One teflon®-like channelled nanoporous polymer with a chiral and new uninodal 4-connected net: sorption and catalytic properties†‡

Angeles Monge,* Natalia Snejko, Enrique Gutiérrez-Puebla, Manuela Medina, Concepción Cascales, Caridad Ruiz-Valero, Marta Iglesias and Berta Gómez-Lor

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$Zn(C_{17}H_8F_6O_4)$ is the first example of a fluoro-lined nanotube organo-inorganic 3D polymeric chiral structure, which possesses two different types of isolated channels, one of them being laid out with a double spiral of CF_3-groups from the ligand molecule; the structure is a new uninodal 4-connected net that only exists when bent ligands connect the centres, and the compound exhibits selective sorption and catalytic chiral recognition properties.

Presently, the design and synthesis of new materials "on demand" is becoming increasingly important. In this sense, new outstanding possibilities are presented in the area of the synthesis of organo-inorganic polymeric materials, where a particularly promising systematic method to achieving the desired design of a material is a building-block approach.[1] It seems also to be very advantageous to consider the chemical properties of the connector and its influence on the structure and properties of the resulting material, and to choose a certain connector contemplating not only its acidic or coordinative capability and geometric shape but, specifically, the composition and shape of the intermediate part of the ligand. Also, the trend towards the application of single enantiomers of chiral compounds is undoubtedly increasing. This is especially the case for pharmaceuticals but also for agrochemicals, flavours and fragrances. In this regard, chiral porous materials have aroused great interest since they are very attractive candidates for use in enantioselective heterogeneous catalysis and separations. Moreover, heterogeneous catalysts have the inherent advantage of being easily separated.[2] Here we present the first example of a fluoro-lined nanotube organo-inorganic 3D polymeric chiral structure, which possesses two different types of isolated parallel channels, one of them being laid out with a double spiral of CF_3-groups from the ligand molecule. The obtained polymer exhibits sorption and chiral recognition properties.

The hydrothermal reaction§ of zinc(II) salt with 4,4′-(hexafluoroisopropylidene)bis(benzoic acid) ($C_{17}H_{10}F_6O_4$, H_2L) in water led to the formation of colorless crystals. Upon determining the crystal structure,¶ the composition was found to be $[Zn(C_{17}H_8F_6O_4)]$ (**1**). The Zn atom is situated on a two-fold axis and the ($C_{17}H_8F_6O_4$) ligand also has imposed crystallographic 2-fold symmetry, thus, the asymmetric unit comprises one half of the formula. The metal centre is surrounded by four oxygen atoms from different ligand molecules in tetrahedral coordination, with two distances of 1.922(1) and two of 1.925(1) Å. Carboxylate groups are bonding the Zn atoms related by the 6_4 axis to give two different helical chains of tetrahedra along the *c* direction (Fig. 1). The complete anion L^{2-} links both of these chains giving rise to a 3D channelled structure with two kinds of very different parallel tunnels. Due to the geometry of the ligand, its central atom being an sp^3 carbon, one of the channels is square shaped with the fluorine atoms pointing outside of them and dimensions of 8 Å × 8 Å. Due to the packing of these squared channels around the 6_4 axis, other channels with hexagonal shapes and a diameter of ~10 Å (interatomic distances) appear along the *c* direction, too. The walls of these latter channels are formed by one double helix of CF_3-groups giving rise to fluoro-lined teflon®-like channels (Fig. 1). The result is a structure with separated parallel hydrophilic and hydrophobic channels (Fig. 2, left). The crystal structure has a fascinating 3D polymeric architecture. It is a chiral and new uninodal 4-connected net that exists only if there are bent ligands connecting the centres. The final topology[3] is a self-penetrated chiral net with maximum symmetry in $P6_422$, and characterized by the Schlafli symbol: $\{6^5.8\}$, vertex symbol with circuits: [6.6.6.6.6(2).8(13)], with rings: [6.6.6.6.6(2).8(11)]. The ideal net presents edges crossing at 1/2, 1/2, 2/3, that are avoided in the real one due to the flexible ligands that bend over (Fig. 3). Topological classification was done with TOPOS[3] and optimized with SYSTRE[3].

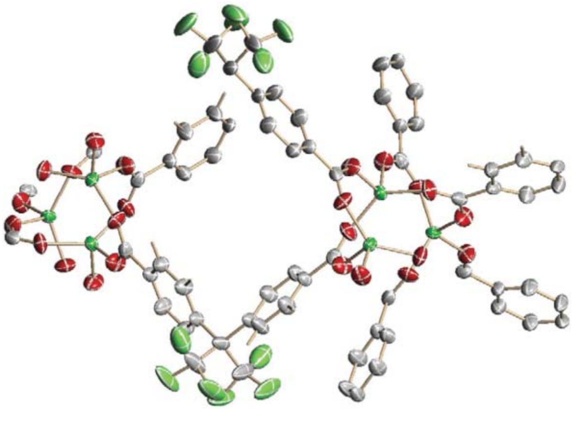

Fig. 1 ORTEP drawing of $Zn(C_{17}H_8F_6O_4)$, including more than one asymmetric unit. Ellipsoids probability 50%. Red ellipsoids: O; small green: Zn; large green: F and gray: C.

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† Electronic supplementary information (ESI) available: nitrogen adsorption and desorption isotherms of **1** at 110 °C, and TGA curves for compounds **1** and **2** up to 800 °C, and complete topological classification. See http://www.rsc.org/suppdata/cc/b4/b415960h/

‡ Dedicated to Professor Josû Elguero on the occasion of his 70th birthday.

*amonge@icmm.csic.es

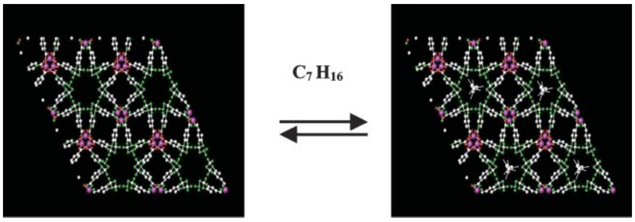

Fig. 2 View of the $Zn(C_{17}H_8F_6O_4)$ framework, left, with both hydrophilic and hydrophobic channels empty, and right, after the treatment with hydrocarbon.

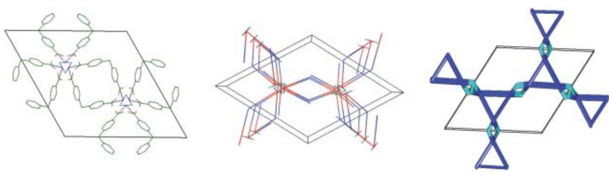

Fig. 3 Real (left), schematic (middle), and ideal (right) $\{6^5.8\}$ topology of the $Zn(C_{17}H_8F_6O_4)$ framework. The structure is simplified by putting a centroid between two Zn in light blue, oxygen connections in red and ligands in dark blue.

The TGA/DTA experiments in N_2 flow (50 ml min^{-1}) reveal that **1** is a thermally stable material: after losing half a molecule of absorbed water from the hydrophilic channel, the framework is stable up to 430 °C. A sharp endothermic loss between 440 and 490 °C corresponds to its total decomposition.

In order to test absorption properties, **1** (after removing the absorbed water) was treated with linear hydrocarbons (140 °C) and, in the case of heptane, its structure was re-determined in the same $P6_422$ space group. Along the hexagonal hydrophobic channels, a continuum of electron density, that was not observed in the structure of **1**, appeared systematically in all the studied crystals. With the purpose of clarifying, as much as possible, this point, the symmetry was lowed to $P3_1$ and $P2$. The electron density found along the fluoro-lined hexagonal channels, with positional disorder due to the 3_1 symmetry, was assigned to the heptane molecules in a ratio of 0.25 per formula weight $[Zn(C_{17}H_8F_6O_4)]\cdot 0{,}25(C_7H_{16})$(**2**) (Fig. 2, right). As the continuous chain of carbon atoms is generated by symmetry with only two maxima of electron density and in order to rule out any false interpretation, the structure of **2** was also solved in the $P2$ space group of the monoclinic system. Although some positional disorder still remained, a row of maxima of electron density at distances and angles assignable to sp^3 atoms was also found in the Fourier difference map. The hydrophilic channels remained empty. Thermal analysis of **2** has confirmed the composition of the compound: a weight loss that appears between 120 and 150 °C corresponds to a loss of 0.25 molecules of C_7H_{16} (calculated 5.20%, observed 5.3%). The second weight loss, beginning at ~440 °C, corresponds to complete pyrolysis of the organic ligand (calculated 77.85%, observed 78.0%). The presence of the hydrocarbon inside the material was also confirmed by gas chromatography analysis.‖ With the purpose of testing the purity of the samples before and after the treatment with heptane and following its evolution, simulations of the X-ray powder patterns with the coordinates obtained from single-crystal structures, without and with hydrocarbon in the channels, were calculated.

The experiments have shown that the process of sorption–desorption can be repeated several times with the structure of **1** remaining intact. The reversibility and reproducibility of the temperature-controlled (140 °C) process of insertion–extraction of heptane in the hexagonal hydrophobic channels is clearly displayed in Fig. 4, in which the most noticeable changes affect the relative intensities of *hkl* reflections with $l = 0$, that correspond to the plane

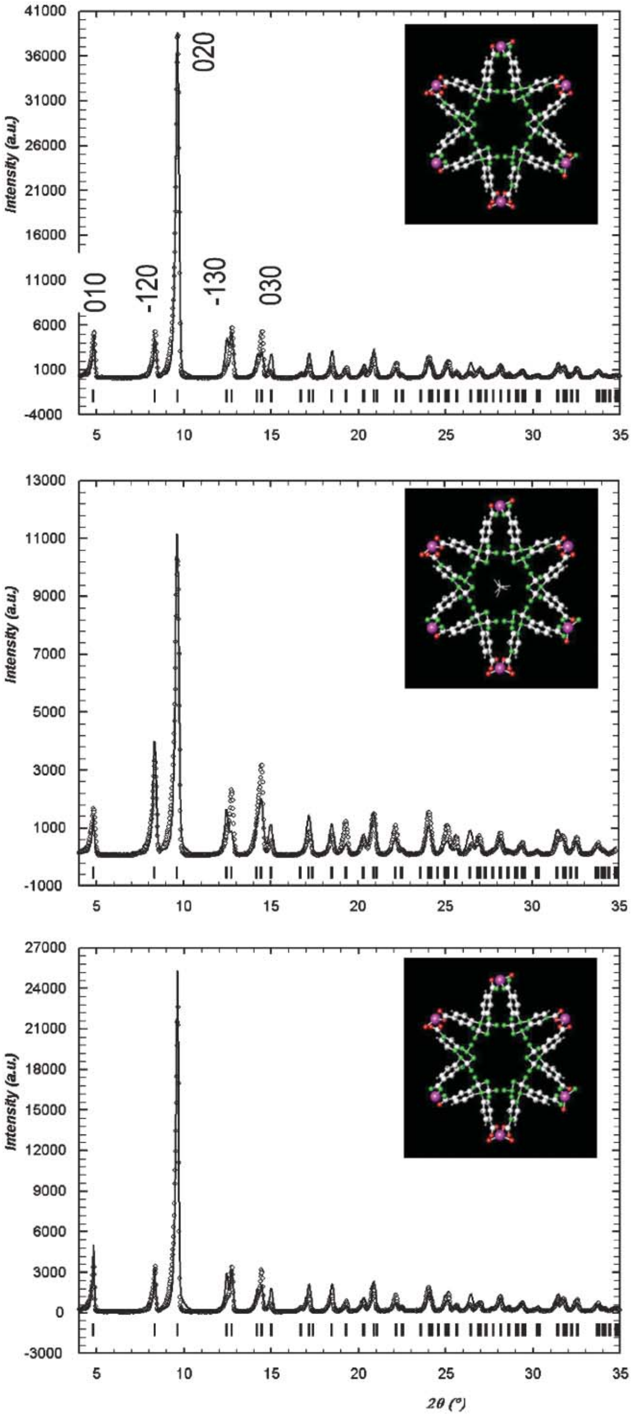

Fig. 4 Evolution of Rietveld X-ray powder profile diagrams through the insertion–extraction of hydrocarbon into the hydrophobic channels: Top, as initially prepared; middle after the treatment with n-heptane for 48 h at 140 °C; bottom, the same sample, after extraction of n-heptane.

perpendicular to the structure's channels. It is noteworthy there is a decrease in the intensity of the (020) reflection and thus a change in the intensity ratio between this reflection and the ($\bar{1}$20) that goes from ~8 in the case of **1** to ~2.7 in that of **2**. Furthermore, it can be seen that the final product fully recovers the characteristic X-ray diffraction pattern of the initial framework.

The surface area of **1** was evaluated by using nitrogen adsorption–desorption measurements on a Micromeritics ASAP 2020 unit. The nitrogen adsorption–desorption isotherm was measured after degassing the sample under vacuum for 3 h at 110 °C. For a monolayer coverage of N_2 we estimate the specific surface area of **1** as 288.9(2) m^2g^{-1} based on the method of Langmuir.

As the current material has a chiral structure and shows considerably high thermal stability, its ability to show chiral recognition was studied on the acetalization of (*R,S*)-2- phenylpropionaldehyde as a test reaction.** This reaction with trimethylorthoformate using **1** as a heterogeneous acid catalyst proceeded with high conversion and moderate enantioselectivity under mild conditions and the corresponding acetals were obtained in a 60% yield after 24 h. The structure of the new material favours the preferable formation of one of the enantiomeric acetals (enantiomeric excess: 30%). Although the material should be racemic existing as a 50% mixture of crystals with Flack parameters of 0 and 1, the above indicated enantiomeric excesses made us determine the crystal structure of 10 randomly chosen crystals of **1**. All of them, being the same enantiomer with the $P6_422$ space group and an average Flack factor number of 0.01(1), indicate that, statistically speaking, the proportion of enantiomers is far from being 50%.

Recently, theoretical and experimental studies[4] on the breaking of chiral symmetry during crystallization, define its mechanism as an advection-mediated nonlinear autocatalytic process. Although it is clear that we have this phenomenon in our hydrothermal synthesis, this is a surprising preliminary result, which is the basis for some of our continued work.

In conclusion, by searching the cooperative effect of both metal and organic species, a multifunctional material has been obtained: the first example of a fluoro-lined channelled compound with selective sorption and catalytic chiral recognition properties. We are currently actively working on the study of selective sorption into the two kinds of channels of **1** depending on the polarity of the absorbed molecules.

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Angeles Monge,* Natalia Snejko, Enrique Gutiérrez-Puebla,
Manuela Medina, Concepción Cascales, Caridad Ruiz-Valero,
Marta Iglesias and Berta Gómez-Lor
Instituto de Ciencia de Materiales de Madrid (CSIC) Cantoblanco,
28049 Madrid, Spain. E-mail: amonge@icmm.csic.es;
Fax: +34 913720623; Tel: +34 913349025

Notes and references

§ Reaction of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.220 g, 1 mmol) with H_2L (0.392 g, 1 mmol) and deionized water (10 mL) in a stainless steel autoclave (PARR, USA) at 170 °C for 72 h resulted in prismatic colorless crystals of **1**.

¶ Crystal data of **1**: $Zn(C_{17}H_8F_6O_4)$, M = 455.6, hexagonal; space group: $P6_422$; a = 21.232(8), c = 7.708(0) Å; V = 3009.4(5) Å^3; Z = 6; D_c = 1.508 mg m^{-3}; μ(Mo-Kα) = 1.296 mm^{-1}; No. of independent reflections = 3107; R_1 = 0.030 for $I > 2\sigma(I)$ reflections. Software for the SMART System V5.04 and SHELXTL V 5.1, Bruker-Siemens Analytical X-ray Instrument Inc., Madison, WI, 1998. CCDC 226851. Determination of the crystal structure in $P3_1$ is also available: CCDC 253973. See http://www.rsc.org/suppdata/cc/b4/b415960h/ for crystallographic data in .cif or other electronic format.

|| Gas chromatography analysis (GC-MS) was performed using a Hewlett-Packard 5890 II with a flame ionization detector in a cross-linked methylsilicone column (mixture of methylsilicone (OV-1701) and permethylcyclodextrine as stationary phase). To confirm the presence of n-heptane in the material, it was heated at 105 °C for 20 h in ethanol. Afterwards the liquid was analyzed by GC-MS and confirmed the presence of the hydrocarbon.

** Catalysis: A solution of (*R,S*)-2-phenylpropionaldehyde (1 mmol) and TMOF (5 mmol) in CCl_4 (5 ml) was added onto the catalyst (20 mg). The resulting samples were taken at regular times and after filtration they were analysed. Chemical yields and enantiomeric excesses of the acetals were measured by GC with a chiral glass capillary column with a 15 : 85 mixture of methylsilicone (OV-1701) and methylsilicone-heptakis[2,3-dipentyl-6-(*t*-butyldimethylsilyl)]-β-cyclodextrin as stationary phase.

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