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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†

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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.

Oligopyridines¹ 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 domains² 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's⁵ or Wang and Hanan's⁶ 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 pyridyl⁹ 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 ZnCl₂ 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 ¹H 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 Hanan⁶ starting from 2,5-bis(octoxy)benzene-1,4-dicarbaldehyde and 4.7 equivalents of 3-acetylpyridine in EtOH in the presence of NH₃. 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 ¹³C 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 CHCl₃ solutions of Co(NCS)₂ and **1**, respectively, resulted in the formation of pink crystals of [Co(NCS)₂(**1**)·4CHCl₃]_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 *Pna*2₁. The Flack parameter of 0.480(10) suggested that it was a twin by inversion¹⁶ as every attempt to either solve or refine the structure in *Pnma* failed and ADDSYM¹⁷ 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 {4²·8⁴} *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(**1**)·4CHCl₃]_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(**1**)·4CHCl₃]_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 CHCl₃ molecules. Fig. 4 illustrates that the chains lie in the *ac*-plane, a consequence of the close CH⋯ π contacts between the terminal CH₂CH₃ 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. 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. 4 Superimposition of the topological representation of the lvt net in $[\text{Co}(\text{NCS})_2(1)\cdot 4\text{CHCl}_3]_n$ 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 coplanar¹³ 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.

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