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## A 3-dimensional {4<sup>2</sup>·8<sup>4</sup>} 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)<sub>2</sub>.

Oligopyridines<sup>1</sup> 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<sup>2</sup> 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.<sup>3</sup> 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.<sup>4</sup>

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<sup>5</sup> or Wang and Hanan's<sup>6</sup> 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.<sup>3</sup> Extension to 3-dimensions is achieved by introducing non-innocent domains such as diphenylphosphino,<sup>7</sup> carboxylato,<sup>8</sup>

or pyridyl<sup>9</sup> functionalities, or by using co-ligands.<sup>10</sup> 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.<sup>11-14</sup> We have demonstrated that 1,4-bis(n-octoxy)-2,5-bis(4,2':6',4"terpyridin-4'-yl)benzene reacts with ZnCl<sub>2</sub> to give a network consisting of (4,4)-sheets engaging in  $2D \rightarrow 2D$  parallel interpenetration,<sup>14</sup> 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.<sup>15</sup> The inclusion of the long alkoxy chains in 1 enhances the solubility of the ligand with respect to analogues with simple phenylene spacers,<sup>14</sup> and also has a stabilizing influence on an infinite architecture.

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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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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Synthetic and crystallographic details; Fig. S1–S2 solution <sup>1</sup>H NMR and absorption spectra of 1. CCDC 1035825. See DOI: 10.1039/c4ce02347a

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Ligand 1 was synthesized† using the one-pot method of Wang and Hanan<sup>6</sup> starting from 2,5-bis(octoxy)benzene-1,4dicarbaldehyde and 4.7 equivalents of 3-acetylpyridine in EtOH in the presence of NH<sub>3</sub>. Compound 1 was isolated in 41% yield. The electrospray mass spectrum exhibited a base peak at m/z 797.8 arising from [M+H]<sup>+</sup>, and <sup>1</sup>H (Fig. S1†) and <sup>13</sup>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<sub>3</sub> solutions of Co(NCS)<sub>2</sub> and 1, respectively, resulted in the formation of pink crystals of  $[Co(NCS)_2(1)\cdot 4CHCl_3]_n$  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 Pna21. The Flack parameter of 0.480(10) suggested that it was a twin by inversion<sup>16</sup> as every attempt to either solve or refine the structure in Pnma failed and ADDSYMM<sup>17</sup> could not identify an alternative space group. The asymmetric unit contains one molecule of 1 and a Co(NCS)<sub>2</sub> 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··· $\pi$  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<sup>v</sup> in Fig. 1) or by two *N*-donors



Fig. 1 The repeat unit (with symmetry generated Co atoms) in  $[Co(NCS)_2(1)\cdot 4CHCl_3]_n$  (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)°.

from each of the two 4,2':6',4"-tpy domains of 1 (e.g. Co1 and Co1<sup>iv</sup> 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.<sup>14</sup> 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  $\{Co(N_{tpv})_4\}$  domain in  $[Co(NCS)_2(1) \cdot 4CHCl_3]_n$  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  $[Co(NCS)_2(1)\cdot 4CHCl_3]_n$  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  $CH\cdots\pi$  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. 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<sup>18</sup> representations of the  $\{4^2, 8^4\}$  **lvt** net in  $[Co(NCS)_2(1).4CHCl_3]_n$ : (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.

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**Fig. 4** Superimposition of the topological representation of the **lvt** net in  $[Co(NCS)_2(1).4CHCl_3]_n$  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  $\{4^2\cdot8^4\}$  **lvt** net. Among metal–organic frameworks, the **lvt** topology is scarce in comparison with other 4-connected nets.<sup>19</sup> 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<sup>13</sup> 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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