ESI to accompany:

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

Y. Maximilian Klein,<sup>a</sup> Alessandro Prescimone,<sup>a</sup> Mateusz B. Pitak,<sup>b</sup> Simon J.Coles,<sup>b</sup> Edwin C. Constable,<sup>a</sup> and Catherine E. Housecroft<sup>\*a</sup>

### Experimental

Ligands 4 and 5 were prepared as previously described.<sup>1</sup>

# $[Co_2(NCS)_4(4)_4]_n$

A MeOH (8 mL) solution of Co(NCS)<sub>2</sub> (5.25 mg, 0.03 mmol) was layered over a CHCl<sub>3</sub> (5 mL) solution of **4** (36.9 mg, 0.09 mmol) and left to stand at room temperature. Pink crystals of  $[Co_2(NCS)_4(4)_4]_n$  (20.3 mg, 0.01 mmol, 17% based on Co) were obtained after 1-2 weeks. The bulk sample was characterized using powder diffraction (see Fig. S1). IR (solid): 2929 (w), 2851 (w), 2050 (s), 1598 (s), 1558 (w), 1539 (w), 1516 (s), 1502 (m), 1468 (w), 1431 (w), 1397 (m), 1291 (w), 1238 (s), 1217 (m), 1180 (s), 1063 (w), 1014 (m), 825 (s), 733 (w), 678 (w), 646 (s), 621 (w), 602 (m), 525 (m). UVVIS (solid) 494, 638 (sh) nm.

# $[Co_2(NCS)_4(5)_4]_n$

A MeOH (8 mL) solution of  $Co(NCS)_2$  (5.25 mg, 0.03 mmol) was layered over a  $CHCl_3$  (5 mL) solution of **5** (40.6 mg, 0.09 mmol) and left to stand at room temperature. Pink crystals of  $[Co_2(NCS)_4(5)_4]_n$  (26.7 mg, 0.011 mmol, 18% based on Co) were obtained after 1-2 weeks. The bulk sample was characterized using powder diffraction (see Fig. S2).

### Crystallography

The single crystal X-ray diffraction data were collected on a Rigaku AFC12 diffractometer equipped with enhanced sensitivity (HG) Saturn724+ CCD detector mounted at the window of an FR-E+ *SuperBright* rotating anode

generator (Mo K $\alpha$ ,  $\lambda$  = 0.71075 Å) with VHF *Varimax* optics (70 µm focus) using Rigaku CrystalClear<sup>2</sup> and CrysalisPro<sup>3</sup> software for data collection and reduction. Unit cell parameters in all cases were refined against all data. Crystal structures were solved by direct methods with ShelXT<sup>4</sup> and then refined on F<sub>o</sub><sup>2</sup> by fullmatrix least-squares refinements using ShelXL<sup>5</sup> within the OLEX2 suite.<sup>6</sup>

All hydrogen atoms were added at calculated positions and refined using a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (Ueq) of the parent atom.

Crystallographic data of  $[Co_2(NCS)_4(4)_4]_n$  (enantiomer I): a = 23.7111(4), Å, b = 23.7111(4) Å, c = 46.9783(7) Å,  $\alpha = \beta = \gamma = 90^\circ$ ; V = 26412.0(9) Å<sup>3</sup>, tetragonal,  $P4_12_12$ , Z = 8,  $\rho_{calc} = 1.000 \text{ Mg/m}^3$ ;  $\mu = 0.362 \text{ mm}^{-1}$ ; T = 100(2) K;  $\theta_{max} = 27.221^\circ$ , 79766 measured reflections, 26743 unique reflections  $[R_{int} = 0.0691]$ , 12814 with F<sup>2</sup> > 2 $\sigma$ ,  $R(F, F^2 > 2\sigma) = 0.0901$ ;  $R_w(F^2$ , all data) = 0.2795, GoF = 0.940, CCDC: 1474325.

Crystallographic data of  $[Co_2(NCS)_4(4)_4]_n$  (enantiomer II): a = 23.68444(16), Å, b = 23.68444(16) Å, c = 46.9716(4) Å,  $\alpha = \beta = \gamma = 90^\circ$ ; V = 26348.8(4) Å<sup>3</sup>, tetragonal,  $P4_32_12$ , Z = 8,  $\rho_{calc} = 1.002 \text{ Mg/m}^3$ ;  $\mu = 0.363 \text{ mm}^{-1}$ ; T = 100(2) K;  $\theta_{max} = 26.6550^\circ$ , 294870 measured reflections, 26290 unique reflections  $[R_{int} = 0.0748]$ , 17361 with F<sup>2</sup> > 2 $\sigma$ ,  $R(F, F^2>2\sigma) = 0.0894$ ;  $R_w(F^2$ , all data) = 0.2836, GoF = 1.032, CCDC: 1474326.

Crystallographic data of [{Co<sub>2</sub>(NCS)<sub>4</sub>(**5**)<sub>4</sub>}·2CHCl<sub>3</sub>·MeOH]<sub>n</sub>: a = 23.88216(9), Å, b = 23.88216(9) Å, c = 46.8514(3) Å,  $\alpha = \beta = \gamma = 90^{\circ}$ ; V = 26722.0(3) Å<sup>3</sup>, tetragonal,  $P4_12_12$ , Z = 8,  $\rho_{calc} = 1.207$  Mg/m<sup>3</sup>;  $\mu = 0.486$  mm<sup>-1</sup>; T = 100(2) K;  $\theta_{max} = 27.5260^{\circ}$ , 292603 measured reflections, 30625 unique reflections [ $R_{int}$  = 0.0437], 28191 with F<sup>2</sup> > 2 $\sigma$ , R(F, F<sup>2</sup>>2 $\sigma$ ) = 0.0913;  $R_w$ (F<sup>2</sup>, all data) =0.2615, GoF = 1.029, CCDC: 1474327.

Crystals of all three studied compounds were sensitive to solvent loss. To prevent crystal decomposition selected crystals were 'cold mounted' on MiTeGen Micromounts<sup>TM</sup> at approximately T = 213 K using Sigma-Aldrich Fomblin Y® LVAC (3300 mol. wt.) with the X-Temp 2<sup>7</sup> crystal cooling system attached to the microscope.

All three reported crystals structures contain molecular fragments, which exhibit a degree of positional disorder. Due to diffuse electron density in the crystal structure of  $[Co_2(NCS)_4(4)_4]_n$  (enantiomer I), fragments of aliphatic chains: C78-C81 as well as C105-C108 were extremely difficult to assign directly from differential electron density map, resulting in number of geometrical restraints DFIX/DANG being applied to maintain reasonable geometry. An attempt to model these labile molecular fragments over two sites has been made, however results were unsatisfactory and led to a spurious models. For this reason, the atomic displacement parameters on these atoms were refined as isotropic. Additionally, two disordered thiocyanate groups (containing S3 and S4) were split and refined over two sites with approximately 61.8/38.2 and 70.3/29.7 ratio each.

In the crystal structure of  $[Co_2(NCS)_4(4)_4]_n$  (enantiomer II), three disordered thiocyanate groups (containing S2, S4 and S6) were modelled over two sites with approximately 62.1/37.9, 60.3/39.7 and 56.4/43.6 ratio respectively. Due to large variations in atomic displacement parameters the heavily disordered -SCN group (S4/S5) was refined as isotropic only. Similarly to enantiomer I, geometrical restraints DFIX/DANG had to be applied to preserve a chemically sensible geometry of aliphatic chains. Attempts to model two of these chains (C48-C53 and C102-C107) over two positions have been made, but obtained results did not improve the overall model. These aliphatic chains were kept in a single orientation with full occupancy. An analogous approach has been applied for the crystal structure of  $[{Co_2(NCS)_4(5)_4} \cdot 2CHCl_3 \cdot MeOH]_n$ Additionally, in this structure one methanol and two chloroform molecules have been successfully assigned, however for one CHCl<sub>3</sub> solvent molecule (C201, Cl4-Cl6) the modelling of positional disorder was unsatisfactory, thus it was refined isotropically.

To model atomic displacement parameters, especially these on disordered fragments, global SIMU, DELU and RIGU restraints were applied to all three crystal structures.

Crystal structures of  $[Co_2(NCS)_4(4)_4]_n$  (enantiomer I and II) represents two enatiomorphic mixtures of varying chirality solved and refined in tetragonal spacegroups P4<sub>1</sub>2<sub>1</sub>2 (enantiomer I) and P4<sub>3</sub>2<sub>1</sub>2 (enantiomer II) as an inversion twin with 0.79(3) /0.21(3) and 0.84(2)/ 0.16(2) ratio respectively. Reported crystal structures contain large accessible voids and channels that are occupied by diffuse electron density of solvent molecules. Such electron density contribution was accounted for by the SMTBX solvent masking routine as implemented in OLEX2 software.<sup>6</sup> This significantly improved the quality of the model and led refinement of the crystal structure to satisfactory convergence.

Powder diffraction data were collected on a Stoe Stadi P powder diffractometer. Structural diagrams and structural analysis were carried out using Mercury v. 3.7<sup>8,9</sup> and TOPOS.<sup>10</sup>



**Fig. S1.** Powder diffraction data (room temperature) for the bulk sample (top) compared to the powder pattern predicted from the single crystal structure (either enantiomorphic lattice, 100 K) of  $[Co_2(NCS)_4(4)_4]_n$ .



(b)

**Fig. S2.** The 4-fold screw axes that define the chirality dominant lattice in each structure of  $[Co_2(NCS)_4(4)_4]_n$ : opposite handednesses in each of space groups (a) right-handed screw in  $P4_12_12$  and (b) left-handed screw in  $P4_32_12$ .



**Fig. S3.** Powder diffraction data (room temperature) for the bulk sample (top) compared to the powder pattern predicted from the single crystal structure (either enantiomorphic lattice, 100 K) of  $[{Co_2(NCS)_4(5)_4} \cdot 2CHCl_3 \cdot MeOH]_n$ .



**Fig. S4.** The interpenetrating *nbo* nets in [Co(NCS)<sub>2</sub>(4'-(pyridin-2-yl)-4,2':6',4''-tpy)]<sub>n</sub> (refcode XUVPAH).

#### References

- 1 Y. M. Klein, E. C. Constable, C. E. Housecroft, J. A. Zampese and A. Crochet, *CrystEngComm*, 2014, **16**, 9915.
- 2 CrystalClear-SM Expert 3.1 b27 (Rigaku, 2012).
- 3 CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).
- 4 G. M. Sheldrick, *Acta Cryst.*, 2015, A**71**, 3.
- 5 G. M. Sheldrick, *Acta Cryst.*, 2015, C**71**, 3.
- 6 O. V. Dolomanov, A. J. Blake, N. R. Champness and M. Schröder, *J. Appl. Crystallogr.*, 2003, **36**, 1283.
- 7 T. Kottke and D. Stalke, J. Appl. Crystallogr., 1993, 26, 615.

- 8 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, 2006, **39**, 453.
- 9 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock,
  L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*,
  2008, 41, 466.
- 10 V. A. Blatov and A. P. Shevchenko, TOPOS Professional v. 4.0, Samara State University, Russia.