Hydrogen-bonded self-assemblies in a polychlorotriphenylmethyl radical derivative substituted with six *meta*-carboxylic acid groups†

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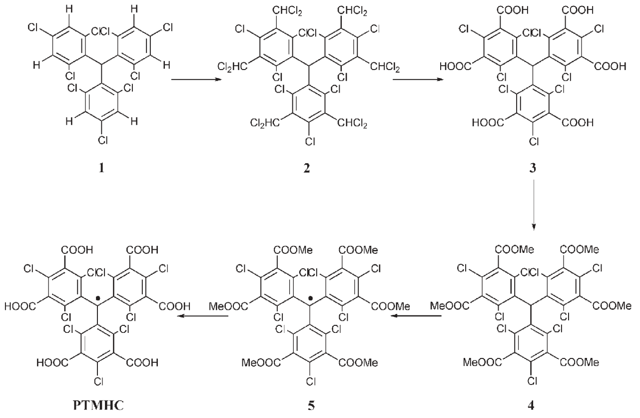
The synthesis, self assembly and magnetic properties of a polychlorotriphenylmethyl radical, substituted with six *meta*-carboxylic groups, are reported showing that radical–radical hydrogen bonds in the solid state yield to very weak intermolecular ferromagnetic interactions.

Over the last few years, there has been a considerable interest in the design of purely organic magnetic materials. In order to fulfil one of the major requirements to obtain magnetic properties, that is to control the structural arrangement of the organic spin-bearing units in the solid state, crystal engineering through hydrogen bonds has been proved to be a powerful methodology.[1] Materials designed following this approach are mainly based on the use of stable nitroxide radical derivatives that are able to act as hydrogen bond acceptors. Very interesting results have been obtained when one or several hydrogen-bond donor groups were introduced directly on the spin bearing molecule.[2] Among them, carboxylic groups are particularly appealing since they possess both hydrogen-bond donor and acceptor character, duality that allows them to add to the expected radical–acid interaction the possibility to form various supramolecular motifs.[3] In a recent article, we have shown that the formation of acid dimers was responsible of the presence of hydrogen-bond mediated weak ferromagnetic interactions between two polychlorotriphenylmethyl radicals substituted in *para*-position by a carboxylic group (PTMA).[4] In order to extend the structural and the magnetic dimensionality in such PTM-based materials, we have designed and studied the self assembly of PTM radicals substituted with two (PTMDC) and three (PTMTC) *para*-carboxylic acid groups. In both cases, carboxylic groups are involved in the formation of hydrogen-bonded rings yielding two dimensional hydrogen-bonded layers. Weak antiferromagnetic interactions are observed in the resulting open-framework of PTMDC, while the self assembly of PTMTC molecules led to the first example of a nanoporous purely organic magnetic material (POROF2), exhibiting a high thermal stability and a long range ferromagnetic ordering.[5] Keeping in mind the remarkable structural and magnetic properties of POROF2, and with the idea of continuing to increase further both structural and magnetic dimensionalities, we report herein for the first time, the synthesis, X-ray structures and magnetic properties of a new PTM derivative (PTMHC), that is one of the rare examples of an organic hexacarboxylic acid ever described, and to the best of our knowledge, the first example with electronic open-shell characteristics.[6] Compared to PTMDC and PTMTC, the increase of the carboxylic/chlorine substituent ratio and the change in the substitution pattern (*meta vs. para*) make this molecule a promising candidate for obtaining hydrogen-bonded purely organic magnetic material.

PTMHC was prepared following an original six step procedure, starting from compound **1** (Scheme 1). Dichloromethyl groups were introduced by reacting **1** with chloroform following a Friedel–Craft reaction using $AlCl_3$ as a catalyst (70%). These groups were converted to carboxylic ones by a hydrolysis–oxidation reaction using 20% oleum (75%). Treatment with diazomethane yielded the hexamethylester **4** (80%), that was then converted to the corresponding hexamethylester radical **5** (80%) in a one pot reaction using subsequently tetrabutylammonium hydroxide, as a strong base, and *para*-chloranil, as oxidant reagent that converts the carbanion to radical. Removal of the methyl ester groups was finally performed with concentrated sulfuric acid, a methodology that allows PTMHC to be obtained in an excellent yield (90%).

Yellow prismatic single-crystals, suitable for X-ray diffraction, of the solvate [PTMHC·$(THF)_6$] were grown from a mixture of THF and *n*-hexane. The radical crystallizes in a trigonal *R*-3 space group with six molecules of PTMHC and thirtysix molecules of



Scheme 1

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† Electronic supplementary information (ESI) available: crystallographic data of [PTMHC·$(THF)_6$] and [PTMHC·$(Et_2O)_3$] solvates and crystal structure of diamagnetic [**3**·$(THF)_3$] solvate (PDF, CIF). See http://dx.doi.org/10.1039/b508952b

THF packed in the unit cell showing a structural disorder.‡ The high molecular C_3 symmetry is reflected by the presence of a crystallographic three-fold rotation axis that passes through the central carbon atom (C3) of the molecule that adopts a three-bladed propeller-like conformation. Thus, the three polychlorinated aromatic rings are symmetry related. Owing to the steric hindrance of the chlorine atoms in *ortho* positions with respect the carboxylic groups, these groups are twisted by 84° and 87° with respect to the plane of the phenyl group to which they are bonded, with the two acidic hydrogen atoms lying above and below the plane of the plane of the phenyl ring, respectively (Fig. 1).

As occurs with other polycarboxylic acid derivatives,[7] the PTMHC radical forms hydrogen bonds with disordered THF molecules. However, the [PTMHC·(THF)$_6$] solvate presents the particularity that all its six carboxylic acid groups are involved in the formation of hydrogen bonds with one THF. Consequently, the resulting "supramolecular radical–THF clusters" (Fig. 2a) avoid direct hydrogen bonds between radical molecules pushing them far away. Thus, the shortest C3···C3 distance, where the most part of the spin density is localized, is of 7.51Å. Close packing of the such supramolecular radical–THF clusters take place through several weak Csp^3–H···O hydrogen bonds between neighboring THF molecules leading to a PTMHC-templated honeycomb arrangement of the solvent molecules (Fig. 2b).[8] Interactions between solvent molecules are not strong enough to avoid the immediate loss of crystallinity that is observed when the crystals are removed from the mother liquor, as confirmed by XRPD experiments.

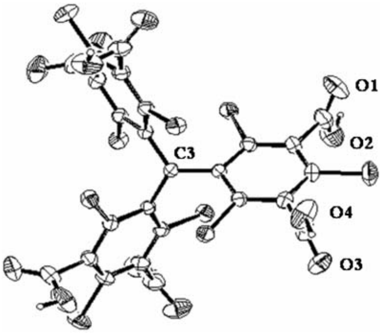

Fig. 1 ORTEP view of the [PTMHC·(THF)$_6$] solvate (thermal ellipsoids set at 20% of probability; THF molecules are omitted for clarity).

In order to increase the structural dimensionality and to disfavour the formation of hydrogen bonds between PTMHC and solvent molecules, several attempts of crystallisation were performed using various solvent mixtures and crystallisation techniques. All these tries failed, mainly because of the lack of solubility of the highly polar radical PTMHC in non oxygenated solvents. We finally succeed in obtaining a new solvate, [PTMHC·(Et$_2$O)$_3$], as orange prismatic crystals, using a mixture of diethyl ether and *n*-hexane. Like in the previous solvate, the radical crystallizes in a trigonal *R*-3 space group with six molecules of PTMHC and eighteen molecules of solvent in the unit cell.§ This solvate also exhibits a three-fold rotation axis passing through the central carbon atom of the radical molecule with dihedral angles between the phenyl rings and the carboxylic groups of 83° and 85°, respectively.

The most striking difference of the [PTMHC·(Et$_2$O)$_3$] solvate with respect to that with THF is the presence of several direct hydrogen bonds between PTMHC molecules that results in the formation of two-dimensional hydrogen bonded corrugated layers in the *ab* plane. The main repeating unit consists of an unusual $R_6^6(48)$ hydrogen-bonded motif formed by six PTMHC molecules with alternating plus and minus helicities in their three-bladed propeller-like conformations (Fig. 3a). In this motif, each radical is hydrogen bonded to two neighbouring radicals through one carboxylic group, with a bond length of 1.86Å (O1···H–O4) and a bond angle of 164° (O1–H–O4). The other carboxylic group localized in the same phenyl ring is involved in one hydrogen bond with a diethyl ether molecule, with a bond length of 1.83Å (O5···H–O2) and a bond angle of 153° (O5–H–02).

Since every radical unit contains six carboxylic groups (three are involved in hydrogen bonds with PTMHC molecules and three in hydrogen bonds with solvent molecules) each radical molecule participates in the construction of three identical hexameric units resulting in open polar windows that propagate along the *ab* plane (Fig. 3b). Three diethyl ether molecules are localized on each side of each polar window contributing to isolate one layer from the two neighbouring ones (the shortest C3···C3 interlayer distance is

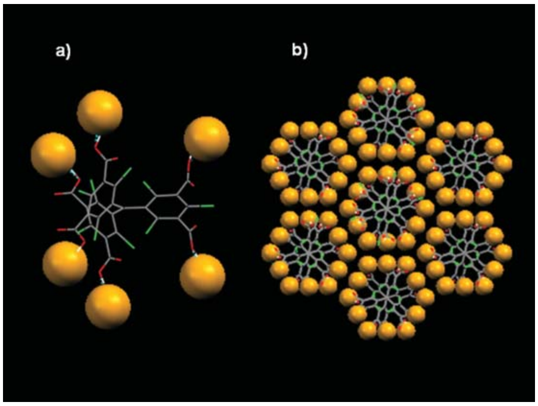

Fig. 2 Crystal structure of the solvate [PTMHC·(THF)$_6$]. a) View of the supramolecular PTMHC·(THF)$_6$ cluster. View, along the *c* axis of PTMHC-templated honeycomb arrangement of solvent THF molecules (THF molecules are represented by orange spheres for clarity).

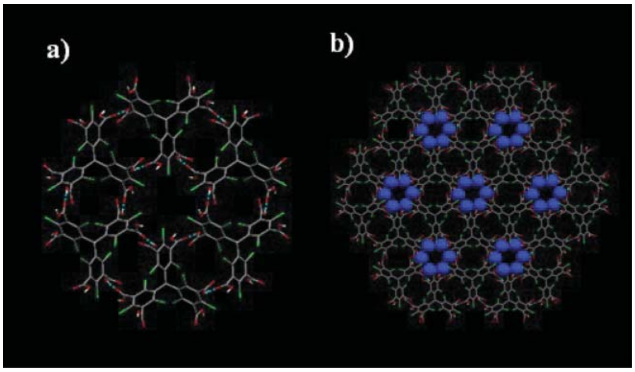

Fig. 3 Crystal structure of solvate [PTMHC·(Et$_2$O)$_3$]. a) $R_6^6(48)$ hexamer, surrounded by six secondary $R_2^2(24)$ dimers, and b) Two dimensional hydrogen-bonded layer, with Et$_2$O molecules lying above and below the polar windows originated by the free carboxylic acid groups (Et$_2$O molecules are represented as blue spheres for clarity).

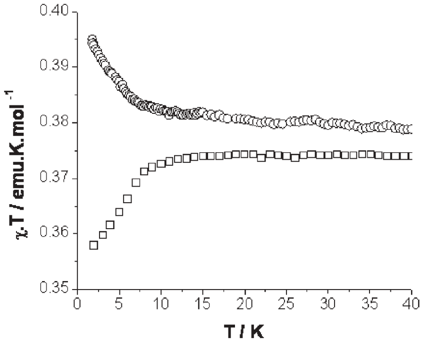

Fig. 4 Magnetic characterization of solvates [PTMHC·(THF)$_6$] (□) and [PTMHC·(Et$_2$O)$_3$] (○) in the presence of their mother liquors. Product of the magnetic susceptibility with the temperature as a function of the temperature in the lower limit.

6.89Å). Interdigitation of diethyl ether molecules, promoted by weak PTMHC–Et$_2$O O1···H–Csp^3 hydrogen bonds (2.71Å, 166°), belonging to neighbouring layers avoid interlayer chlorine–chlorine short contacts and/or hydrogen bonding between PTMHC molecules, leading to an ABC arrangement of the layers along the *c* axis (Fig. 3c). As in the first THF solvate, crystallinity is immediately lost when the crystals are removed from their mother liquor.

Variable temperature magnetic susceptibility data for as-synthesized crystalline samples of both solvates were obtained on a SQUID susceptometer, under a temperature range of 2–300 K, in the presence of their mother liquors. In both cases, a paramagnetic behavior was observed in the 20–300 K temperature range, with χ.T product values that fully agree with the theoretically value of 0.375 emu.K.mol^{-1}, expected for uncorrelated spins (S = ½) with g = 2.0. Main differences were observed below 20 K. For [PTMHC·(THF)$_6$], the χ.T value smoothly decreases upon decreasing temperature until a value of 0.358 emu.K.mol^{-1} at 2 K (Fig. 4)., consistently with the presence of very weak intermolecular antiferromagnetic interactions (through space), in agreement with the lack of direct hydrogen bonds between PTMHC radicals in that solvate. For [PTMHC·(Et$_2$O)$_3$], the χ.T value smoothly increases upon decreasing temperature to reach a value of 0.395 emu.K.mol^{-1} at 1.8 K (Fig. 4). This result is in agreement with the presence of very weak intermolecular ferromagnetic interactions, which are ascribed to the presence of direct hydrogen bonds between radical molecules in this crystal structure.[9]

In summary, we have described the synthesis of a new PTM radical derivative that is the first example of hexacarboxylic acid with an electronic open-shell characteristic. Depending on the solvent used, the self assembly of PTMHC molecules yield to isolated radicals surrounded by THF molecules or to radical hydrogen-bonded layers which are isolated by diethyl ether layers. While weak antiferromagnetic interactions are obtained in the first case, the presence of hydrogen bonds in the second one yields very weak intermolecular ferromagnetic interactions in the solid state. Taking into account the structural resemblance between the [PTMHC·(Et$_2$O)$_3$] solvate and POROF-2,[4b] we can also expect a ferromagnetic ordering at lower temperatures in the order of few millikelvin. Further work to confirm this behaviour is undergoing together with new crystallisation tries in order to increase both structural and magnetic dimensionalities.

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Notes and references

‡ *Crystal data* for α-PTMHC [(C$_{25}$H$_6$Cl$_9$O$_{12}$·6(C$_4$H$_8$O)]: trigonal, *R*-3, a = 24.9133(6), b = 24.9133(8), c = 15.0874(8) Å, $\alpha = \beta = 90$, $\gamma = 120°$, V = 8109.7(5) Å^3, Z = 6, λ(Mo–Kα) = 0.71073 Å, 13298 reflections collected, 1761 independent reflections with $I > 2\sigma(I)$, $R1$ = 0.0678, $wR2$ = 0.1884, GOF = 1.044. Both kind of THF-molecule present disorder. For C10–C13–O5, the disorder was not solved. For C14–C17–06 a 1 : 1 disorder model with partial overlying position (C15 = C15A and C17 = C17A) and bond restraints was used. Hydrogen atoms of both THF-molecules were neither found nor calculated. CCDC 276959. See http://dx.doi.org/10.1039/b508952b for crystallographic data in CIF or other electronic format.

§ *Crystal data* for β-PTMHC [(C$_{25}$H$_6$Cl$_9$O$_{12}$·3(C$_4$H$_{10}$O)]: trigonal, *R*-3, a = 15.6488(8), b = 15.6448(6), c = 33.8402(7) Å, $\alpha = \beta = 90$, $\gamma = 120°$, V = 7.1767(5) Å^3, Z = 6, λ(Mo–Kα) = 0.71073 Å, 12097 reflections collected, 1880 independent reflections with $I > 2\sigma$ (I), $R1$ = 0.0588, $wR2$ = 0.1624, GOF = 1.037. Data were measured on a Nonius KappaCCD. Structure solutions were done using SHELXS86 and refinements with SHELXL97. CCDC 276958. See http://dx.doi.org/10.1039/b508952b for crystallographic data in CIF or other electronic format.

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8 A structure presenting comparable cell parameters and without disorder for THF molecules has been obtained for compound **3** ([**3**·(THF)$_6$]. See Electronic Supplementary Information.
9 A similar behaviour was observed for crystalline α and β-phases of PTMA. See Ref. 4.