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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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The reaction of a 3-connecting PTMTC radical and a 2-connecting 4,4′-bipyridine ligands with $Co(MeCOO)_2\cdot 4H_2O$ forms a paramagnetic non-interpenetrated supramolecular network, $Co(PTMTC)(4,4'\text{-bpy})(H_2O)_3\cdot 6EtOH\cdot 2H_2O$ (MOROF-2), with an unprecedented $(6^3)\cdot(6^9.8^1)$ topology exhibiting helical nanochannels.

The endless versatility of molecular chemistry to design organic building blocks has provided chemists with a huge variety of polyfunctional ligands to arrange transition metal ions through the space, affording an extended array of porous architectures.[1] Among them, carboxylic-based ligands have attracted much attention for their ability to construct open-framework networks with a wide diversity of topologies and pore shapes and sizes.[2] In this context, our group have recently established a new strategy focused on the use of a 3-connecting open-shell ligand based on a perchlorinated triphenylmethyl radical skeleton with three carboxylic groups [(4,4′,4″-tricarboxydodecaclorotriphenyl) methyl radical, PTMTC][3] as a polyfunctional ligand to build new supramolecular nanoporous materials with additional magnetic properties.[4] This approach is based on the open-shell character of PTM radicals, which are expected to interact magnetically with transition metal ions[5] enhancing the magnetic dimensionality of the nanoporous materials. Recent results in the obtaining of the first Metal–Organic Radical Open-Framework (MOROF-1) material, a non-interpenetrated (6,3) honeycomb porous molecular Cu(II)-based magnet with very large pores (28 Å), has confirmed the outcome of this approach.[4] We report herein a new supramolecular Co(II)-based network, $Co(PTMTC)(4,4'\text{-bpy})(H_2O)_3\cdot 6EtOH\cdot 2H_2O$ (MOROF-2), based upon the 3-connecting trigonal PTMTC and an additional linear 2-connecting 4,4′-bipyridine.[6] To the best of our knowledge, MOROF-2 represents the first example of a metal–organic framework with an unprecedented $(6^3)\cdot(6^9.8^1)$ topology in terms of connectivity, nanochannel-like architecture and magnetic properties.

Slow diffusion of an ethanol solution of 4,4′-bpy onto a solution of ethanol and water of $Co(MeCOO)_2\cdot 4H_2O$ and PTMTC radical yielded red prism crystals of MOROF-2. X-ray analysis performed on a single crystal of MOROF-2 revealed a highly porous structure sustained by coordinative and hydrogen bonds.‡ The crystal structure of MOROF-2 is illustrated in Fig. 1. The octahedral Co(II) ions are linked by 4,4′-bpy spacers to generate monodimensional coordinative chains along the [011] and $[0\bar{1}1]$ directions, where each metal ion is additionally bound to one carboxylate group of PTMTC radical in a monodentate fashion and three water ligands. Moreover, the remaining carboxylic and carboxylate groups of PTMTC are responsible for linking these chains along the [101] plane. Each COO(H) group of PTMTC strongly interacts with two water molecules of a Co(II) unit of an adjacent *quasi* perpendicular chain through two hydrogen bonds (d(O–O) = 2.74 and 2.79 Å). Taking into account the directional nature of these H–bonds, PTMTC radical can be considered a trigonal 3-connecting spacer unit and each Co(II) unit as a 5-connecting center since all three coordinated water molecules form H-bonds with two COO(H) groups of different PTMTC radicals. The supramolecular arrangement of both 3- and 5-connecting units creates (6,3) hexagonal planes (each hexagon is defined by three PTMTC radicals and three octahedral Co(II) centres). Furthermore, 4,4′-bpy ligands interconnect the Co(II) centers of neighboring layers leading to a supramolecular 3D structure, which can be described by (6,3) planes linked through chains running along [011] and $[0\bar{1}1]$ axes. As a result, a (3,5)-connected network with a circuit symbol of $(6^3)\cdot(6^9.8^1)$ is created. Topologically, this network resembles those $4^6 6^4$ and $(6^3)\cdot(6^9.8^1)$ networks recently obtained in metal–organic polymers,[7,8] since all of them could be described as the connection of (6,3) hexagonal layers (Fig. 2). However, the main difference lies in the fact that structure of MOROF-2 presents a 2-fold screw axis perpendicular to the hexagonal (6,3) sheet. Thus, the connectivity between hexagonal sheets in $4^6 6^4$ and $(6^3)\cdot(6^9.8^1)$ networks takes place exclusively through one crystallographic axis, whereas in the case of MOROF-2 arises along two perpendicular axis

The partial overlap of two-directional linked hexagonal plane nets along the [010] direction produces surprising helical nano-

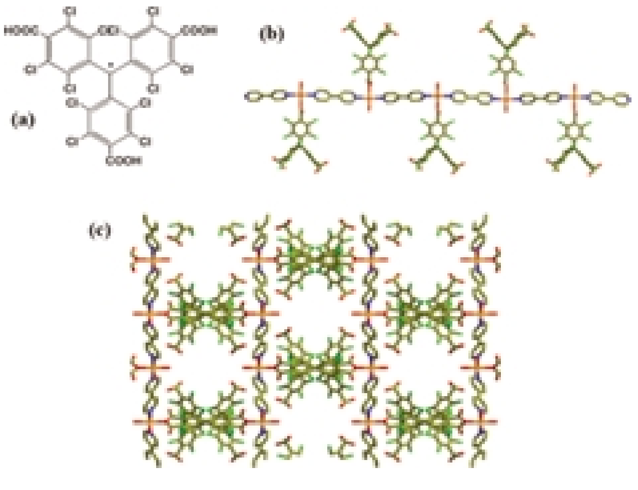

Fig. 1 Crystal structure of MOROF-2. a) PTMTC radical, b) One-dimensional coordinative chain of Co(II) units linked by 4,4′-bpy; c) Crystal packing along the [010] direction, showing the nanochannels and the *quasi* perpendicular neighboring coordinative chains.

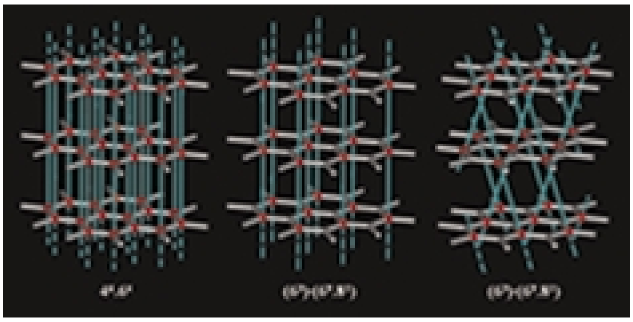

Fig. 2 Schematic views of the $4^6.6^4$ and the two $(6^3)\cdot(6^9.8^1)$ topologies.

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† Electronic supplementary information (ESI) available: additional crystallographic data. See http://www.rsc.org/suppdata/cc/b3/b315147f/

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channels of dimensions 16.6 × 12.9 Å, with an effective size of 13.2 × 9.4 Å when van der Waals radius are considered (Fig. 3). Thus, the calculated porosity reflects a void volume of 54.5% of the total volume cell, or 4171 $Å^3$ per 7560 $Å^3$ of the unit cell.[9] The channels are filled with six disordered ethanol and two water molecules. Thermogravimetric analysis of MOROF-2 revealed a weight loss of 20% after 150 minutes at room temperature, which is consistent with the liberation of guest solvent molecules (calculated loss of 23% for six molecules of ethanol and two molecules of H_2O), as also confirmed by elemental analysis. MOROF-2 remains crystalline upon desolvation. X-ray powder diffraction (XRPD) studies of MOROF-2 confirm that principal peaks remain unchanged after desolvation process at room temperature. However, local distortions in the pore structure are probable since broadening and a slight shift of the diffraction lines have been detected.[10]

When the desolvated material is heated, the thermogravimetric analysis shows a second weight loss of 5% at 80–110 °C attributed to the loss of the three water ligands (as confirmed by elemental analysis), with the collapse of the framework (as confirmed by XRPD). A further increase of the temperature shows a sharp weight loss at 240 °C attributed to the decomposition of the amorphous solid.

Magnetic properties of desolvated MOROF-2 shows that χT product is equal to 3.69 emu·K·mol^{-1} at room temperature, a value that diverges from the expected for a non-interacting Co(II) ion (S = 3/2) and 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 it decreases more abruptly to 1.22 emu·K·mol^{-1} at 1.8 K. Due to the difficulties of analysing the orbital contribution, the temperature magnetic data was only fitted above 50 K. A magnetic model, based on a two-spin system radical–Co(II), showing a relatively strong antiferromagnetic exchange coupling (J), with an effective Hamiltonian $H = -2JS_1 \cdot S_2$ that does not take into account the ZFS contribution, was used. 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 $g = 2.29$. The approximated value of −39 K for metal ion-carboxylic-based PTM radical is in the range of previous findings.[5]

In summary, MOROF-2 shows an unprecedented paramagnetic non-interpenetrated (3,5)-connected network with helical nanopores. This topology, along with others recently described,[7,8,11] promises great advances in crystal engineering, especially for the design of future new multifunctional materials with useful structural properties, such as porosity, or additional physical properties, such as magnetism. In such a context, the possibility of carboxylic groups of PTMTC participating in coordination bonds as well as hydrogen bonds makes PTMTC an excellent open-shell organic building block to design new magnetic porous metal–organic architectures. Further work aimed at designing a Co(II)-based network composed of a completed coordinated PTMTC radical where both the rigidity of the open-framework and/or the magnetic properties are increased is in progress.

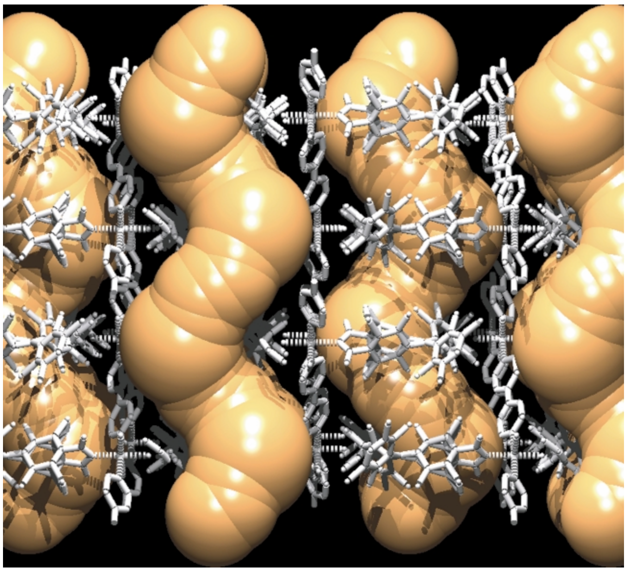

Fig. 3 View of the helical nanochannels along the [010] direction.

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Notes and references

‡ *Crystallographic data:* X-ray single-crystal diffraction data for MOROF-2 was collected on a Nonius KappaCCD diffractometer with an area detector and graphite-monochromized Mo-K_α radiation (λ = 0.7107 Å). Single crystal of MOROF-2 was measured in a sealed capillary containing mother liquor to prevent desolvation. In the asymmetric unit is a half PTMTC, and a 2-fold axis, that is not completely consistent with the symmetry of the molecule, which generates the other part in a disordered manner. The 2-fold axis goes through the oxygen atom, co-ordinated on the Co(II) ion, and through the methyl carbon atom, leading to a 1:1 disorder for one ring with partial overlying positions.

Crystal data for MOROF-2: $C_{32}H_{14}Cl_{12}CoN_2O_9 \times 2\ H_2O \times 6$ EtOH, orthorhombic space group *Pnna*, a = 29.312(4), b = 15.887(2), c = 16.428(2) Å, vol = 7650(2) $Å^3$, Z = 4, D_c = 1.187 g cm^{-3}, μ = 0.694 mm^{-1}, $F(000)$ = 2796, T = 293 K, $2\theta_{max}$ = 38° ($-25 \leq h \leq 26$, $-13 \leq k \leq 14$, $-15 \leq l \leq 15$). Final results (for 344 parameters) were R_1 = 0.1363 and wR_2 = 0.3477 for 1635 reflections with $I > 2\sigma(I)$, and R_1 = 0.1880, wR_2 = 0.3783 and *GooF* = 1.361 for all 2687 reflections. CCDC reference number is CCDC 224920. See http://www.rsc.org/suppdata/cc/b3/b315147f/ for crystallographic data in .cif or other electronic format.

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