A Robust Nanocontainer Based on a Pure Organic Free Radical

Daniel Maspoch,[†] Neus Domingo,[‡] Daniel Ruiz-Molina,[†] Klaus Wurst,[§] Javier Tejada,[‡] Concepció Rovira,[†] and Jaume Veciana*,[†]

Institut de Ciència dels Materials de Barcelona (CSIC), Campus UAB, 08193, Cerdanyola, Catalonia, Spain, Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028-Barcelona, Spain, and Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 52a, A-6020, Innsbruck, Austria
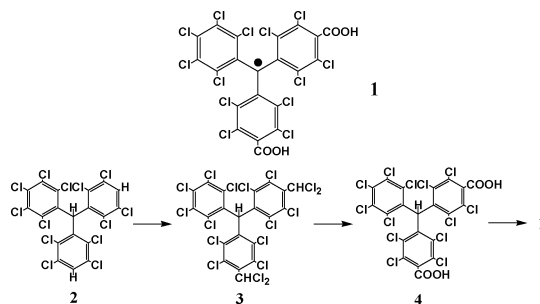
Received October 10, 2003; E-mail: vecianaj@icmab.es

Proper supramolecular self-assembly of organic molecules in the solid state is one of the most important challenges for the development of multifunctional molecular materials.[1] Among them, recently much more effort has been focalized toward the obtaining of magnetic nanoporous materials. Indeed, thus far several metal-organic open-framework structures that combine the inherent characteristics of nanoporous materials and the occurrence of magnetic exchange interactions between transition metal ions have been obtained.[2,3] However, even though several examples of pure organic nanoporous systems have already been described,[4,5] to the best of our knowledge, none of them exhibit magnetic properties due to the lack of transition-metal ions and the diamagnetic character of the organic molecular bricks used thus far. Herein, we present the first example of a purely organic magnetic and robust nanoporous lattice based on the supramolecular arrangement of an open-shell molecule, the dicarboxylic perchlorinated triphenylmethyl (PTM) radical 1. The use of this free radical as a supramolecular synthon has several advantages:[6] (1) radical 1 exhibits a high thermal and chemical stability, (2) its trigonal symmetry provides a typical template for getting channels held together by hydrogen bonds through the two carboxylic groups, (3) the molecular bulkiness and rigidity of PTM radicals is expected to prevent close packing of molecular units, and (4) besides their structural control, hydrogen bonds have also been shown to favor magnetic exchange interactions between bound organic radical molecules.[7] Crystallization of the dicarboxylic radical 1[8] generates the pure organic radical open-framework (POROF-1) material, combining large hydrophobic nanocavities with hydrophilic windows along with magnetic characteristics.

Radical 1 was prepared following a new three-step procedure, starting from compound 2.[9] Dichloromethyl groups were introduced by reacting 2 with chloroform following a Friedel–Crafts reaction using $AlCl_3$ as catalyst (78%) and subsequently were converted to carboxylic groups by a hydrolysis-oxidation reaction using oleum 20% (31%). Finally, the subsequent treatment of the hydrocarbon precursor 4 with excess of NaOH, I_2, and HCl gave radical 1 (90%). Single crystals of POROF-1, suitable for X-ray diffraction, were obtained by a diffusion of *n*-hexane into a solution of 1 in dichloromethane.[9]

Radical 1 crystallizes in a trigonal *R*-3 space group with 18 molecules of radical 1 packed in the unit cell. Molecular arrangement of 1 creates a primary structure consisting of two-dimensional hydrogen-bonded sheets along the *ab* plane, where each molecule of 1 participates in the construction of two different hydrogen-bonded motifs. The repetitive unit consists of an unusual hexamer of radicals hydrogen-bonded through one carboxylic group $[R_6^6 (24)]$, with bond distances of 1.837 Å and bond angles of 168.5° (Figure 1). The second carboxylic group of each radical acts as a connecting element between hexameric units by the formation of

† Institut de Ciència dels Materials de Barcelona.
‡ Universitat de Barcelona.
§ Universität Innsbruck.

Scheme 1

two complementary hydrogen bonds between two carboxylic groups $[R_2^2 (8)]$, with a bond distance of 1.865 Å and bond angle of 163.2°.[11] In this way, each hexamer is linked with six more identical units in an hexagonal topology, extending the infinitely hydrogen-bonded net along the *ab* plane (Figure 1). Further supramolecular interactions, in particular four H-bonds between chlorine atoms and carboxylic groups and six Cl···Cl contacts per molecule,[12] contribute to an additional stabilization of the hydrogen-bonded network.

A view down the *c* axis of the crystal structure of POROF-1 reveals a stacking of laterally shifted layers held together through several Cl···Cl contacts (Figure 2), yielding an ABCABC arrangement. The packing of these pillared sheets leads a pure organic open-framework structure with one-dimensional nanochannels formed by narrowed polar windows and larger hydrophobic cavities. Indeed, as illustrated in Figure 2, these channels contain large hydrophobic nanocavities where a sphere 10 Å in diameter can fit inside them and smaller windows with a highly hydrophilic environment due to the presence of the carboxylic groups at the inner rims. The diameter of such hydrophilic windows is 5 Å, considering van der Waals radius. The unusual combination of connected nanocavities and windows gives way to solvent-accessible voids in the crystal structure that amount to 31% (5031 Å[3] per unit cell) of the total volume (16 158 Å[3]).[13]

To evaluate the structural robustness of POROF-1, we have examined, by a combination of thermal gravimetric analysis and X-ray powder diffraction (XRPD) experiments, an as-synthesized crystalline sample of POROF-1.[14] In the as-synthesized material, the large hydrophobic cavities are occupied by six *n*-hexane solvate molecules (one molecule of *n*-hexane per one molecule of radical 1). Accordingly, when an as-synthesized sample of POROF-1 was heated to 100 °C, a weight loss of 9%, ascribed to the complete loss of all guest *n*-hexanes molecules, was observed. Such a loss was confirmed by complementary elemental analysis. Beyond this temperature, thermal analysis does not exhibit any significant change up to 275 °C, whereupon an abrupt weight loss attributed to the decomposition of 1 was observed. Simultaneously, XRPD studies confirmed that POROF-1 remains crystalline and stable up to 275 °C. Indeed, the XRPD pattern of a sample that was heated
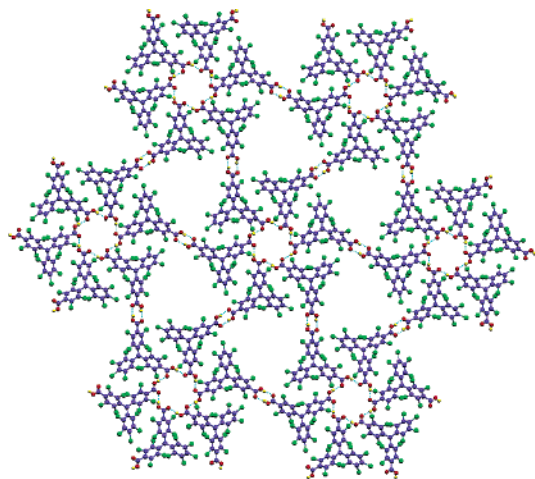
Figure 1. Crystal structure of POROF-1. Two-dimensional hydrogen-bonded layer. Within one layer, the repetitive $R_6^6(24)$ H-bonded hexamer originates a polar window due to the presence of six carboxylic groups, whereas linking of each hexamer with six more identical units in an hexagonal topology originates six trigonal-shaped hydrophobic voids.
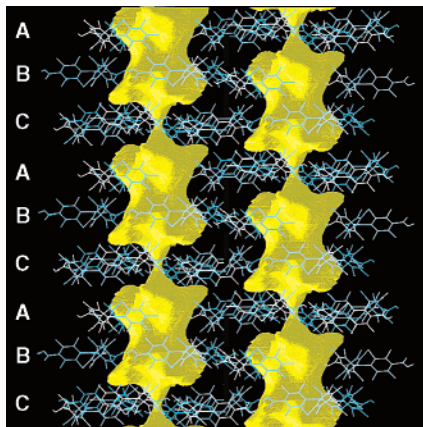

Figure 2. Space-filling view along the *b* axis of the large nanocontainers formed along the one-dimensional channel.

at 265 °C shows that the positions and intensities of all lines remain unchanged when compared with the XRPD pattern of an as-synthesized sample. Such a thermal stability is highly remarkable and comparable to those observed for other stable supramolecular systems, such as multi H-bonded aggregates derived from the cyanuric acid and melamine.[15]

Variable temperature magnetic susceptibility data for an as-synthesized crystalline sample of POROF-1 were obtained on a SQUID magnetometer, under a temperature range of 1.8−300 K. POROF-1 exhibits a paramagnetic behavior in the 50−300 K temperature range, with a $\chi \cdot T$ product value of 0.385 emu K mol^{-1} at 300 K, that fully agrees with the theoretical value of 0.375 emu K mol^{-1} expected for an uncorrelated spin ($S = 1/2$). Below 50 K, the $\chi \cdot T$ value decreases upon decreasing temperature, consistently with the presence of weak intermolecular antiferromagnetic interactions. This magnetic behavior remains constant in the absence of guest solvent molecules.

In summary, self-assembly of radical **1** generates a paramagnetic open-framework structure with one-dimensional nanochannels formed by narrowed polar windows and large hydrophobic nanocontainers. Moreover, POROF-1 is one of the scarce examples of pure organic porous materials that remains stable up to 275 °C, even after removal of internal solvate guest molecules.[16] Such structural features, joined to its solubility in polar organic solvents, give to POROF-1 the possibility to be a good candidate for future ship-in-bottle synthesis applications.[17] Further studies to validate the use

of polycarboxylic organic radicals as building blocks for obtaining pure organic magnetic nanoporous molecular materials are currently underway.

Supporting Information Available: Crystallographic data, thermal gravimetric analysis, and XRPD patterns and magnetic properties of POROF-1 (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) *Supramolecular Chemistry*, Lehn, J. M., Ed., VCH: Weinheim, Germany, 1995. (b) Aakeröy, C. B.; Beatty, A. M.; Helfrich, B. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3240.
(2) For recent examples on metal-organic open frameworks, see: (a) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keefe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021. (b) Noro, S. I.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem., Int. Ed.* **2000**, *12*, 2081.
(3) For recent examples on magnetic metal-organic open frameworks, see: (a) Maspoch, D.; Ruiz-Molina, D.; Domingo, N.; Wurst, K.; Cavallini, M.; Biscarini, F.; Tejada, J.; Rovira, C.; Veciana, J. *Nat. Mater.* **2003**, *2*, 195. (b) Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 12096. (c) Barthelet, K.; Marrot, J.; Riou, D.; Férey, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 281. (d) Moulton, B.; Lu, J.; Hajndl, R.; Hariharan, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2821. (e) Price, D. J.; Tripp, S.; Powell, A. K.; Wood, P. T. *Chem.−Eur. J.* **2001**, *7*, 200. (f) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148.
(4) For recent reviews on organic nanoporous open-framework materials, see: (a) Nangia, A. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 115. (b) Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3052. (c) Langley, P. J.; Hulliger, J. *Chem. Soc. Rev.* **1999**, *28*, 279. (d) Desiraju, G. R. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 451.
(5) For recent examples on organic open-framework materials, see: (a) Miyahara, Y.; Abe, K.; Inazu, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 3020. (b) Bong, D. T.; Ghadiri, M. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2163. (c) Sada, K.; Sugahara, M.; Kato, K.; Miyata, M. *J. Am. Chem. Soc.* **2001**, *123*, 4386. (d) Müller, T.; Hulliger, J.; Seichter, W.; Weber, E.; Weber, T.; Wübbenhorst, M. *Chem.−Eur. J.* **2000**, *6*, 54. (e) Kobayashi, K.; Shirasaka, T.; Sato, A.; Horst, E.; Furukawa, N. *Angew. Chem., Int. Ed.* **1999**, *38*, 3483. (f) Biradha, K.; Dennis, D.; MacKinnon, V. A.; Sharma, C. V. K.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 11894. (g) Russel, V. C.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575.
(6) For recent reviews on magnetism of organic materials, see: (a) *Magnetic Properties of Organic Materials*, Lahti, P. M., Ed.; Marcel Dekker: New York, 1999. (b) Veciana, J.; Iwamura, H. *MRS Bull.* **2000**, *25*, 41. (c) *Magnetism: Molecules to Materials*; Miller, J. S., Drillon, M., Eds.; Wiley-VCS: Weinheim, Germany, 2001; Vols 1−3.
(7) Domingo, V. M.; Castañer, J.; Riera, J.; Labarta, A. *J. Org. Chem.* **1994**, *59*, 2604.
(8) Maspoch, D.; Gerbier, P.; Catala, L.; Vidal-Gancedo, J.; Wurst, K.; Rovira, C.; Veciana, J. *Chem.−Eur. J.* **2002**, *8*, 3635.
(9) Ballester, M.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O. *Synthesis* **1986**, 64.
(10) X-ray structure analysis. Crystal data: $C_{21}H_2Cl_{13}O_4 \cdot C_6H_{14}$, trigonal, space group R-3, $a = 31.4651(6)$ Å, $b = 31.4651(7)$ Å, $c = 18.8447(7)$ Å, $V = 16157.6(8)$ Å^3, $Z = 18$, $T = 233(2)$ K, λ-Mo Kα = 0.7173 Å, $F(000) = 7758$, $\mu = 1.032$ mm^{-1}, ρcalcd = 1.601 g/cm^3, red prism 0.15 × 0.08 × 0.08 mm^3. Data collection: Nonius Kappa CCD, 19 275 measured reflections were corrected with the program SCALEPACK. Structure solution and refinement: anisotropic refinement on F2 (SHELXL 97), hydrogens of the acid groups were refined with isotropic parameters; R-values for 421 parameters and 2592 observed reflections [$I > 2\sigma(I)$] R1 = 0.0461 and wR2 = 0.1183.
(11) Similar hydrogen-bonded dimers were observed in the monocarboxylic perchlorotriphenylmethyl radical; see ref 7. In this case, bond distance and angle are 1.955 Å and 144°, respectively.
(12) (a) Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222. (b) Desiraju, G. R.; Parthasarathy, R. *J. Am. Chem. Soc.* **1989**, *111*, 8725.
(13) Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 1998.
(14) Thermal gravimetric analyses were done with as-synthesized microcrystals of radical **1** which were heated to 350 °C at a constant rate of 3 °C/min.
(15) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37.
(16) There are only four examples of pure organic open-framework materials remaining structurally ordered when the guest molecules are removed: (a) Sozzani, P.; Comotti, A.; Simonutti, R.; Meersman, T.; Logan, J. W. *Angew. Chem., Int. Ed.* **2002**, *39*, 2695. (b) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737. (c) Ung, A. T.; Gizachew, D.; Bishop, R.; Scudder, M. L.; Dance, I. G.; Craig, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 8745. (d) Ibragimov, B. T.; Talipov, S. A. *J. Inclusion Phenom. Mol. Recognit.* **1994**, *17*, 317.
(17) There is a previous example of a metal-organic open-framework material suitable for ship-in-bottle synthesis: Pan, L.; Liu, H.; Lei, X.; Huang, X.; Olson, D. H.; Turro, N. J.; Li, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 542.

JA038988V