{\text{Zn}_2\text{Cl}_4(\mathbf{14})\} \cdot 4\text{H}_2\text{O}]_n$. (c) Side view of a single 2D net in $[\{\text{Zn}_2\text{Br}_4(\mathbf{10})\} \cdot 2\text{C}_6\text{H}_4\text{Cl}_2]_n$ showing that the methoxy groups are directed above and below the sheet.

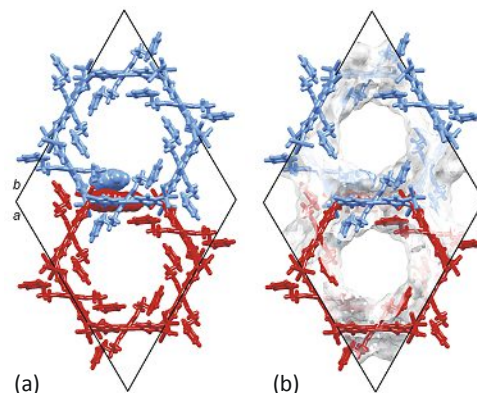


Fig. 8. Views down the *c*-axis of the trigonal unit cell in $[\{\text{Zn}_2\text{Br}_4(\mathbf{16})\} \cdot \text{H}_2\text{O}]_n$: (a) showing π -stacking between parts of the two interpenetrating nets, and (b) a representation of the solvent accessible void space.

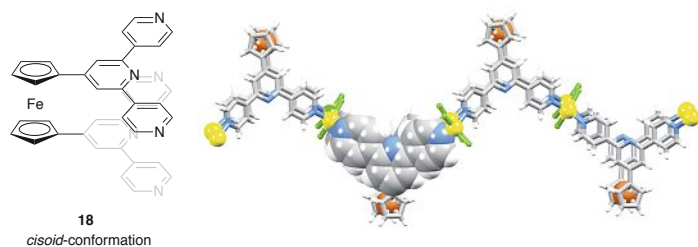


Fig. 9. Structure of ligand **18** in a *cisoid*-conformation and part of the double-stranded chain in $[\{Zn_2Cl_4(\mathbf{18})\}_n]3CHCl_3$.

concerned. However, in reality the face-to-face π -stacking of the two 4,2':6',4''-tpy domains that results from a *cisoid*-conformation (Fig. 9) seems to be so highly preferred that assemblies with zinc(II) halides are reduced to double-stranded chains.^[28]

4. Assembly Constrained to a 2D Platform

In the networks discussed above, anions and solvent molecules play a significant role in the crystal lattice. In all the examples presented, the anions (NCS^- , NO_3^- , Cl^- , Br^-) occupy two or more coordination sites at each metal centre. Although we have not discussed packing interactions involving solvents in this article, it is obvious that solvent molecules play a vital role in filling otherwise empty cavities and helping to stabilize the crystal lattice. What happens if the solvent molecules and anions are absent? In practice, we have approached this fascinating question by constraining the coordination assembly to a 2D Au(111) or Cu(111) platform using the ditopic ligands **19–21** (Scheme 5) with adsorbed copper atoms *in vacuo* and imaging the surface assemblies using scanning tunnelling microscopy (STM).^[29] Highly ordered ladder assemblies result and the presence of the ethyl substituent in **21** permits precise molecular resolution by STM, the pyrimidinyl substituent being easily distinguished from the two outer pyridinyl units of the 4,2':6',4''-tpy. When **21** is deposited on an Au(111) surface by thermal sublimation followed by *in situ* addition of Cu adatoms, long straight ladders are observed as shown in Fig. 10a. Essentially the same assemblies are observed when **21** is deposited on a Cu(111) surface (Fig. 10b). Fig. 10c shows a molecular interpretation of part of one chain showing the ethyl substituent pointing outwards from the ladder.

5. Conclusions

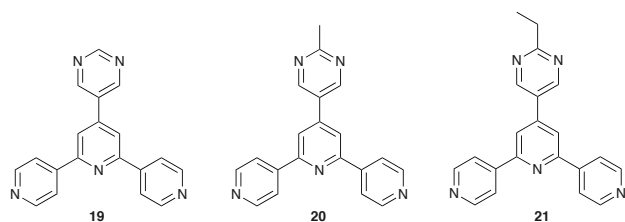
Over the last decade, we have explored the coordination chemistry of ditopic and tetratopic ligands with 4,2':6',4''-tpy metal-binding domains and have demonstrated the versatility of these as divergent N,N' - or N,N',N'',N''' -donor building blocks in 2D- and 3D-coordination networks. While the ditopic ligands in Scheme 3 are limited to a role as a linker in coordination assemblies, the tetratopic ligands in Scheme 4 can be 4-connecting nodes. Functionalization in the 4'-position of ditopic 4,2':6',4''-tpys with different length alkyloxy tails provides a means of switching the dimensionality of the coordination network. Combinations of 4-connecting ligand nodes with metal-linkers have produced both 2D- and 3D-networks, while combinations of 4-connecting metal and ligand nodes lead to 3D-architectures. The length and steric properties of the alkyloxy chains attached to the ligand-spacer are highly influential in directing the coordination assembly. Finally, we have constrained the coordination assembly to 2-dimensions by depositing ditopic ligands onto Au(111) or Cu(111) platforms with Cu adatoms in the former case. The highly ordered assemblies that result are independent of solvent molecules or anions.

Acknowledgements

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Scheme 5. Structures of ligands **19–21**.

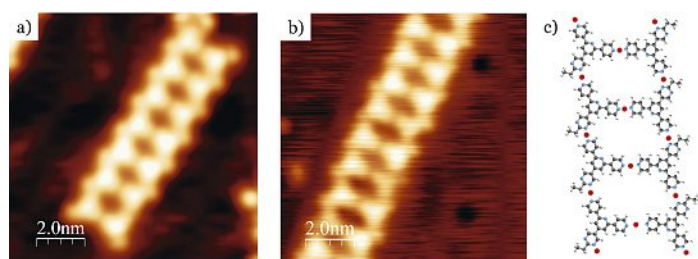


Fig. 10. Comparison of parts of **21** (a) on Au(111)+Cu adatoms and (b) on Cu(111). (c) Model of part of one chain showing the ethyl substituent pointing to the outside of the ladder. (Reprinted with permission from *J. Am. Chem. Soc.* **2018**, *140*, 2933. Copyright 2018 American Chemical Society.)

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