A 3-dimensional \( \{4 \times 8\} \) \( \text{liv} \) net built from a ditopic bis(3,2\(^{\prime}\):6,3\(^{\prime}\)-terpyridine) tecton bearing long alkyl tails.
A 3-dimensional \{4^{2}\cdot8^{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}\cdot8^{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 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 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. 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.

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 or Wang and Hanani’s strategies. With coordinatively innocent 4′-substituents, reactions between 4,2′:6′,4″-terpyridines and metal ions yield metallocamacrocycles, 1-dimensional chains or 2-dimensional nets. Extension to 3-dimensions is achieved by introducing non-innocent domains such as diphenylphosphino, carboxylato, or pyridyl functionalities, or by using co-ligands. 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. 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, 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. 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}\cdot8^{4}\} lvt net. The inclusion of the long alkoxy chains in 1 enhances the solubility of the ligand with respect to analogues with simple phenylene spacers, 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‡ starting from 2,5-bis(octoxy)benzene-1,4-dicarbaldehyde and 4.7 equivalents of 3-acyetylpyridine 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 ¹³C NMR spectra (assigned using COSY, DEPT, HMOC 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 π* → n and π* → π 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)]₄ 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 Pnma by inversion¹⁶ as every attempt to either solve or refine the structure in Pnma failed and ADDSYM⁷ could not identify an alternative space group. The asymmetric unit contains one molecule of 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′ 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 Co1w 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 {2-8⁴} net.¹⁴ The two 4-connected nodes are Co1 and the centroid of the aren spacer in 1, which are planar and approximately tetrahedral, respectively. Although the local {Co[Ntpy]₄} domain in [Co(NCS)₂(1-4CHCl₃)]₄ is square planar (Ntpy-Co-Ntpy 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)]₄ 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
are orthogonal, ligand 1 can combine with a planar 4-connecting metal node to produce a \{4^2,8^3\} \textit{lt} net. Among metal-organic frameworks, the \textit{lt} topology is scarce in comparison with other 4-connected nets.\textsuperscript{19} The conformational flexibility of ditopic bis(4,2′,3′,4′-tpy) and bis(3,2′,3′,6′-tpy) ligands allows the two tpy units to lie on a path between coplanar\textsuperscript{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′- 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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Notes and references


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