Supporting Materials

Solvent-controlled assembly of supramolecular isomers: 2D (4,4) network, 1D ribbons of ring, and both 2D (4,4) networks and 1D ribbons of rings polycatenated in a 3D array

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1. Synthesis of [Mn(btb)$_2$(NCS)$_2$](CH$_2$Cl)$_2$ (1), [Mn(btb)$_2$(NCS)$_2$](CH$_3$NO)$_2$ (2)

A EtOH solution (10 mL) of Mn(NCS)$_2$ (0.5 mmol) was layered onto a solution of btb (1.0 mmol) in 10 mL CH$_2$Cl$_2$, or CH$_3$NO$_2$. The resulting solutions stood for several days to give single crystals 1 and 2, respectively. The crystals of 1 and 2 lose the included solvent and turn opaque immediately upon removal from the mother liquor, give [Mn(btb)$_2$(NCS)$_2$] (1a) (Yield 42%), [Mn(btb)$_2$(NCS)$_2$] (2a) (Yield 51%), respectively. Anal. calc. for C$_{18}$H$_{24}$MnN$_{14}$S$_2$ (1a and 2a) (%) C 38.91, H 4.35, N 35.30; found C 38.76, H 4.21, N 35.18 for 1a and C 38.73, H 4.34, N 35.24 for 2a.

2. Synthesis of [2D-Mn(btb)$_2$(NCS)$_2$][1D-Mn(btb)$_2$(NCS)$_2$] (3)

A EtOH solution (10 mL) of btb (1.0 mmol) was layered onto an aqueous solution (10 mL) of Mn(NCS)$_2$ (0.5 mmol). The resulting solutions stood for two weeks to give single crystal 3 (Yield 57%). Anal. calc. for C$_{36}$H$_{48}$Mn$_2$N$_{28}$S$_4$ (%) C 38.91, H 4.35, N 35.30; found C 38.84, H 4.29, N 35.23.
Fig. S1 The packing of two 2D (4,4) networks in 1.
Fig. S2 The packing of the 1D ribbons of rings in 2.
Fig. S3 Schematic view of the overall entanglement of 3. The btb ligands of planar 2D (4,4) networks are omitted for clarity.

Table S1 The parameters of the btb ligand in 1, 2 and 3.

| Complex     | Structure      | Conformation | Distance of Two donor nitrogen atoms | Torsion $\text{N}_{\text{triazole}}$-(C-C-C)$_b$ | Torsion (C-C-C)$_b$-(C-C-C)$_b$-
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