Supplementary Material (ESI) for Chemical Communications

Supporting Information

A new $(6^3)\cdot(6^9.8^1)$ non-interpenetrated paramagnetic network with helical nanochannels based on a tricarboxylic perchlorotriphenylmethyl radical.

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Supplementary information of the crystal structure.

Topology. Topologically, crystal structure of MOROF-2 is a (3,5)-connected network since each PTMTC radical can be considered a trigonal 3-connecting unit and each Co(II) unit as a 5-connecting center. Each PTMTC radical has three carboxyl groups, where one of them is directly coordinated to the Co(II) ion, whereas the remaining two carboxyl groups form four H-bonds with four coordinated water molecules of two different Co(II) ions. Otherwise, each 5-connecting Co(II) center is formed by two 4,4'-bpy ligands, one coordinated PTMTC radical and two more H-bonded PTMTC radicals. Both PTMTC radicals are H-bonded with two coordinated water molecules thought one carboxyl group.

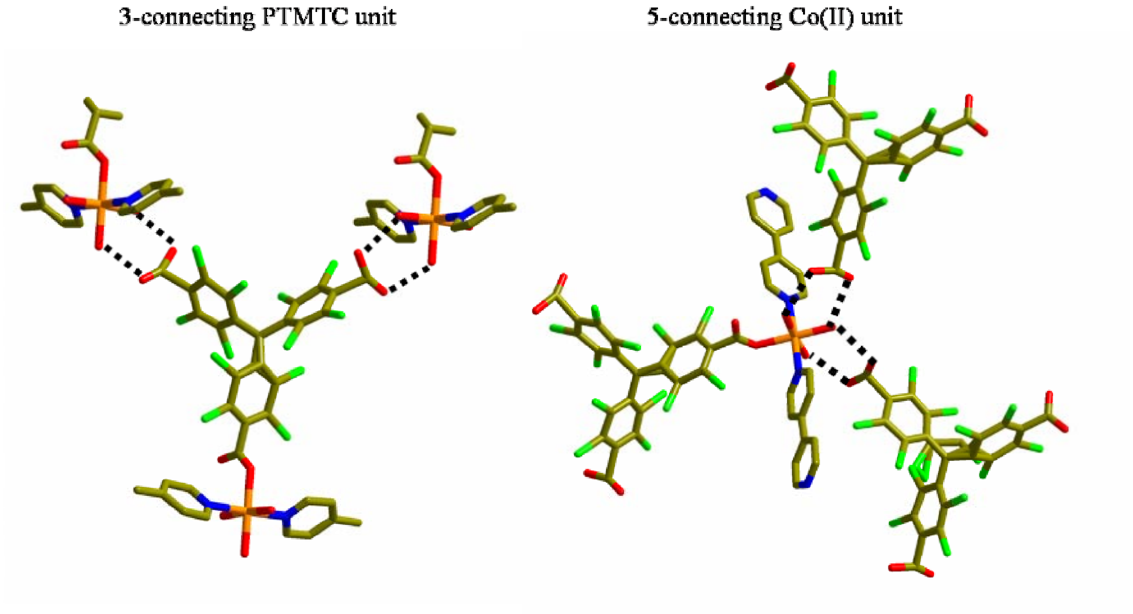

Fig 1. 3- and 5-connecting centers of MOROF-2.

Crystal packing.

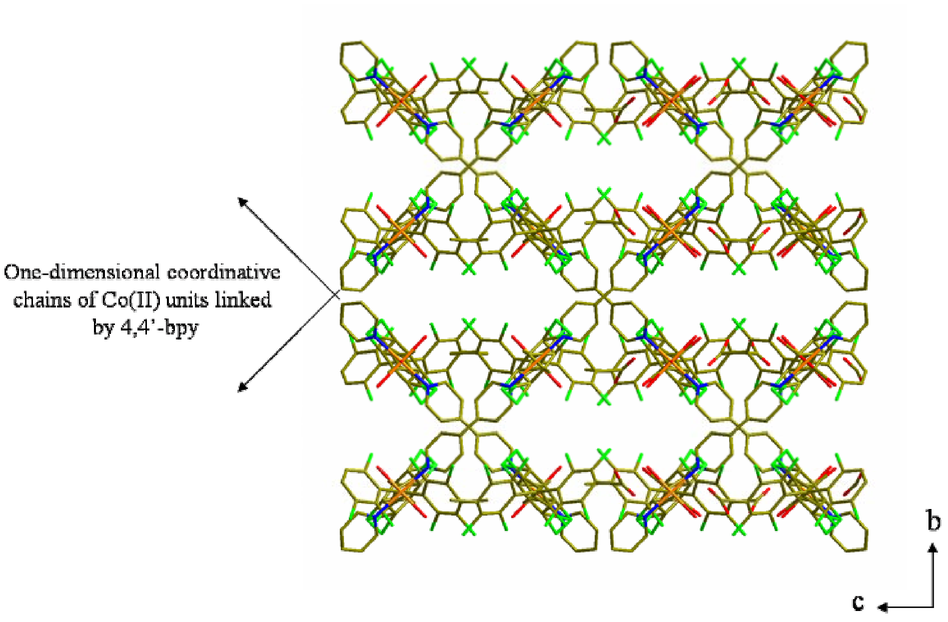

Fig 2. Crystal packing of MOROF-2 along the [100] direction.

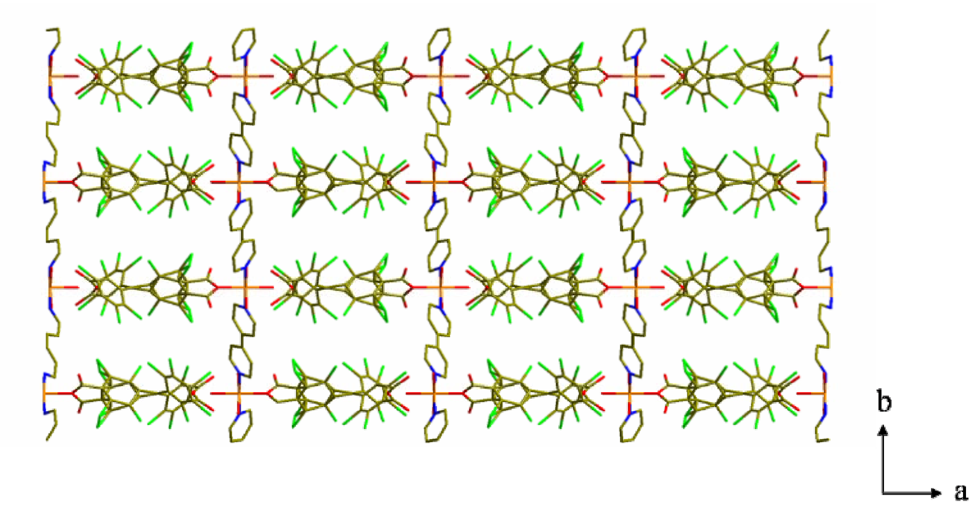

Fig 3. Crystal packing of MOROF-2 along the [001] direction.

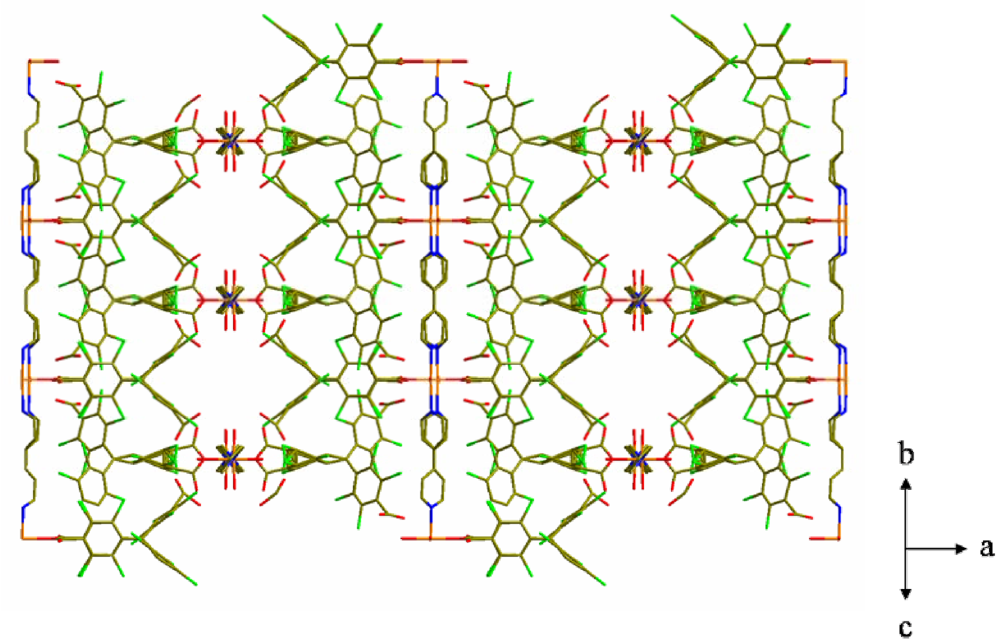

Fig 4. Crystal packing of MOROF-2 along the [011] direction.

Crystallographic data. Although the value of R_1 with 0.136 is quite large, similar values for supramolecules are not unusual in the literature as a consequence of numerous factors, for example, having large unit cells or disordered guest solvent molecules and fragments of the molecule. Specially common are reported crystal structures of open-framework networks with highly disordered solvent molecules, where values of R_1 and wR_2 are in the range of 0.10-0.15 and 0.20-0.45, respectively (for some examples see references below). The final agreement factors for MOROF-2 are owing to highly disordered solvent molecules that fill 54.5% of the volume unit cell, the partially disordered phenyl rings and the accompanying poor data quality. For some related recent examples, see: B. Molton, J. Lu, A. Mondal, M. Zaworotko, *Chem. Commun.*, 2001, 863; F. A. Cotton, C. Lin, C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 575; L. Carlucci, G. Ciani, D. M. Proserpio, F. Porta, *Angew. Chem. Int. Ed.*, 2003, **42**, 317; L. Pan, H. Liu, S. P. Kelly, X. Huang, D. H. Olson, J. Li, *Chem. Commun.,* 2003, 854.

Supplementary information of the magnetic properties.

Magnetic properties of MOROF-2[10] shows that χT product is equal to 3.69 emu·K·mol^{-1} at room temperature, a value that diverge from the expected one for a non-interacting Co(II) ion (S=3/2) and one PTMTC radical (S=1/2), in accordance with the well-documented orbital contribution of octahedral Co(II) ions. As the temperature is lowered, χT smoothly decreases to 2.68 emu·K·mol^{-1} at 50 K whereupon decreases more abruptly to 1.22 emu·K·mol^{-1} at 1.8 K. Due to the difficulties to make an analysis with the orbital contribution, the higher temperature magnetic data was only fitted above 50 K on the basis of a magnetic model based on a two-spin system, composed by one organic radical and one Co(II) ion, with relatively strong antiferromagnetic exchange coupling (J), defined by an effective Hamiltonian $H=-2JS_1 \cdot S_2$. The model was corrected by a molecular field approximation (zJ') to take into account the magnetic interactions through the bridging 4,4'-bpy ligands and additional interchain magnetic interactions. The best fit was obtained for J/k = -39 K, zJ'/k = -6 K and g = 2.29.

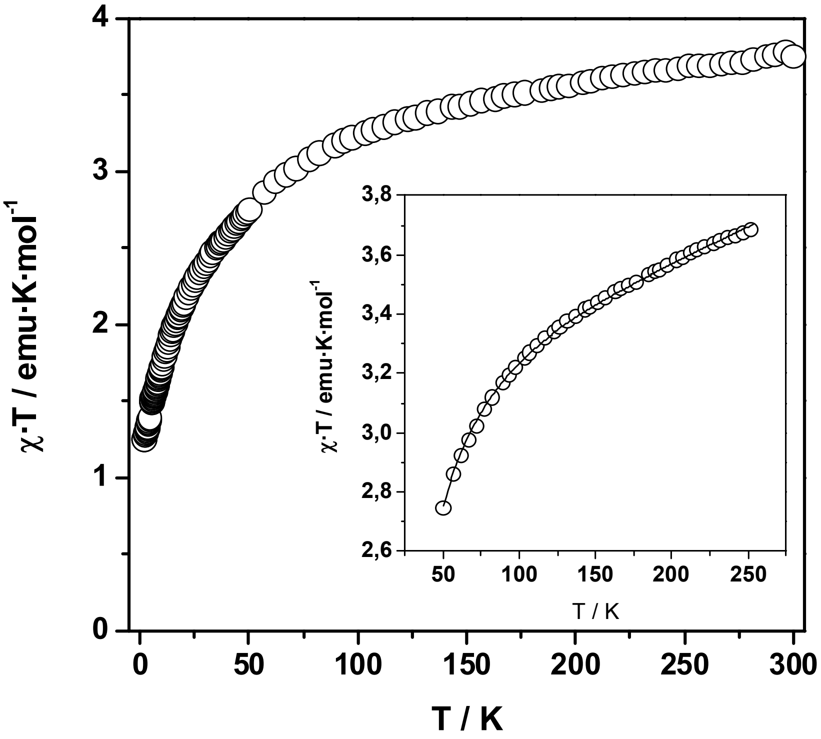

Fig 5. χ·T vs T for MOROF-2. Insert. χ·T vs T in the range of 1.8 K to 300 K. The solid line represents the best-fit calculated data.