

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 $[\text{Mn}(\text{btb})_2(\text{NCS})_2](\text{CH}_2\text{Cl}_2)$ (**1**), $[\text{Mn}(\text{btb})_2(\text{NCS})_2](\text{CH}_3\text{NO}_2)_2$ (**2**)

A EtOH solution (10 mL) of $\text{Mn}(\text{NCS})_2$ (0.5 mmol) was layered onto a solution of btb (1.0 mmol) in 10 mL CH_2Cl_2 , or CH_3NO_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 $[\text{Mn}(\text{btb})_2(\text{NCS})_2]$ (**1a**) (Yield 42%), $[\text{Mn}(\text{btb})_2(\text{NCS})_2]$ (**2a**) (Yield 51%), respectively. Anal. calc. for $\text{C}_{18}\text{H}_{24}\text{MnN}_{14}\text{S}_2$ (**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 $[2\text{D-Mn}(\text{btb})_2(\text{NCS})_2][1\text{D-Mn}(\text{btb})_2(\text{NCS})_2]$ (**3**)

A EtOH solution (10 mL) of btb (1.0 mmol) was layered onto an aqueous solution (10 mL) of $\text{Mn}(\text{NCS})_2$ (0.5 mmol). The resulting solutions stood for two weeks to give single crystal **3** (Yield 57). Anal. calc. for $\text{C}_{36}\text{H}_{48}\text{Mn}_2\text{N}_{28}\text{S}_4$ (%) C 38.91, H 4.35, N 35.30; found C 38.84, H 4.29, N 35.23.

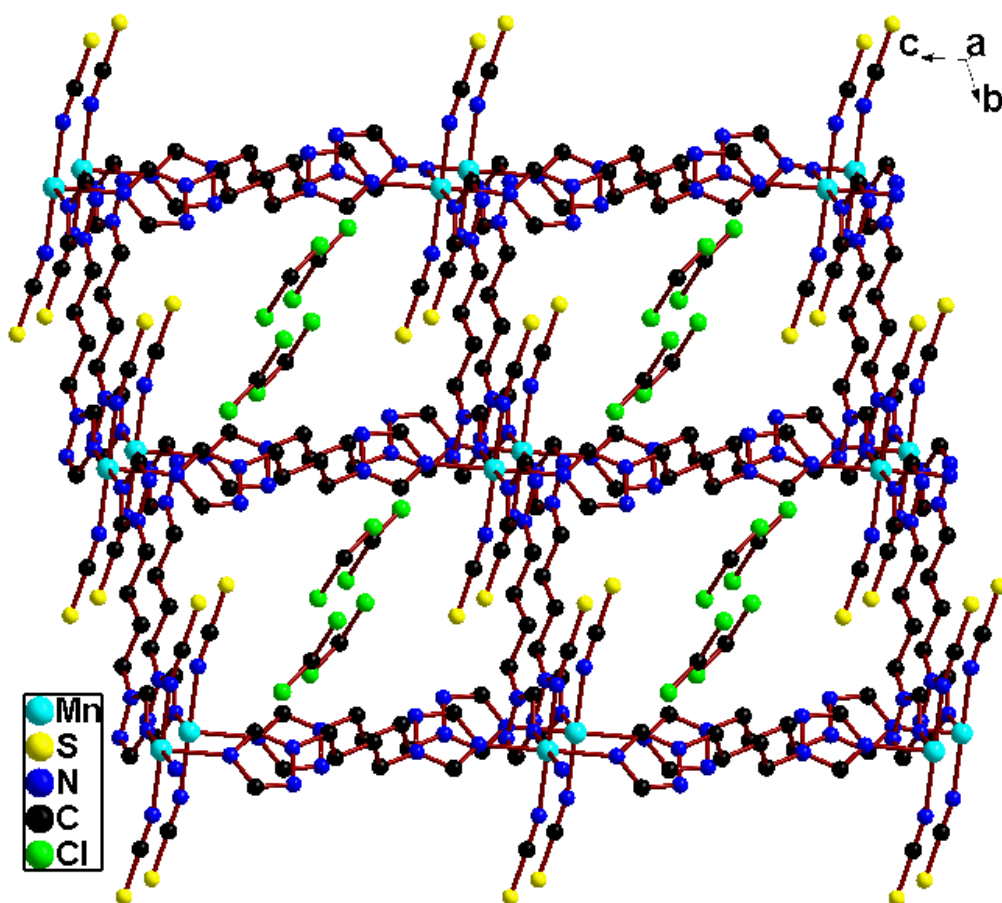


Fig. S1 The packing of two 2D (4,4) networks in 1.

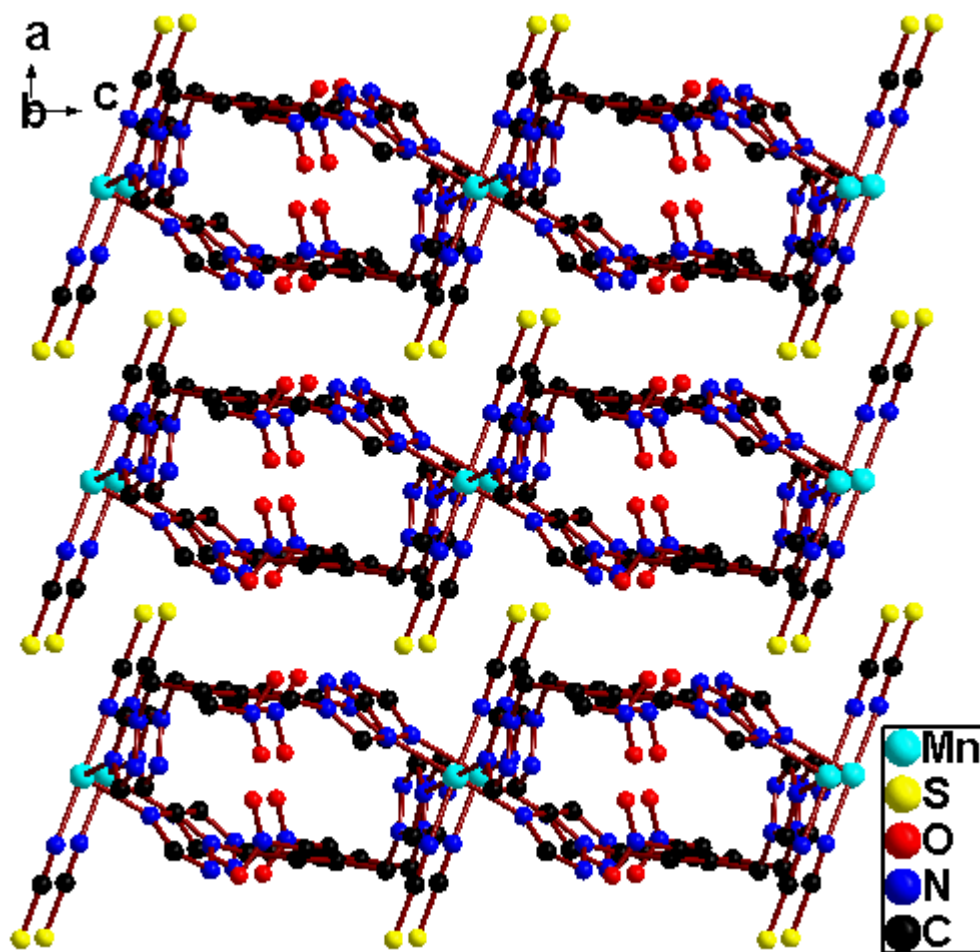


Fig. S2 The packing of the 1D ribbons of rings in 2.

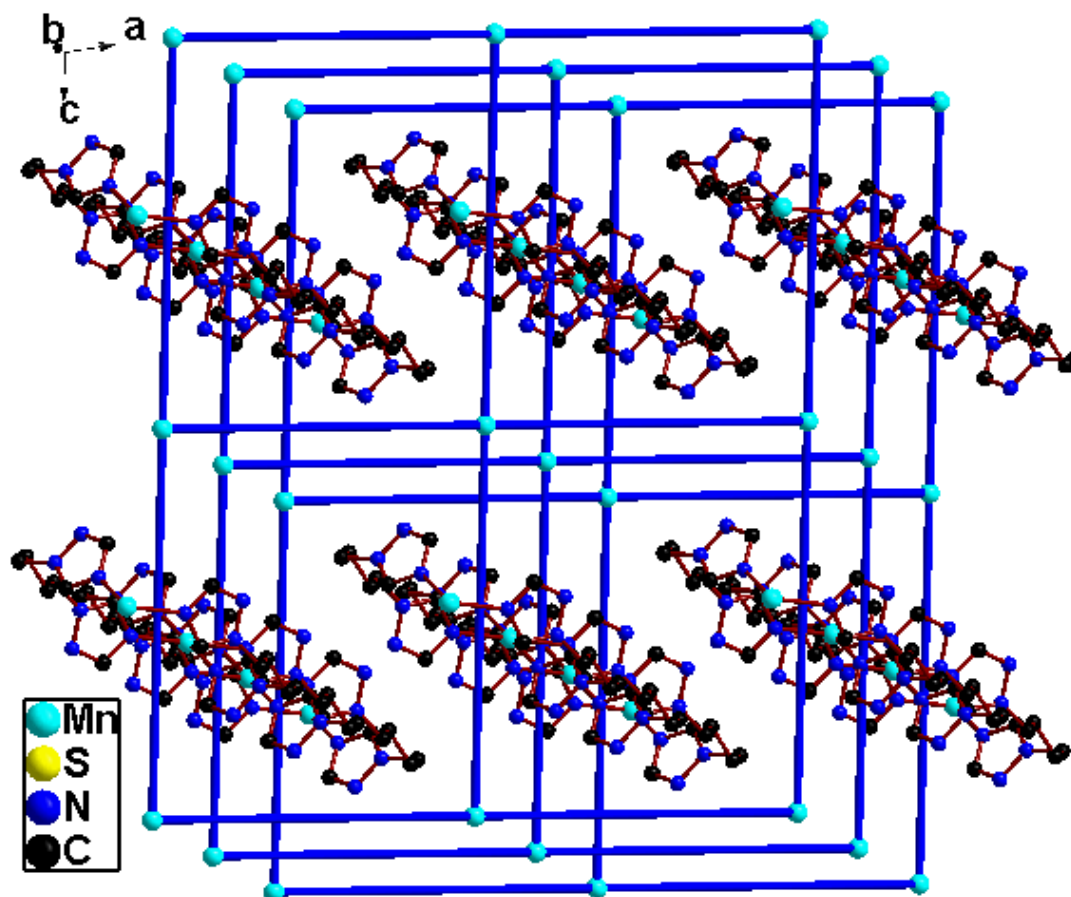


Fig. S3 Schematic view of the overall entanglement of **3**. The btb ligands of planar 2D (4,4) networks are omitted for clarity.

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

Complex	Structure	Conformation	Distance of Two donor nitrogen atoms	Torsion		
				$N_{\text{triazole}}-(C-C-C)_{\text{butane}}$	$(C-C-C-C)_{\text{butane}}$	$(C-C-C)_{\text{butane}}-N_{\text{triazole}}$
1	(4,4) network	<i>anti-anti-anti</i>	10.020	-175.8	180.00	175.8
			10.264	179.7	180.00	-179.7
2	ribbons of rings	<i>anti-anti-gauche</i>	7.648	172.2	172.2	58.8
3	(4,4) network	<i>anti-anti-anti</i>	10.572	-175.3	180.00	175.3
			<i>gauche-anti-gauche</i>	9.236	-62.2	180.00
	ribbons of rings	<i>anti-anti-gauche</i>	7.840	169.9	-179.6	68.7