Magnetic Materials

A Robust Purely Organic Nanoporous Magnet**

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In the last few years, the construction of purely organic-molecule-based magnetic materials has become a topic of interest.[1] Since the first organic ferromagnet was discovered in 1991,[2] a number of other purely organic radicals exhibiting bulk ferromagnetic ordering at very low temperatures (generally below 1.5 K) have been found.[3] For this property to be achieved, synthetic tailoring of open-shell building blocks that allow both a proper control over their supramolecular assembly and the establishment of correct magnetic interactions, are required. Crystal engineering through hydrogen-bonding interactions is a powerful method for achieving both conditions. From a structural point of view, the directional and often predictive nature of hydrogen bonds may allow control of the long-range supramolecular order in solid state.[4] Besides their structural control, hydrogen bonds have also been shown to favor magnetic exchange interactions between bound radical molecules of α-nitronyl nitroxides, α-imino nitroxide, or *tert*-butyl nitroxide derivatives.[5] For instance, attempts to control packing, and therefore magnetic ordering, in phenyl nitronyl aminoxyl radicals substituted by one or two OH groups have been carried out.[6] However, even though

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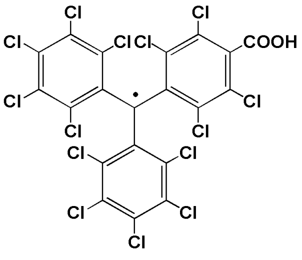
efforts on this direction have been undertaken by different groups, the ultimate design of high-level structures with a ferromagnetic macroscopic behavior must be left in most cases to serendipity, as additional, undesirable intermolecular interactions compete in the solid state.

To circumvent such inconvenience, we have initiated an approach based on the synthesis and study of perchlorotriphenylmethyl (PTM) radicals functionalized with carboxylic groups. PTM radicals, in addition to eminent thermal and chemical stabilities,[7] are bulky molecules which minimize additional through-space intermolecular magnetic interactions.

We have already described the supramolecular arrangement of the monocarboxylic radical **1**.[8] In the solid state radical **1** formed hydrogen-bonded dimers that promoted the transmission of a weak ferromagnetic interaction. Herein we report the supramolecular arrangement and magnetic characterization of the new radical **2** (PTMTC), which offers a rational mechanism to expand the structural, and hence, the magnetic dimensionality of the supramolecular architecture owing to the presence of three carboxylic groups, which are able to form hydrogen bonds. Furthermore, from a strict structural point of view, radical **2**, by analogy with trimesic acid,[9] is expected to generate an open-framework nanoporous structure, a goal within the crystal-engineering field.[10,11] An example of purely organic-radical open-framework (POROF-1), with dominant antiferromagnetic interactions has been obtained by the self-assembly of the dicarboxylic radical **3**.[12] The hydrogen-bonded assembly (named POROF-2) generated from radical **2** has the advantages associated with both mono- and biscarboxylic PTM radicals, it has a robust porous extended network and an architecture that not only combines the presence of highly polar nanotubular channels but also magnetic ordering at low temperatures.



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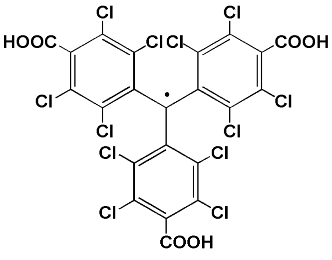

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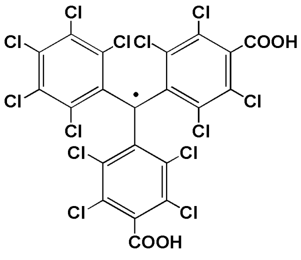

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Hexagonal single-crystals of POROF-2 suitable for X-ray diffraction were grown from a mixture of dichloromethane and *n*-hexane. Radical **2** crystallizes on a trigonal $P\bar{3}c1$ space group with four molecules of **2** packed in the unit cell.[13] The high molecular symmetry of the crystal lattice is reflected by the presence of a C_3 symmetry axis that passes through the central carbon (C8) of the radical (see Figure 1a) Thus, the three polychlorinated aromatic rings of radical **2** are identical. Owing to the steric hindrance of the chlorine atoms in *ortho* positions of the phenyl groups, the carboxylic group is twisted by 87° with respect to the plane of the phenyl group to which it is bonded.

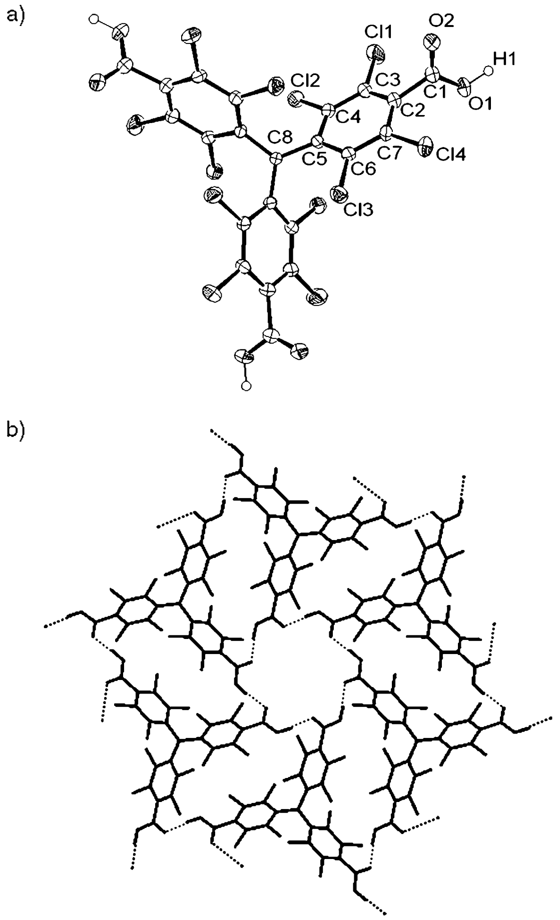

Figure 1. Crystal structure of POROF-2. a) ORTEP plot, thermal ellipsoids set at 50% probability, and b) hydrogen-bonded hexamer.

The molecular arrangement of such crystalline radical building blocks creates a primary structure consisting of two-dimensional hydrogen-bonded layers along the *ab* plane. As shown in Figure 1b, the repeating unit consists of a nontypical hexameric $R_6^6(24)$ hydrogen-bonded motif formed by six molecules of **2** with alternating plus and minus helicities in their three-bladed propeller-like substructures (Figure 1b). In this motif, each radical is hydrogen-bonded to two neighboring radicals through one carboxylic group, with bond lengths of 1.70 Å and bond angles of 169°. Since every radical unit contains three carboxylic groups, each PTMTC molecule participates in the construction of three identical hexameric units that propagate along the *ab* plane (see Figure 2a).

Several chlorine–chlorine contacts (twelve per molecule) between neighboring layers have significant implications for the rigidity of this porous framework, in particular for the

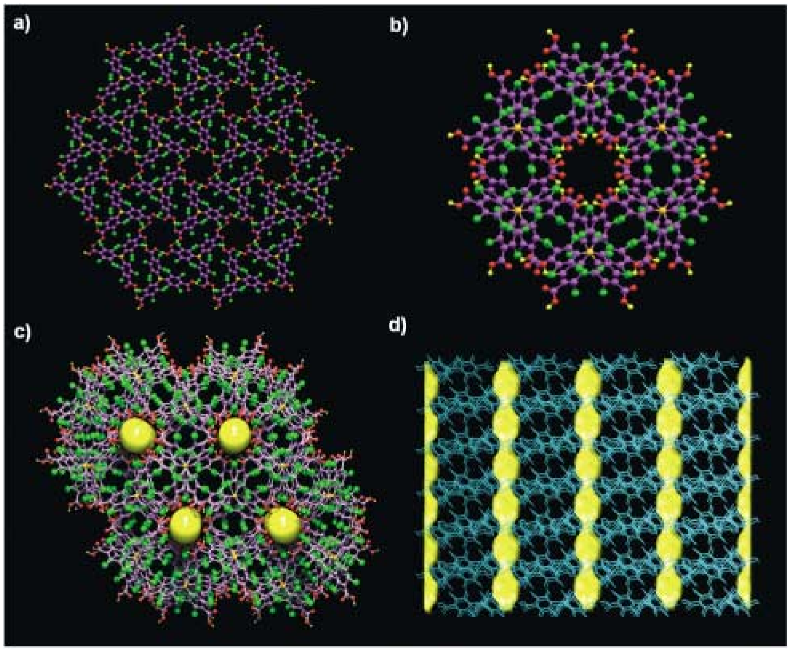

Figure 2. Crystal packing of POROF-2. a) Open-framework network in *ab* plane, b) tubular nanochannel, c) pore view along the *c* axis, the large yellow sphere indicates the dimensions of the tublular channels, and d) pore view along the *a* axis, showing the tubular channels. C violet or orange; O red; Cl green; H yellow. In (a)–(c) the carbon atoms in orange have most of the spin density of radical **2**.

secondary structure of POROF-2 that consists of the stacking of different layers with an ABAB alternation along the *c* axis.[14] Surprisingly, the stacking of layers along the *c* axis generates a three-dimensional structure that has tubular channels, into which a sphere 5.2 Å in diameter can fit (see Figure 2b,c). In addition, such nanochannels are surrounded by a second set of small pores with a diameter of 3.3 Å. The combination of both sets of channels gives solvent-accessible voids in the crystal structure that amount to up to 15% (450 Å^3 per unit cell) of the total volume.[15] The significant steric congestion caused by the large number of bulky chlorine atoms, can be ascribed as the main reason for obtaining this noncatenated crystal packing.[16]

As can be observed more in detail in Figure 2b, the location of carboxylic groups at the inner walls of the largest channels furnish these pores with a highly polar and hydrophilic environment. This arrangement may account for the lack of guest solvent molecules (*n*-hexane and/or CH_2Cl_2) within the nanochannels, a situation confirmed not only by X-ray crystallography but also by thermogravimetric studies and elemental analysis. Thermogravimetric analysis of a few single crystals of radical **2** showed no weight loss in the temperature range 25–300 °C, in fact POROF-2 remains crystalline and stable up to 300 °C. Indeed, the powder X-ray diffraction pattern of a sample that was heated up to 300 °C shows that the positions and intensities of all lines remain unchanged when compared with the powder X-ray diffraction pattern of an as-synthesized sample. A further increase of the temperature above 300 °C reveals a decomposition of POROF-2, as confirmed by combined powder X-ray diffraction and FT-IR characterization. Such a thermal stability is remarkable since most nanoporous organic materials reported to date incorporate guest solvent molecules, that once eliminated, induce a collapse of the crystalline material. To our knowledge, there are only a few previous examples of nanoporous organic hydrogen-bonded networks that remain ordered even when most of the guest molecules are removed.[17]

Variable-temperature magnetic-susceptibility data for a crystalline sample of POROF-2 was obtained on a SQUID susceptometer, under a temperature range of 2–300 K and an applied magnetic field of 200 Oe (see inset Figure 3). The χT value is 0.38 emu K mol^{-1} at 300 K, which is in agreement with the theoretical value expected for a noninteracting S = 1/2 spin in each molecule. Upon cooling, the χT value remains constant down to 5 K, whereupon the χT value increases according with the presence of weak ferromagnetic interactions. This behavior was fitted to the Curie–Weiss law with a Weiss constant of $\theta = +0.2$ K. To investigate the existence of magnetic ordering at very low temperatures, variable temperature magnetic susceptibility experiments down to 0.07 K were performed in a dilution cryostat (see Figure 3). A considerable increase of the χT value up to a maximum around 0.110 K was observed on cooling down below 2 K, which shows a transition to a ferromagnetic ordered state at very low temperatures. The intensity of the peak decreases whereas its maximum shifts slightly to higher temperatures on increasing the external applied magnetic field. For instance, for an applied magnetic field of 200 Oe a value of 2.2 emu K mol^{-1} was obtained, whereas for an external field of 500 Oe the value is reduced to 1.4 emu K mol^{-1}. This behavior originates in the saturation of magnetization for fields of few hundred Oe. Magnetization curves were measured above and below the critical temperature and are illustrated in Figure 4. At 1.35 K, POROF-2 remains in the paramagnetic region and therefore the magnetization curve has a slight gradient. On

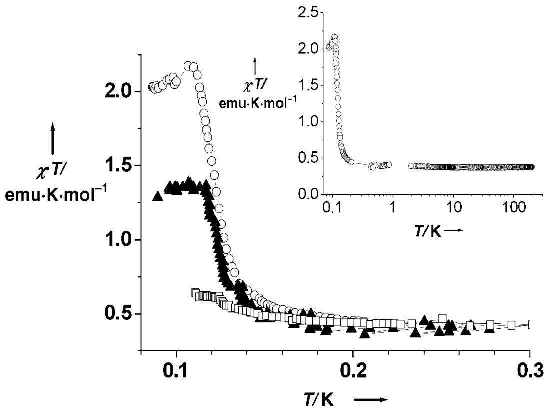

Figure 3. χT as a function of temperature for different applied magnetic fields *H*: (○) *H* = 200 Oe, (▲) *H* = 500 Oe, and (□) *H* = 1000 Oe. The inset shows the logarithmic dependence of χT function on the temperature up to 200 K, measured with an applied magnetic field of 200 Oe.

the contrary, the curve at 0.80 K, even if it is very close to the critical temperature, traces a hysteretic loop characteristic of a soft ferromagnet. The magnetization is almost saturated at about 400 Oe, and though the coercitive force is of the order of 50 Oe (see inset of Figure 4), the remnant magnetization at zero field is of about 35 % of the saturation value.

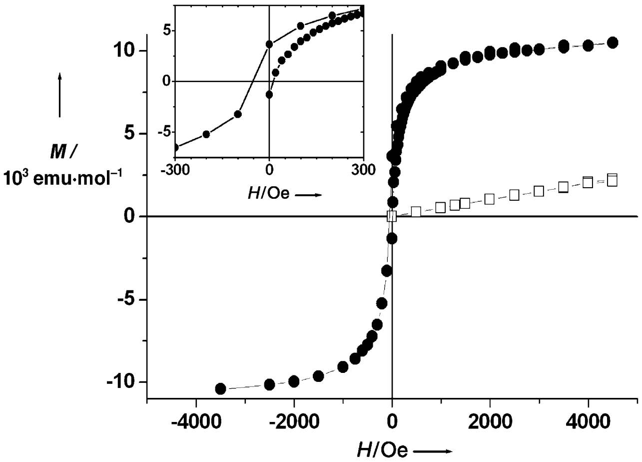

Figure 4. Magnetization curves as a function of the applied magnetic field, measured at different temperatures. (●) 0.08 K, (□) 1.35 K. The inset shows the detail of the curve at 0.08 K around zero field.

In conclusion, we have reported the first example of a supramolecular, nanoporous purely organic, "zeolite-like" material exhibiting an unusual thermal stability, a hydrophilic nanoporous architecture, and a long-range ferromagnetic ordering. Nanoporous materials exhibit a wide range of applications, such as molecular sieves, catalysis, separation, and sensors. Such properties, along with the magnetic properties of the organic framework, may open a new avenue to the development of new multifunctional materials.

Experimental Section

Radical **2**: A mixture of tris(2,3,5,6-tetrachlorophenyl)methane[18] (1.70 g, 2.58 mmol), chloroform (30 mL), and aluminum chloride (0.40 g, 3.00 mmol) was heated at 160 °C for 8 h in a glass pressure vessel. The mixture was then poured onto ice/1N hydrochloric acid and extracted with chloroform. The white solid collected was mixed in 20 % oleum (100 mL) and heated at 150 °C for 12 h. The final solution was cooled and poured into cracked ice. The solid was washed with water, dissolved in Et_2O, extracted with aqueous sodium hydrogen carbonate, acidified, extracted with Et_2O, and dried in vacuo. A solution of the resultant white precipitate in DMSO was shaken with an excess of powdered NaOH for 72 h. The mixture was filtered and immediately a stoichiometric amount of iodine was added to the filtrate. The solution was left undisturbed in the dark (45 min), washed with an aqueous solution of sodium hydrogen sulfite (39 %, 50 mL), and treated with Et_2O (100 mL). Radical **2** was extracted with aqueous sodium hydrogen carbonate, and this aqueous layer was acidified and extracted with Et_2O. The extracted solid was recrystallized from Et_2O/*n*-pentane to give radical **2** as red powder. IR (KBr): $\tilde{\nu} = 3500–2500$, 1740, 1694, 1662, 1537, 1441, 1408, 1352, 1326, 1290, 1251, 1226, 1040, 931, 752, 722, 665, 574, 522, 462 cm^{-1}. Elemental analysis (%) calcd: C 33.50, H 0.38; found C 33.65, H 0.32. Crystals suitable for X-ray diffraction were grown from a mixture of dichloromethane and *n*-hexane.

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[13] X-ray single-crystal diffraction data for POROF-2 was collected on a Kuma KM-8 diffractometer with a CCD area detector and silicon-monochromized synchroton radiation ($\lambda = 0.53378$ Å) Crystal data for OROF-2: trigonal, space group $P\bar{3}c1$, dimensions $0.15 \times 0.15 \times 0.01$ mm, $a = 15.9283(7)$, $b = 15.9283(7)$, $c = 13.8886(11)$ Å, $V = 3051.6(3)$ Å^3, $Z = 4$, $\lambda = 0.53378$ Å, $\mu = 0.572$ mm^{-1}. A total range of 24868 reflections were collected in the range of $1.0 \leq \theta \leq 20.5$, of which 2232 were unique reflections. Least-squares refinement based on 2084 reflections with $I > 2\sigma(I)$ led to converge, with a final $R1 = 0.0585$, $wR2 = 0.1418$, and GOF = 1.133. CCDC-223669 (POROF-2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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