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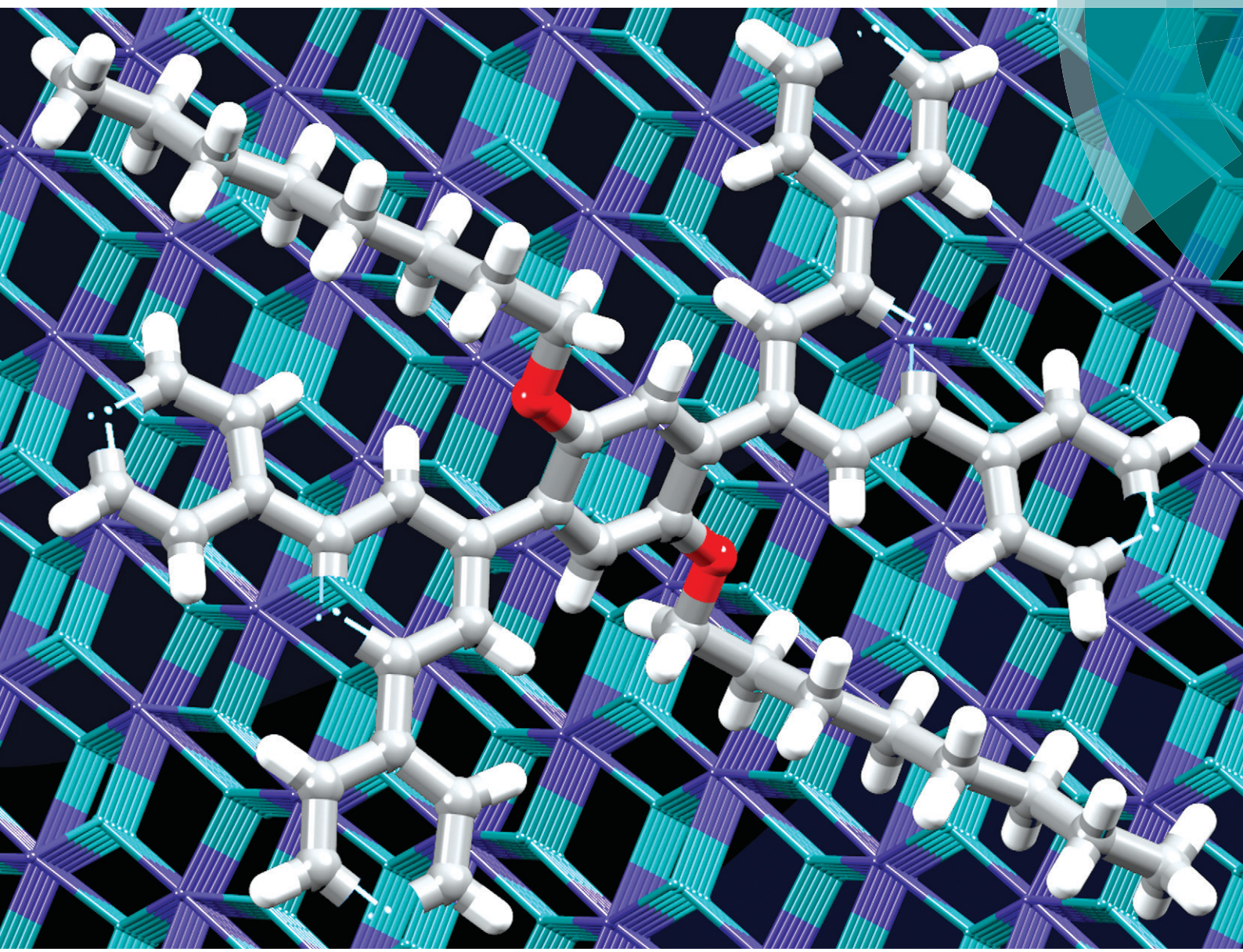

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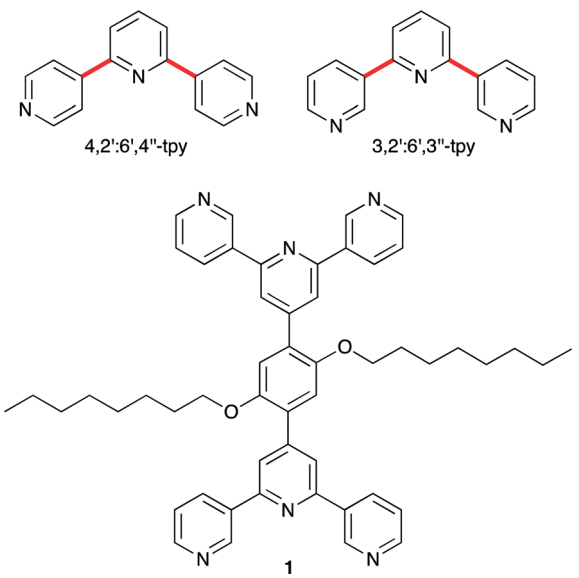
A 3-dimensional $\{4^2{\cdot}8^4\}$ lvt net built from a ditopic bis(3,2′:6′,3″-terpyridine) tecton bearing long alkyl tails†

Y. Maximilian Klein, Edwin C. Constable, Catherine E. Housecroft* and Alessandro Prescimone

Divergent bis(terpyridine) tectons are versatile ligands for the assembly of coordination networks; we demonstrate the assembly of a 3-dimensional $\{4^2{\cdot}8^4\}$ **lvt** net (still relatively sparse among 4-connected nets in metal–organic frameworks) from the reaction of 1,4-bis(*n*-octoxy)-2,5-bis(3,2′:6′,3″-terpyridin-4′-yl)benzene and $Co(NCS)_2$.

Oligopyridines[1] remain as one of the most widespread building blocks in the toolbox of a coordination chemist. The bis(chelate) 2,2′:6′,2″-terpyridine (2,2′:6′,2″-tpy) is especially popular and multitopic ligands containing peripheral 2,2′:6′,2″-tpy domains[2] have been used in a wide variety of architectures. 4,2′:6′,4″-Terpyridine (4,2′:6′,4″-tpy, Scheme 1) and 3,2′:6′,3″-terpyridine (3,2′:6′,3″-tpy, Scheme 1) are less familiar isomers of terpyridine, but in the last decade, the use of 4,2′:6′,4″-tpy as a building block of coordination polymers has grown significantly.[3] In metal complexes of 4,2′:6′,4″-tpy, the central pyridine ring is non-coordinated and the remaining *N*,*N*′-donor set presents a divergent domain, with vectorial properties that are unaffected by inter-ring bond rotation (red bonds in Scheme 1). In contrast, rotation about the interannular bonds in 3,2′:6′,3″-tpy alters its divergent coordination mode.[4]

The beauty of terpyridine metal-binding domains is the ease with which substituents can be introduced into the 4′-position, for example by using Kröhnke's[5] or Wang and Hanan's[6] strategies. With coordinatively innocent 4′-substituents, reactions between 4,2′:6′,4″-terpyridines and metal ions yield metallomacrocycles, 1-dimensional chains or 2-dimensional nets.[3] Extension to 3-dimensions is achieved by introducing non-innocent domains such as diphenylphosphino,[7] carboxylato,[8] or pyridyl[9] functionalities, or by using co-ligands.[10] An alternative approach to increase dimensionality is through the coordination capacity of multitopic 4,2′:6′,4″-tpy ligands, although such compounds have received scant attention.[11–14] We have demonstrated that 1,4-bis(*n*-octoxy)-2,5-bis(4,2′:6′,4″-terpyridin-4′-yl)benzene reacts with $ZnCl_2$ to give a network consisting of (4,4)-sheets engaging in 2D → 2D parallel interpenetration,[14] and a report on a triply interpenetrating network formed between cobalt(II) and 1,3-di((4,2′:6′,4″-terpyridin)-4′-yl)benzene has appeared.[12] We now describe the synthesis of the bis(3,2′:6′,3″-tpy) ligand **1** (Scheme 1) and its reaction with $Co(NCS)_2$ to give a 3-dimensional $\{4^2{\cdot}8^4\}$ **lvt** net.[15] The inclusion of the long alkoxy chains in **1** enhances the solubility of the ligand with respect to analogues with simple phenylene spacers,[14] and also has a stabilizing influence on an infinite architecture.



Scheme 1 Structures of divergent isomers of terpyridine and the ditopic ligand **1**. See text for significance of the bonds marked in red.

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† Electronic supplementary information (ESI) available: Synthetic and crystallographic details; Fig. S1–S2 solution ^{1}H NMR and absorption spectra of **1**. CCDC 1035825. See DOI: 10.1039/c4ce02347a

Ligand **1** was synthesized† using the one-pot method of Wang and Hanan[6] starting from 2,5-bis(octoxy)benzene-1,4-dicarbaldehyde and 4.7 equivalents of 3-acetylpyridine in EtOH in the presence of NH_3. Compound **1** was isolated in 41% yield. The electrospray mass spectrum exhibited a base peak at *m*/*z* 797.8 arising from $[M+H]^+$, and ^1H (Fig. S1†) and ^{13}C NMR spectra (assigned using COSY, DEPT, HMQC and HMBC techniques) were consistent with the symmetrical structure shown in Scheme 1. The absorption spectrum of **1** has broad and intense, high energy bands arising from $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions which extend into the visible region (Fig. S2†).

Layering of MeOH and $CHCl_3$ solutions of $Co(NCS)_2$ and **1**, respectively, resulted in the formation of pink crystals of $[Co(NCS)_2(\mathbf{1})\cdot 4CHCl_3]_n$ within 2–4 weeks in 14% yield. The crystal selected for single crystal X-ray diffraction was solved and refined in the non-centrosymmetric space group $Pna2_1$. The Flack parameter of 0.480(10) suggested that it was a twin by inversion[16] as every attempt to either solve or refine the structure in *Pnma* failed and ADDSYMM[17] could not identify an alternative space group. The asymmetric unit contains one molecule of **1** and a $Co(NCS)_2$ unit; the octoxy chain containing atom C19 was refined isotropically and three of the C–C distances were restrained to chemically reasonable values. The cobalt ion is octahedrally coordinated, and **1** binds through the outer *N*-donors to four cobalt centres (Fig. 1), leaving the central nitrogen atoms N2 and N6 uncoordinated. Atom Co1 coordinates to two $[NCS]^-$ ligands in a *trans*-arrangement and to four different **1** ligands in the equatorial plane. The two independent octoxy chains are in non-extended conformation, and each is folded over a 3,2′:6′,3″-tpy unit with close C–H···π contacts (H···centroid = 3.19 and 3.23 Å for the pyridine rings containing N1 and N4).

Pairs of cobalt atoms are either bridged by a single 4,2′:6′,4″-tpy (*e.g.* Co1 and Co1^{v} in Fig. 1) or by two *N*-donors from each of the two 4,2′:6′,4″-tpy domains of **1** (*e.g.* Co1 and Co1^{iv} in Fig. 1). The latter coordination mode extends to the formation of [2 + 2] metallomacrocycles (Fig. 2a) which are interlinked through the cobalt centres, as shown in Fig. 2b. The structure propagates into a 2-nodal $\{4^2\cdot 8^4\}$ **lvt** net.[14] The two 4-connected nodes are Co1 and the centroid of the arene spacer in **1**, which are planar and approximately tetrahedral, respectively. Although the local $\{Co(N_{tpy})_4\}$ domain in $[Co(NCS)_2(\mathbf{1})\cdot 4CHCl_3]_n$ is square planar (N_{tpy}–Co–N_{tpy} angles = 90.9(3), 89.1(3), 92.9(3) and 87.1(3)°), the cobalt node is distorted in the topological description of the net (centroid–Co–centroid angles = 96.6, 64.6, 132.2 and 67.4°) while remaining planar. Topological representations of the framework in $[Co(NCS)_2(\mathbf{1})\cdot 4CHCl_3]_n$ are shown in Fig. 3. The view down the *a*-axis in Fig. 3a is directly comparable with the structure in Fig. 2b.

The voids in the net are occupied by the octoxy chains and $CHCl_3$ molecules. Fig. 4 illustrates that the chains lie in the *ac*-plane, a consequence of the close CH···π contacts between the terminal CH_2CH_3 units of each chain and pyridine rings (see above).

In conclusion, we have shown that, by adopting a conformation in which the two 3,2′:6′,3″-tpy metal-binding domains

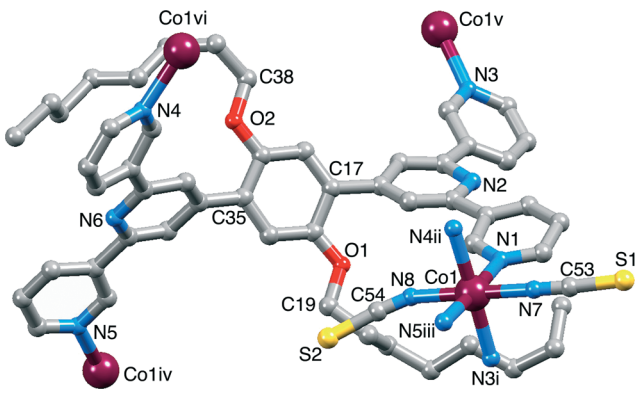

Fig. 1 The repeat unit (with symmetry generated Co atoms) in $[Co(NCS)_2(\mathbf{1})\cdot 4CHCl_3]_n$ (H atoms and solvent molecules are omitted). Symmetry codes: i = 1/2 + *x*, 1/2 − *y*, *z*; ii = −*x*, 1 − *y*, −1/2 + *z*; iii = 1/2 − *x*, 1/2 + *y*, 1/2 − *z*; iv = 1/2 − *x*, −1/2 + *y*, 1/2 + *z*; v = −1/2 + *x*, 1/2 − *y*, *z*; vi = −*x*, 1 − *y*, 1/2 + *z*. Selected bond parameters: Co1–N1 = 2.185(8), Co1–N3i = 2.212(7), Co1–N4ii = 2.204(8), Co1–N5iii = 2.181(8), Co1–N7 = 2.096(8), Co1–N8 = 2.079(8) Å; Co1–N7–C53 = 161.0(8), Co1–N8–C54 = 151.2(8), N1–Co1–N5iii = 176.2(3), N3i–Co1–N4ii = 178.6(3)°.

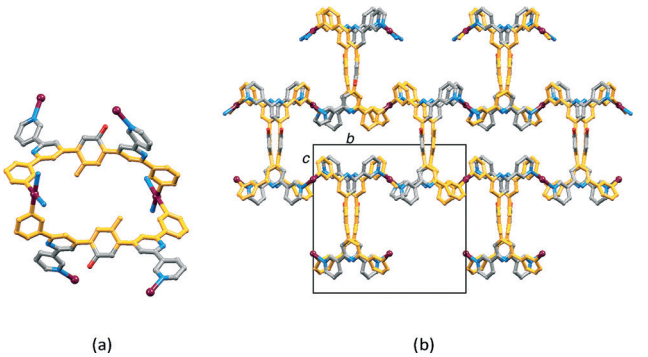

Fig. 2 (a) A [2 + 2] metallomacrocycle formed from two Co1 atoms and two half-ligands (in orange). (b) Interconnection of metallomacrocycles with the unit cell viewed down the *a*-axis.

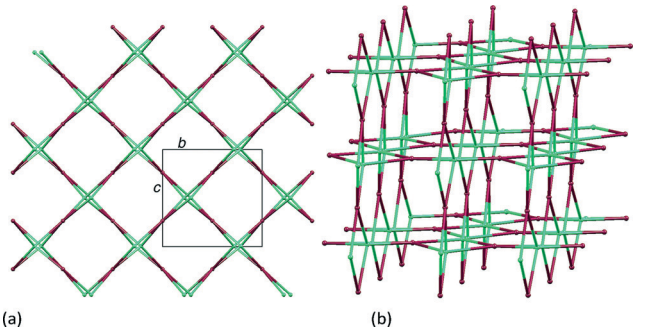

Fig. 3 TOPOS[18] representations of the $\{4^2\cdot 8^4\}$ **lvt** net in $[Co(NCS)_2(\mathbf{1})\cdot 4CHCl_3]_n$: (a) view down the *a*-axis for comparison with Fig. 2b, and (b) showing the 4- and 8-membered metallomacrocycles. Metal nodes, purple; ligand–centroid nodes, green.

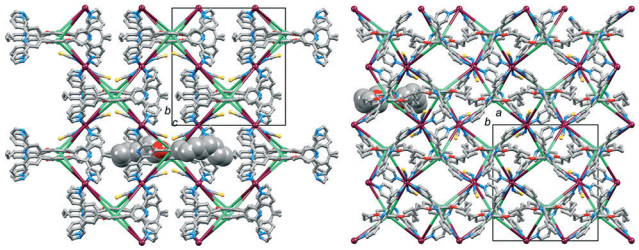

Fig. 4 Superimposition of the topological representation of the **lvt** net in $[Co(NCS)_2(\mathbf{1})\cdot 4CHCl_3]_n$ and the structure (H atoms and $CHCl_3$ molecules are omitted); the octoxy chains of one ligand are shown in the space-filling representation: views down the (a) *a*-axis and (b) *c*-axis.

are orthogonal, ligand **1** can combine with a planar 4-connecting metal node to produce a $\{4^2\cdot 8^4\}$ **lvt** net. Among metal–organic frameworks, the **lvt** topology is scarce in comparison with other 4-connected nets.[19] The conformational flexibility of ditopic bis(4,2′:6′,4″-tpy) and bis(3,2′:6′,3″-tpy) ligands allows the two tpy units to lie on a path between coplanar[13] and orthogonal (as in the current work), making these isomeric ligands attractive tectons. We are currently developing the coordination chemistry of multitopic 4,2′:6′,4″-tpy and 3,2′:6′,3″-tpy ligands to investigate which building blocks favour the assembly of 2- *versus* 3-dimensional networks.

Acknowledgements

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