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Constructing chiral MOFs by functionalizing 4,2':6',4''-terpyridine with long-chain alkoxy domains: rare examples of *neb* nets†

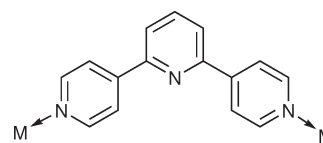
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Reactions of 4'-(4-*n*-alkyloxyphenyl)-4,2':6',4''-terpyridines (alkyl = hexyl or nonyl) with Co(NCS)₂ lead to three structurally characterized chiral 3D assemblies which adopt rare *neb* topologies. For the *n*-hexyl-functionalized ligands, both enantiomorphic lattices of the *neb* nets (crystallizing in the tetragonal space groups *P*4₁2₁2 and *P*4₃2₁2, respectively) are presented.

The coordination chemistry of the divergent ligands 4,2':6',4''- and 3,2':6',3''-terpyridine is dominated by the assembly of extended 1D chain or 2D sheet structures or discrete metallomacrocycles.^{1–4} 4,2':6',4''-Terpyridines (4,2':6',4''-tpy) coordinate only through the outer two pyridine donors, providing the V-shaped tecton shown in Scheme 1. This coordination motif is well-established and entry into higher-dimensionality architectures is typically accomplished by introducing donor groups in the 4'-position. In addition to the widespread use of pyridinyl^{5–7} and carboxylate^{8–13} functionalities, sulfonate donors have also been used to access 3D frameworks.¹⁴ 3D-networks utilizing only the two pendant donors of the 4,2':6',4''-tpy domain are relatively rare, although the reaction of 4'-(pyridin-2-yl)-4,2':6',4''-tpy and Co(NCS)₂ gives a 3D structure in which the pyridinyl substituent is not coordinated.¹⁵ This is an unusual case where combination of a simple 4,2':6',4''-tpy ligand and Co(NCS)₂ leads to a 3D framework; more usually, 2D (4,4) or (6,3) nets result.^{16–18} A (4,4) net also forms when CoCl₂·6H₂O reacts with 4'-(3,4-dimethoxyphenyl)-4,2':6',4''-tpy.¹⁹

Although coordination polymers and networks containing a wide variety of 4,2':6',4''-tpy or 3,2':6',3''-tpy ligands are known, it remains a challenge to code for 3D frameworks rather than 1D-chains or 2D-nets in the absence of additional coordination domains or of co-ligands. To direct the assembly of 3D architectures predicated upon 4,2':6',4''- and 3,2':6',3''-tpy motifs, we have adopted two strategies. In the first, we have used ditopic ligands²⁰ containing 'back-to-back' 4,2':6',4''-tpy or 3,2':6',3''-tpy domains.^{21–23} In the second, we have selected metal-nodes which prefer 6-(or higher) coordination numbers, *e.g.* reaction between the tpy ligands and Co(NCS)₂ (ref. 16–18) or Cd(NO₃)₂·4H₂O.^{24–26}

One way to modify assembly algorithms is with 4'-(4-alkyloxyphenyl)-4,2':6',4''-terpyridines (Scheme 2) in which the steric demands of the 4'-substituent are altered. We have shown that 1D [Zn₂(OAc)₄(4'-(4-ROC₆H₄)-4,2':6',4''-tpy)]_n coordination polymers in which the main packing interactions are π -stacking between arene domains are favoured for small R groups, whereas with longer-chain alkoxy units in which van der Waals interactions are important, discrete complexes [Zn₂(OAc)₄(4'-(4-ROC₆H₄)-4,2':6',4''-tpy)₂] form.²⁷ In a second example, functionalization of the spacer in ditopic 4,2':6',4''-tpy ligands with *n*-octyloxy chains directs the formation of 2D \rightarrow 2D parallel interpenetrated nets, whereas single nets result with methoxy-substituents.^{21,22} We recently reported the assembly of 2D (4,4) nets in the reactions of Co(NCS)₂ with ligands 1–3 (Scheme 2).¹⁷ In each net, the Co atom acts as a 4-connecting, planar node; subtle differences in packing resulted in inter-sheet separations increasing from 8.936 Å (R = Me, Scheme 2) to 9.228 Å (R = Et) to 9.305 Å (R = *n*Pr). The



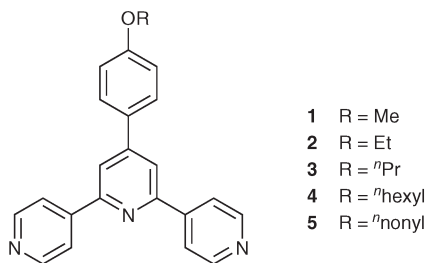
Scheme 1 Divergent coordination mode of the archetype 4,2':6',4''-tpy ligand.

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† Electronic supplementary information (ESI) available: Experimental and crystallographic details. Fig. S1 and S3: powder diffraction data and additional figures of lattices in [Co₂(NCS)₄(4)₄]_n; Fig. S4: interpenetrating *nbo* nets in [Co(NCS)₂(4'-(pyridin-2-yl)-4,2':6',4''-tpy)]_n (refcode XUVPAH). CCDC 1474325–1474327. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6ce00939e





Scheme 2 The structures of the 4'-(4-alkoxyphenyl)-4,2':6',4"-terpyridine ligands 1–5.

most significant differences in packing arose from the intrusion of the longer alkoxy chains through the cavities in adjacent sheets.¹⁷ These results prompted us to investigate the effects of further increasing the length of the alkyl chains, and we report here the assembly of infrequently observed *neb* nets with 6⁶ cage units.²⁸

Ligands 4 and 5 were prepared as previously reported.²⁷ Single crystals of $[\text{Co}_2(\text{NCS})_4(4)_4]_n$ were grown at room temperature by layering an MeOH solution of anhydrous $\text{Co}(\text{NCS})_2$ over a CHCl_3 solution of 4 (36.9 mg, 0.09 mmol). Two different crystals were selected from the bulk material for single-crystal structure determination. These crystallized in the tetragonal space groups $P4_12_12$ and $P4_32_12$, respectively. Since $P4_12_12$ and $P4_32_12$ constitute an enantiomorphic pair, the structure of $[\text{Co}_2(\text{NCS})_4(4)_4]_n$ is inherently chiral. However, since the Flack parameters are 0.21(3) and 0.16(2), respectively, each structure contains 21% or 16% of the second enantiomorph. We discuss the local details of the structure for only one structure (that in space group $P4_32_12$). The bulk sample was characterized by powder diffraction (see Fig. S1†).

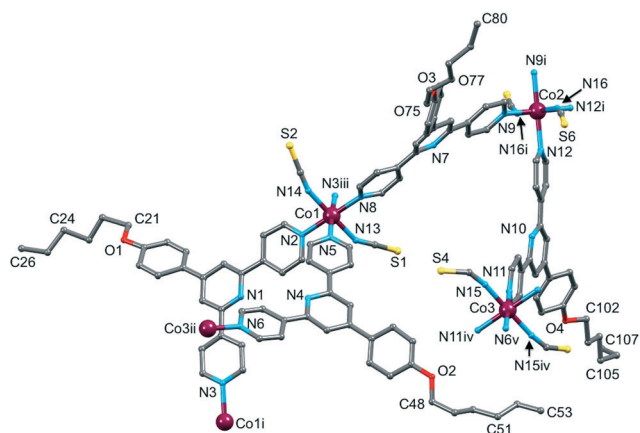


Fig. 1 The asymmetric unit of $[\text{Co}_2(\text{NCS})_4(4)_4]_n$ with symmetry-generated atoms (space group $P4_32_12$); H atoms are omitted and only the major sites of the disordered sites (see text) are shown. Symmetry codes: i = $y, x, 1 - z$; ii = $-\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z$; iii = $\frac{1}{2} - y, -\frac{1}{2} + x, -\frac{1}{2} + z$; iv = $1 - y, 1 - x, \frac{3}{2} - z$; v = $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. Selected bond distances: Co1–N2 = 2.166(5), Co1–N3iii = 2.173(5), Co1–N5 = 2.129(5), Co1–N8 = 2.159(5), Co1–N13 = 2.100(6), Co1–N14 = 2.082(6), Co2–N12 = 2.209(5), Co2–N12i = 2.209(5), Co2–N16 = 2.093(7), Co2–N9 = 2.170(3), Co3–N6 = 2.163(5), Co3–N11 = 2.182(5), Co3–N15 = 2.073(7) Å.

Fig. 1 shows the asymmetric unit of $[\text{Co}_2(\text{NCS})_4(4)_4]_n$ with symmetry-generated atoms. Each of the three independent Co atoms is octahedrally sited with a *trans* arrangement of N-bonded thiocyanato ligands. The thiocyanates containing S2, S4 and S6 are disordered and each has been modelled over two sites of 60.3/39.7, 62.1/37.9 and 56.4/43.6% occupancies, respectively. Each of the four independent ligands 4 coordinates through the outer two pyridine rings, consistent with previously reported coordination modes.^{1,2} The Co–N bond distances (see caption to Fig. 1) and bond angles within the coordination spheres are unexceptional. No significant deviations from planarity are noted for the tpy units; twist angles between pairs of bonded pyridine rings range from 6.5 to 16.3°. Each phenyl ring is, as expected on steric grounds, twisted with respect to the pyridine ring to which it is attached (range of angles = 36.1 to 37.6°).

The structure shown in Fig. 1 propagates into a 3D framework. The differences in coordination environments about Co1, Co2 and Co3 in $[\text{Co}_2(\text{NCS})_4(4)_4]_n$ are structurally insignificant and the framework is uninodal. Fig. 2 shows views down the crystallographic *c* and *b*-axes, generated using a combination of TOPOS²⁹ and Mercury (v. 3.7).^{30,31} The 4-fold screw axes that define the chirality (*i.e.* opposite handednesses in each of space groups $P4_12_12$ and $P4_32_12$, Fig. S2†) of the lattice run along the *c*-axis. Views down either the *a* or *b*-axes (Fig. 2, right) reveal the 6-membered rings present in the 4-connected net. The combination of 4-coordinate nodes and 6-membered rings is reminiscent of diamond. However, whereas a diamond net consists of interconnected 6⁴ cage units, Fig. 3 illustrates that the 4-connected framework in $[\text{Co}_2(\text{NCS})_4(4)_4]_n$ is constructed from 6⁶ cage units.²⁸ Each Co···Co edge of the 3D framework is spanned by one ligand 4 and the hexyloxy-chains are in close to extended conformations, directed along the *a* and *b*-axes (Fig. 4).

The reaction of 5 with $\text{Co}(\text{NCS})_2$ led to single crystals of $[\{\text{Co}_2(\text{NCS})_4(5)_4\} \cdot 2\text{CHCl}_3 \cdot \text{MeOH}]_n$. The compound crystallizes in the tetragonal space group $P4_12_12$, once again signifying a chiral network. The asymmetric unit contains three independent Co atoms and four independent ligands 5, and structural details within the coordination sphere of each Co atom are analogous to those shown in Fig. 1 for $[\text{Co}_2(\text{NCS})_4(4)_4]_n$. As in the latter, the Co–N(NCS) bond distances (range 2.065(5) to 2.107(5) Å) in $[\{\text{Co}_2(\text{NCS})_4(5)_4\} \cdot 2\text{CHCl}_3 \cdot \text{MeOH}]_n$ are shorter than the C–N(tpy) bond lengths (range 2.153(5) to

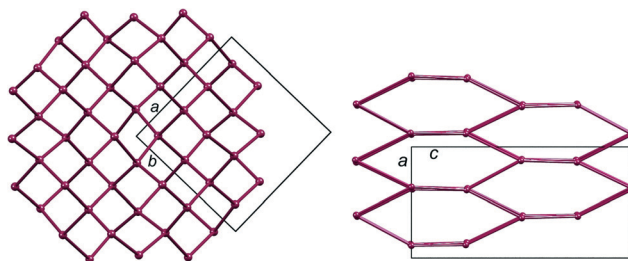


Fig. 2 $[\text{Co}_2(\text{NCS})_4(4)_4]_n$ (space group $P4_32_12$): views down the crystallographic *c* and *b* axes, generated using TOPOS and Mercury.



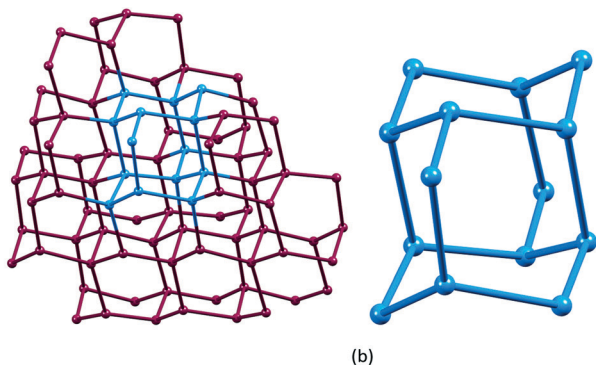


Fig. 3 (a) TOPOS/Mercury representation of the structure of $[\text{Co}_2(\text{NCS})_4(4)_4]_n$ showing Co nodes. (b) The fundamental 6^6 unit of the *neb* topology excised from the framework shown in (a).

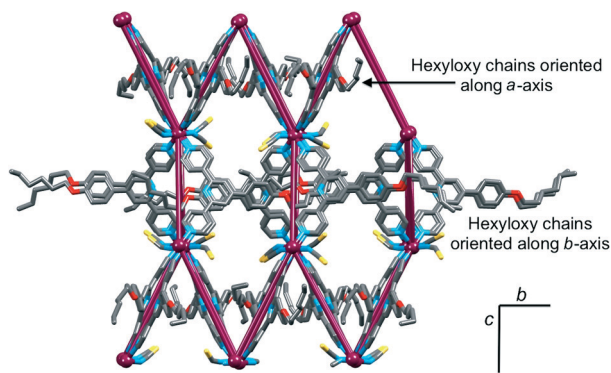


Fig. 4 TOPOS/Mercury representation of $[\text{Co}_2(\text{NCS})_4(4)_4]_n$ with superimposed ligand structures (H atoms omitted) viewed down the *a*-axis.

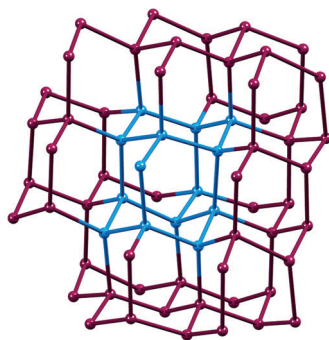


Fig. 5 TOPOS representation of part of the *neb* net in $[(\text{Co}_2(\text{NCS})_4(5)_4)_2 \cdot 2\text{CHCl}_3 \cdot \text{MeOH}]_n$ showing Co nodes; one 6^6 cage that characterizes the *neb* net is shown in blue.

2.175(4) Å). All thiocyanate ligands and solvent molecules are ordered. The bulk material for $[(\text{Co}_2(\text{NCS})_4(5)_4)_2 \cdot 2\text{CHCl}_3 \cdot \text{MeOH}]_n$ was characterized by powder diffraction (see Fig. S3†).

Replacing ligand 4 (hexyloxy chains) by 5 (nonyloxy chains) has little effect on the overall structure, although the unit cell expands slightly along the *a* and *b* axes in response to the accommodation of the longer alkyl chains which are oriented along these axes (Fig. 4). In the two enantiomorphs

of $[\text{Co}_2(\text{NCS})_4(4)_4]_n$, $a = b = 23.7111(4)$ and $c = 46.9783(7)$ Å ($V = 26412.0(9)$ Å³), and $a = b = 23.68444(16)$ and $c = 46.9716(4)$ Å ($V = 26348.8(4)$ Å³), respectively, while in $[(\text{Co}_2(\text{NCS})_4(5)_4)_2 \cdot 2\text{CHCl}_3 \cdot \text{MeOH}]_n$, $a = b = 23.88216(9)$ and $c = 46.8514(3)$ Å ($V = 26722.0(3)$ Å³). This expansion also leads to inclusion of solvate of crystallization. Fig. 5 reveals the assembly of the chiral *neb* net in $[(\text{Co}_2(\text{NCS})_4(5)_4)_2 \cdot 2\text{CHCl}_3 \cdot \text{MeOH}]_n$, confirming that a change from "hexyloxy to "nonyloxy functionality has no effect on the overall architecture.

In addition to the scarcity of the *neb* net among coordination polymers and hydrogen-bonded networks,³² we note that the space groups $P4_12_12$ and $P4_32_12$ are relatively rare. A search of the Cambridge Structural Database^{33,34} (CSD which contains ~800 000 entries) using Conquest³⁵ v. 5.37 (with November 2015 update) revealed 1563 and 1346 hits for $P4_12_12$ and $P4_32_12$, respectively.

To assess the impact of the long alkoxy chains, we have four benchmark structures. In $[\text{Co}(\text{NCS})_2(4'-(\text{pyridin-2-yl})-4,2':6',4''\text{-tpy})]_n$, the pyridin-2-yl substituent is non-coordinating¹⁵ and spatially analogous to the phenyl spacer in ligands 4 and 5. Although the 3D network was not defined in the original work,¹⁵ inspection of the structure (CSD refcode XUVPAH) reveals interpenetrating *nbo* frameworks (Fig. S4†). Modification with small alkoxy domains leads to 2D (4,4) nets in $[(\text{Co}(\text{NCS})_2(1)_2) \cdot 4\text{CHCl}_3]_n$ and $[(\text{Co}(\text{NCS})_2(2)_2) \cdot 4\text{CHCl}_3]_n$ and $[(\text{Co}_2(\text{NCS})_4(3)_4) \cdot 2\text{CHCl}_3 \cdot 1.5\text{MeOH}]_n$; these structures all exhibit head-to-tail π -stacking of 4'-(4-alkoxyphenyl) units with the alkyl units protruding into the holes in adjacent sheets. In the current work, we have demonstrated that longer tails switch the structure to an unusual 3D *neb* network in which the extended alkyl chains thread through the lattice. We also note that the chiral MOFs described in this work assemble from achiral nodes and linkers.³⁶

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