Article J

Títol: 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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Publicació: Chem. Commun., en premsa.

(No presentat a la Comissió de Doctorat)

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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)$_2$·4H$_2$O forms a paramagnetic non-interpenetrated supramolecular network, Co(PTMTC)(4,4'-bpy)(H$_2$O)$_3$·6EtOH·2H$_2$O (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 stablished a new strategy focalized in the use of a 3-connecting open-shell ligand based on a perchlorinated triphenylmethyl radical skeleton with three carboxylic groups (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'-bpy)(H$_2$O)$_3$·6EtOH·2H$_2$O (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)$_2$·4H$_2$O 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 [0-11] 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
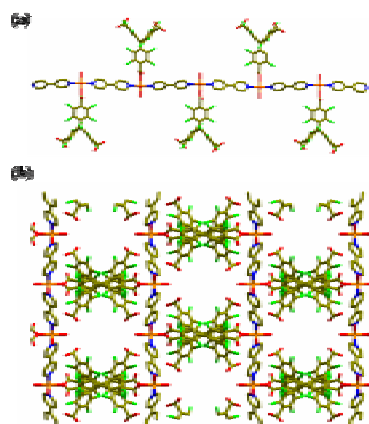
Fig 1. Crystal structure of MOROF-2. a) One-dimensional coordinative chain of Co(II) units linked by 4,4'-bpy; b) Crystal packing along the [010] direction, showing the nanochannels and the *quasi* perpendicular neighboring coordinative chains.

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 [0-11] 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 to 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 nanochannels of dimensions 16.6 x 12.9 Å, with an effective size of 13.2 x 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
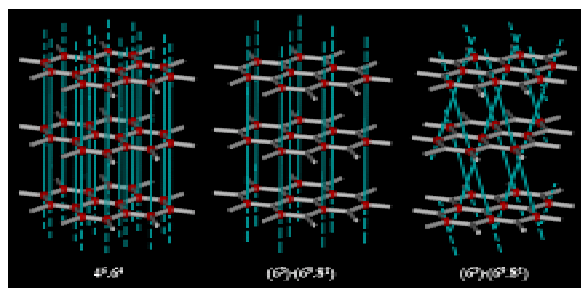
Fig. 2. Schematic views of the $4^6.6^4$ and the two $(6^3) \cdot (6^9.8^1)$ topologies.

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 confirms that principal peaks remain unchanged after desolvation process at room temperature. However, local distortions in the pore structure are probably 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 80-110ºC 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 240ºC attributed to the decomposition of the amorphous solid.
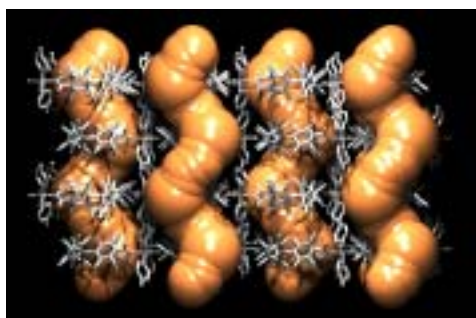

Fig. 3. View of the helical nanochannels along the [010] direction.

Magnetic properties of desolvated MOROF-2[10] shows that χT product is equal to 3.69 emu·K·mol^{-1} at room temperature, value that diverge 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 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 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$_1$·S$_2$, 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. A 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, joined to other recently described,[7,8,11] supposes great advances on crystal engineering, specially to 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 to participate in coordination bonds as well as hydrogen bonds confers to PTMTC to be an excellent open-shell organic building block to design new magnetic porous metal-organic architectures. Further work aimed at the designing of 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.

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Supporting Information

A new $(6^3)•(6^9.8^1)$ 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.
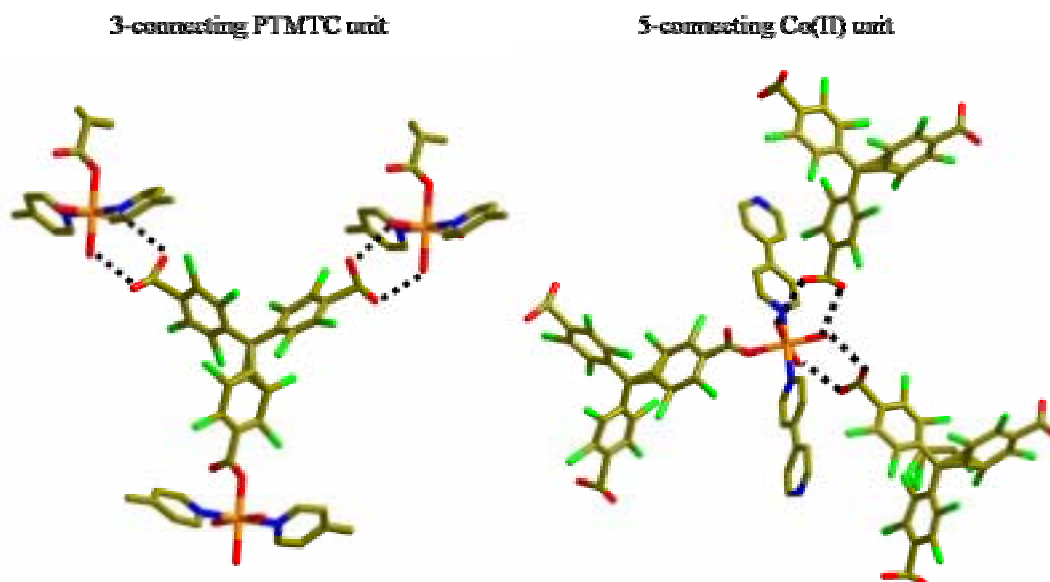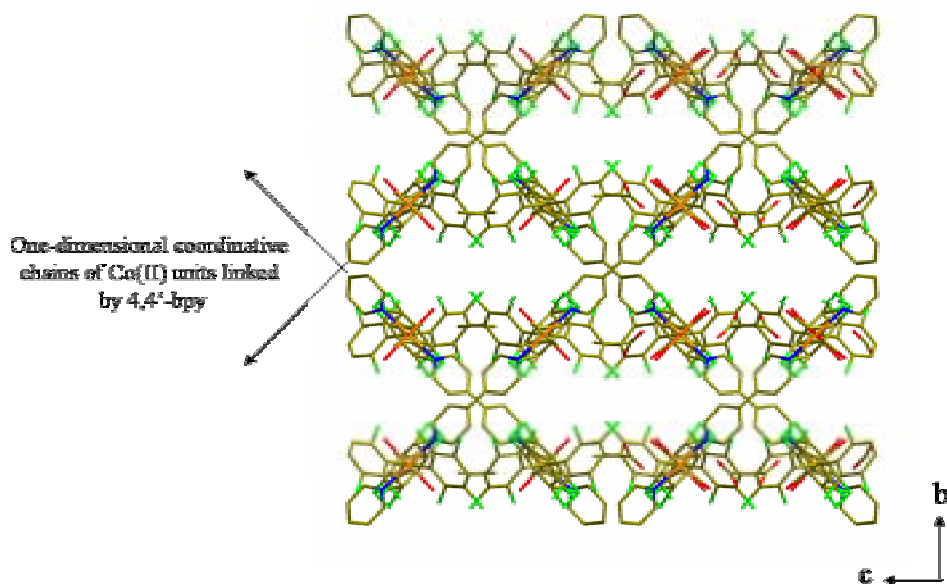
Crystal packing.

One-dimensional coordinative chains of Co(II) units linked by 4,4'-bpy

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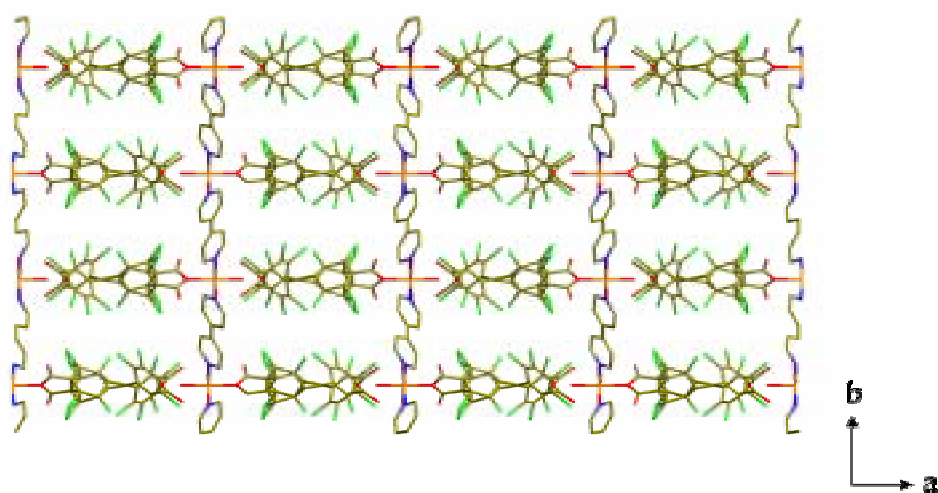

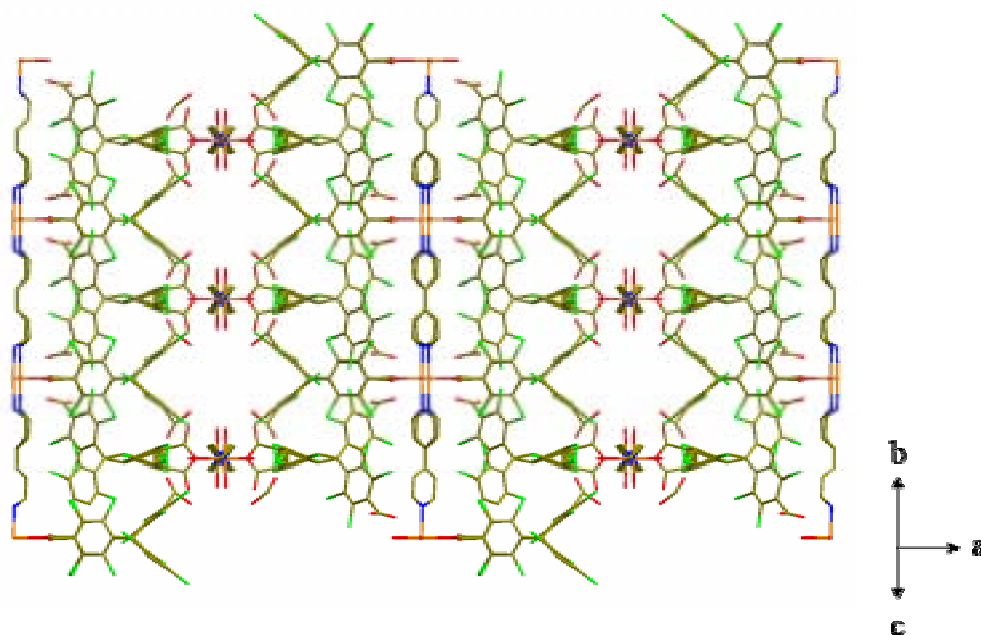**Fig 3.** Crystal packing of MOROF-2 along the [001] direction.

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 T 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, T 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$_1$·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.
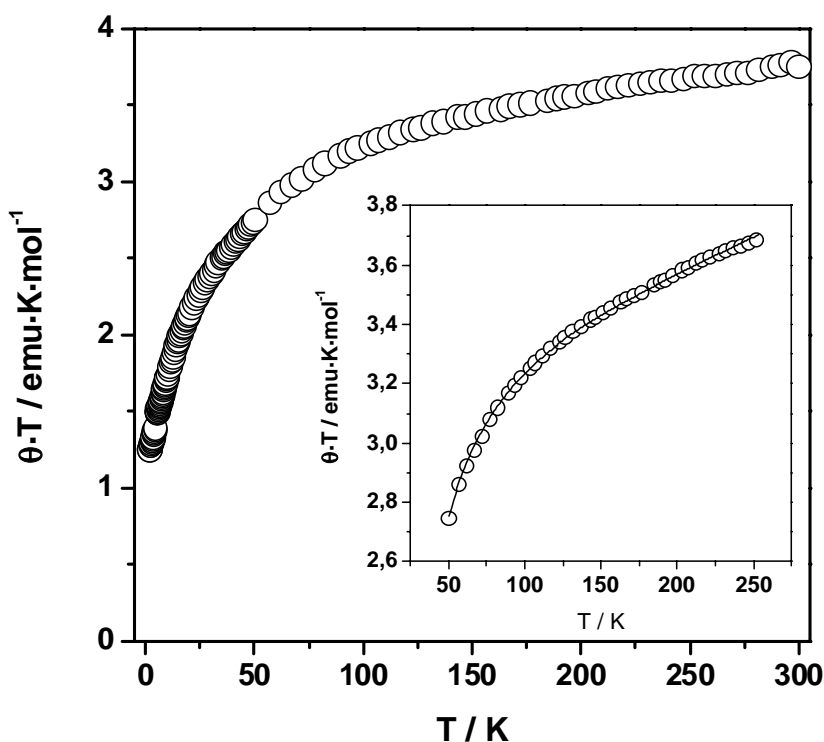
Fig 5. θ·T vs T for MOROF-2. Insert. θ·T vs T in the range of 1.8 K to 300 K. The solid line represents the best-fit calculated data.

Article K

Títol: A non-interpenetrated nanoporous helical (6,3) network exhibiting magnetic ordering based on a tricarboxylic perchlorotriphenylmethyl radical.

Autors: D. Maspoch, N. Domingo, D. Ruiz-Molina, K. Wurst, G. Vaughan, J. Tejada, C. Rovira, J. Veciana.

Publicació: En preparació.

(No presentat a la Comissió de Doctorat)

A Non-Interpenetrated Nanoporous Helical (6,3) Network Exhibiting Ferrimagnetism based on a Tricarboxylic Perchlorotriphenylmethyl Radical.**

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Rapid development in the self-assembly of transition metal ions and multifunctional organic ligands has yield a wide variety of one-, two- and three-dimensional metal-organic architectures that have specific properties.[1] In

the field of porous metal-organic materials, the endless versatility of molecular chemistry to design new polytopic ligands has become an excellent tool to obtain a long list of open-framework structures[2] with different topologies[3] and surprising porosity properties.[4] However, besides classical applications of porous solids in molecular sieves, sensors, ion-exchangers and catalysis, the construction of open-frameworks from transition metal ions opens the possibility to design porous materials with additional electrical,[5] optical or magnetic properties. Among them, attainment of magnetic porous solids has attracted considerable efforts in the last few years.[6]

In this context, in our laboratory we have recently described a new strategy consisting in the use of purely organic radicals as "spacer" paramagnetic ligands to obtain magnetic nanoporous metal-organic materials.[7] To implement this idea, we have designed and synthesized a first polyfunctional open-shell specie, a new thermical and chemical stable perchlorinated triphenylmethyl radical[8] with three carboxylic groups (PTMTC). Indeed, PTMTC radical fulfils all requirements. In terms of topology, PTMTC is expected that behave as a trigonal bridging 3-connected ligand. In particular, it can be considered an expanded version of trimesic acid[4f,9,10] with the additional presence of bulky chlorine atoms in all the remaining phenyl positions, which could also prevent interpenetration phenomena.[11] Otherwise, from a magnetic point of view, the open-shell character of such organic radical is particularly appealing since it is expected to interact magnetically with transition metal ions enhancing the magnetic dimensionality of the porous material.[12,13] Success of this approach has been demonstrated in a noninterpenetrated (6,3) honeycomb porous molecular material (MOROF-1) with very large pores (2.8 Å) and magnetic ordering.[7]

-Insert Scheme 1 here-

Herein, we report what is to our knowledge the first example of a noninterpenetrated nanoporous helical (6,3) network that act as a molecular ferrimagnet: $Co_6(PTMTC)_4(py)_{17}(H_2O)_4(EtOH)$ (MOROF-3), an open-framework structure formed by the self-assembly of Co(II) ions and 3-connected bridging PTMTC radicals.

Red needle crystals of MOROF-3 were obtained by the slow diffusion of a solution of pyridine in ethanol onto a solution of $Co(ClO_4)_2 \cdot 6H_2O$ and PTMTC in ethanol and water. The single-crystal X-Ray analysis[14] of MOROF-3 reveal a three-dimensional framework build from seven crystallographic different octahedral Co(II) units,[15] although coordination environment for all sites are nearly identical (Figure 1). Each Co(II) unit is formed by two coordinated PTMTC radicals. Two carboxylate groups of two different PTMTC moieties coordinate to two Co(II) ions in a bidentate mode, whereas each of the other carboxylate groups coordinate Co(II) ions in a monodentate fashion. The remaining positions on the metal centers are occupied by two or three pyridine molecules and one or two water or ethanol molecules.

– **Insert Figure 1 here**–

The shortest circuits in the architecture contain six PTMTC radicals and six Co(II) atoms (Figure 2a). Thus, the network can be classified as a (6,3) net,[17] if the Co(II) are considered spacers and the moieties of PTMTC to be 3-connected nodes. This configuration gives a 3-D network with one finite direction. Along the [100] direction, this arrangement can be regarded as a non-chiral helical network,[16] growing in a pseudo-hexagonal topology (Figure 2). Each helical strand is composed of four Co(II) units per turn with a pitch of 9 Å. In this topology, PTMTC radical plays a key role to create such helical arrangement. For their propeller-shape conformation, family of PTM radicals have torsion angles between the mean planes of the three polychlorinated aromatic rings and that formed by the three bridgehead C atoms and the methyl one –the

reference plane— that amount 38 to 62°.[18] In such a context, the dihedral angles of PTMTC ligands with values in the range of 45 to 56° favor the helical nature of MOROF-2. Furthermore, trigonal geometry of PTMTC also awards angles in the range of 112 to 124° between carboxylate groups and methyl carbon atom. This geometry originates that methyl carbon atoms of each PTMTC ligand (C(19), C(38), C(57) and C(76)) occupy four of six hypothetical vertices positions of distorted hexagons (Figure 2c). Remaining vertices are occupied by two Co(II) metal ions at Co(2) and Co(4) or Co(5) and Co(7). All Co(II) units have angles of 154 to 149° between metal ion and coordinated PTMTC radicals.

— **Insert Figure 2 here—**

The overall structure thus formed could be regarded as the packing of individual (6,3) nets along the [011] direction (Figure 3). The infinite nets are stacked with a (0,b/4,c/4) displacement and connected by noncovalent interactions such as non-classical H-bonds, face-to-face φ–φ interactions and Cl-Cl contacts.

-Insert Figure 3 here-

A remarkable feature of the hexagonal helical growth is that without interpenetration it intrinsically generates the formation of large monodimensional nanochannels, with minimum distances of 16.9 x 9.4 Å between their limits. Indeed, these cavities are large enough to endow this material with a total void volume of 38.1 % of the cell volume.[19] In absolute terms, it represents a volume of 5492 $Å^3$ per 14412 $Å^3$ of the unit cell.[20] Such volume is occupied by reaction solvent molecules. An X-ray study confirmed that ethanol and water molecules located close to the inner walls are hydrogen bonded to carboxylate groups of PTMTC and water ligands. Because of disorder, additional guest

molecules in the pore channels could not be directly located in the crystal structure analysis.

Thermal variation of magnetic susceptibility for a crystalline sample of MOROF-3 was measured on a SQUID magnetometer in the temperature range of 1.8-300K, under external applied magnetic fields of 0.1 to 10 kG (Figure 4). The product of molar magnetic susceptibility ($\theta_m \cdot T$) with temperature (T) equals 24 emu•K•mol-1 at room temperature, value that differs from the expected spin-only value of 12.75 emu•K•mol-1, corresponding to six Co(II) ions and four PTMTC radicals with local spins S_{Co}=3/2 and S_{PTMTC}=1/2, in accordance with the well documented orbital contribution of octahedral Co(II) ions. Upon lowering the temperature to ca. 30K, $\theta_m \cdot T$ smoothly decreases until it reaches a minimum of 14.5 emu•K•mol-1 at 15K. The magnetic susceptibility in the range of 30-300K obeys the Curie-Weiss law, with a Curie constant C = 24.5 emu•K•mol-1, and a negative Weiss constant χ of -15K, which indicates the presence of antiferromagnetic coupling between nearest-neighboring Co(II) ions and PTMTC radicals within the helical framework. As the temperature is further decreased, the $\theta_m \cdot T$ abruptly increases up to a maximum value of 34.6 emu•K•mol-1 at 1.8 K, which can be explained by an increase of the correlation length of antiferromagnetic coupled units as randomising thermal effects are reduced, either via in-helical (6,3) net long-range antiferromagnetic coupling or inter helical nets ferromagnetic interactions. Moreover, the value of $\theta_m \cdot T$ exhibits a considerable dependence on the applied external magnetic field, similar to that observed for MOROF-1.[7]

Magnetic order is also confirmed by the presence of peaks on both, the in phase θ_m' and the out of phase θ_m'' components of ac magnetic susceptibility below 3 K (Figure 4b). The position of the peaks shows negligible frequency dependence over a range of 3-100 Hz. Furthermore, magnetic field dependence of MOROF-3 at 1.8K rapidly increases from

0 to 1.5T, but no saturation value is observed up to 5T. Maximum measured value of magnetization of 12 σB is quite agree with the expected for a ferrimagnetic ground state (14 σB) due to the presence of antiferromagnetic coupling interactions between Co(II) ions and PTMTC radical moieties. No evidence of hysteresis loop was observed in this system at 1.8K. Currently we are evaluating the field dependence of the magnetization at lower temperatures.

-Insert Figure 4 here-

The results of this study show the huge coordinating versatility exhibited for the open-shell PTMTC ligand to build nanostructured networks with large pores and interesting magnetic properties. Further experimentation aimed at the chemical modification of perchlorotriphenylmethyl skeleton. The possibility to functionalize different positions of the three phenyl rings allows the design of a whole range of carboxylic substituted PTM radicals. Such new radical units are expected to produce a new family of 1-D, 2-D and 3-D magnetic metal-organic radical open-frameworks (MOROF) with surprising topologies.

Experimental Section

MOROF-3: Slow diffusion of a solution of pyridine (0.5 mL) in ethanol (2 mL) onto a solution of $Co(ClO)_2 \cdot 6H_2O$ (0.0684 mmol) and PTMTC (0.0456 mmol) in ethanol (1.6 mL) and water (0.4 mL). After 28 days, red needle crystals of MOROF-3 were extract from the solution. Crystals of MOROF-3 appears to lose solvent and crystallinity slowly in the absence of solvent. IR (KBr, cm^{-1}): 3422, 1603, 1488, 1446, 1399, 1347, 1321, 1040, 757, 723, 699, 579, 528.

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[21]   Magnetic measurements done with MOROF-3 were performed in contact and not of solvent. The magnetic behaviour of a sample that was in contact with the atmosphere for one week was identical from that obtained for the as-synthesized MOROF-3.

Figure Captions.

Figure 1. ORTEP view of the asymmetric unit of MOROF-3 (thermal ellipsoids set at 30% probability). All H atoms are omitted for clarity.

Figure 2. The crystal structure of MOROF-3. a) Shortest circuit composed of six PTMTC moieties and six Co(II) ions, which are space-filling represented b) Portion of the adjacent infinite helices viewed along [0½½]. Note the opposite hands of adjacent helices, which build the non-chiral (6,3) net. c) An hexagonal pore. Methyl carbon atoms of PTMTC radicals and Co(II) ions, which are located in the vertex of hexagons, are space-filling represented. d) Illustration of the (6-3) net viewed along [100]. Co, violet; C, brown; O, red; Cl, green; N, blue; H, yellow. In a), b), and c) pyridine, water and ethanol ligands are omitted for clarity. Guest solvent molecules are also omitted.

Figure 3. a) Illustration of the crystal packing of (6,3) nets viewed along [100]. b) Space-filling representation.

Figure 4. Magnetic properties. a) θT value as a function of the temperature for MOROF-1 at an applied field of 1000 Oe. b) Magnetic AC susceptibility measurements as a function of the temperature at 3 (•), 5 (•), 10 (•) and 100 (•) Hz and at an applied field of 3000 Oe.
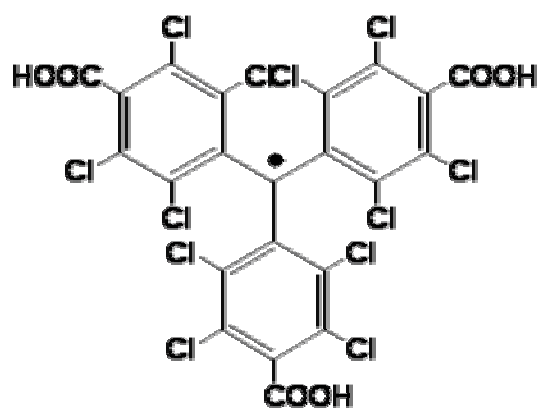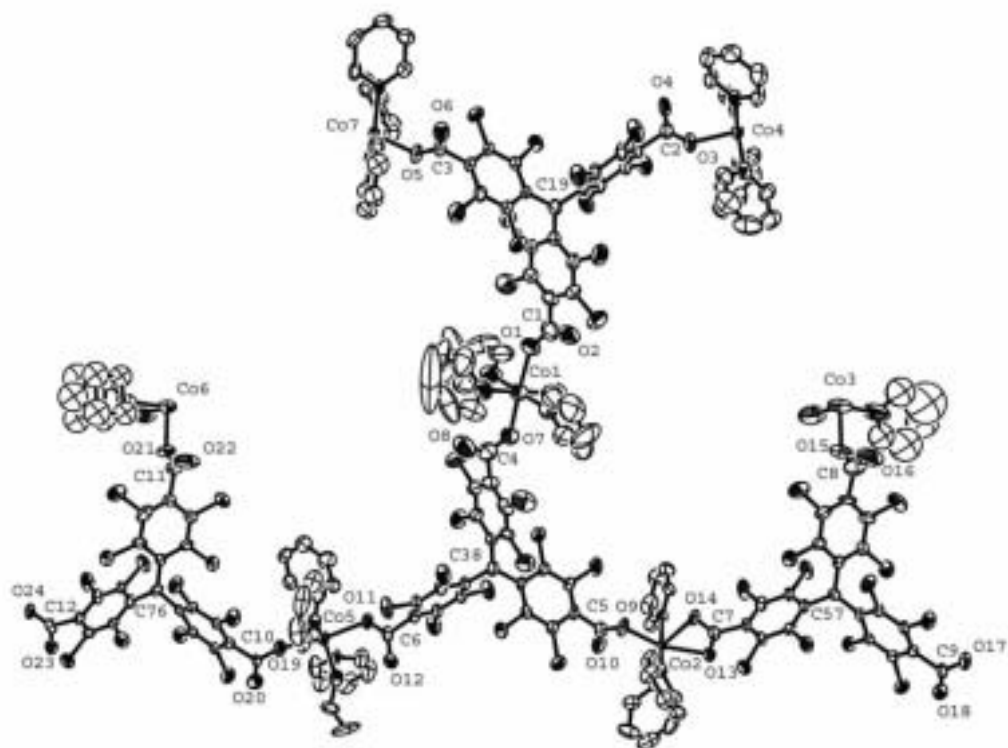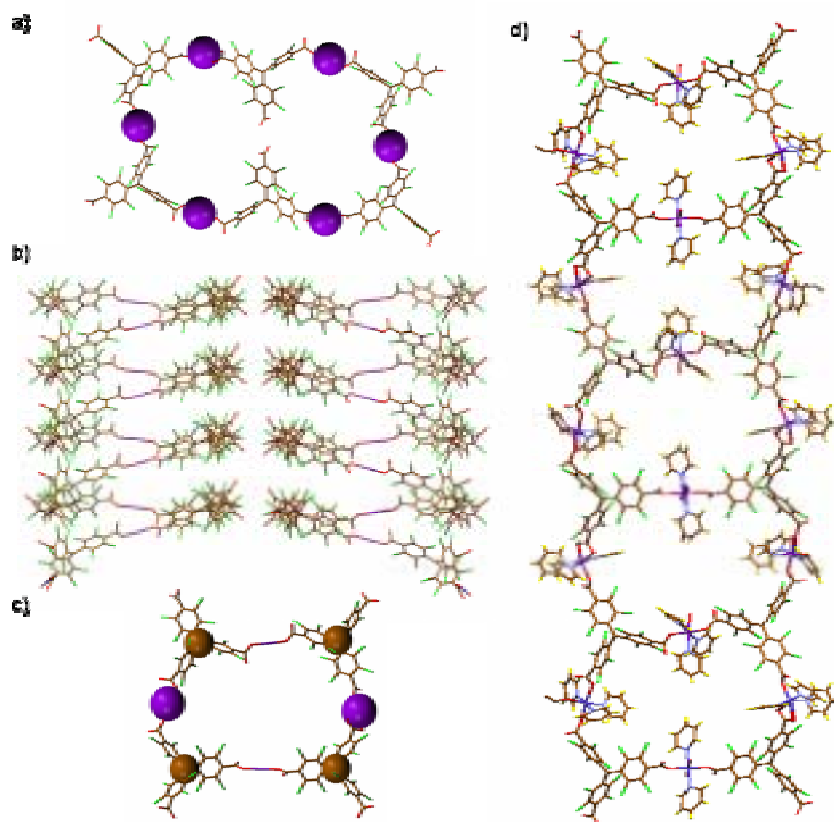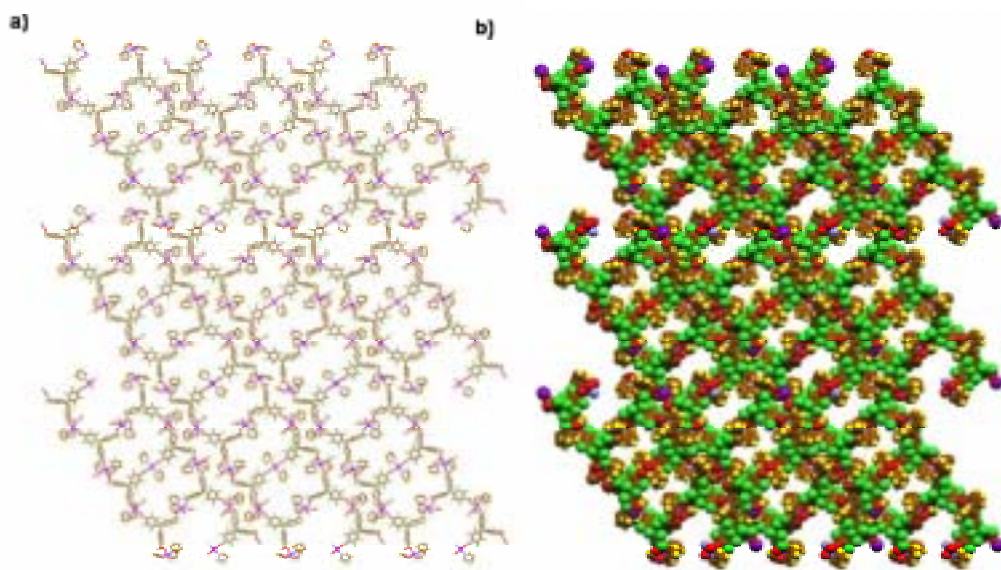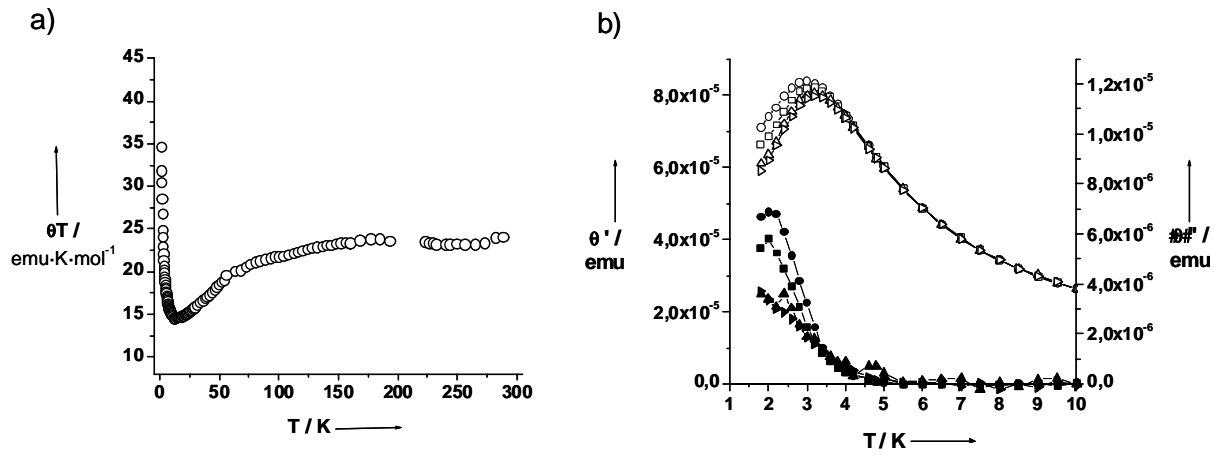
PTMTC

Scheme 1

Figure 1

Figure 2

Figure 3

a)

b)

Figure 4