

**SELF-ASSEMBLY OF PTM RADICALS:
FROM WEAK FERROMAGNETIC INTERACTIONS TO ROBUST AND
NANOPOROUS PURELY ORGANIC MAGNETS.**

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Control of molecular organization is an essential aspect for the development of purely organic solids with remarkable physical or chemical properties and characteristics. Whereas supramolecular chemistry has allowed the access to numerous examples of molecular organization in one and two dimensions, that in the third dimension is still a challenging proposition. The fairly limited number of three-dimensional purely organic assemblies previously reported may be explained by the difficulty to synthesize well-programmed molecular building blocks, with respect to the position of the noncovalent interactive sites, molecular shape, rigidity and amphiphilicity, and by the complexity to get *in fine* the inquired sophisticated self-assemblies through non-covalent interactions.

Such synthetic and structural considerations are even much more difficult to solve when an open-shell character is wanted for the tecton, and when its self-assembly is expected to yield remarkable magnetic properties for the resulting pure organic material. Open-shell tectons used in this field are mainly based on α -nitronyl nitroxide, α -imino nitroxide or *tert*-butyl nitroxide derivatives because of their high stability and the ability of their nitroxide groups to act as acceptors of hydrogen bonds. Thus, the self-assembly of such nitroxide based building-blocks substituted with one or several hydrogen bond donors such as phenol, boronic acid, imidazole, benzimidazole, triazole, uracil, pyrazole, phenyl acetylene or benzoic acid has been extensively studied. The resulting synthons, which are involving the nitroxide groups, allow both structural control and transmission of magnetic interactions between the radical molecules through strong (OH \cdots O) or weak (CH₃ \cdots O) hydrogen bonds. This approach shows that with the design of radical molecules that bear hydrogen-bond donor and acceptor groups, the structural dimensionality of the material may be controlled to some extent, and, hence, also the propagation of the magnetic interactions through the supramolecular structure [1]. However, the difficulty lies in determining the strength and the nature of the magnetic interactions through the supramolecular pathway, since additional undesired intermolecular through space interactions are often present in the solid state.

Five years ago, we have initiated an approach based on the synthesis and study of thermally and chemically stable perchlorotriphenylmethyl (PTM) radicals functionalized with carboxylic groups (Fig. 1). For structural considerations, the rigidity of this family of open-shell molecules was expected to prevent close packing of molecular units and to form robust networks. PTM were also chosen for their bulkiness with the objective to minimize undesired through space magnetic interactions in the solid state, while the carboxylic groups were introduced to control the structural arrangement and to allow the transmission of the magnetic interactions between the paramagnetic units [2].

Herein we present the most striking results we obtained by studying the self-assembly of PTM radicals substituted by one, two, three and six carboxylic acid functions [3-6]. The remarkable properties and characteristics of the resulting purely organic magnetic materials will be described in detail (Fig. 2).

References:

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Figures:

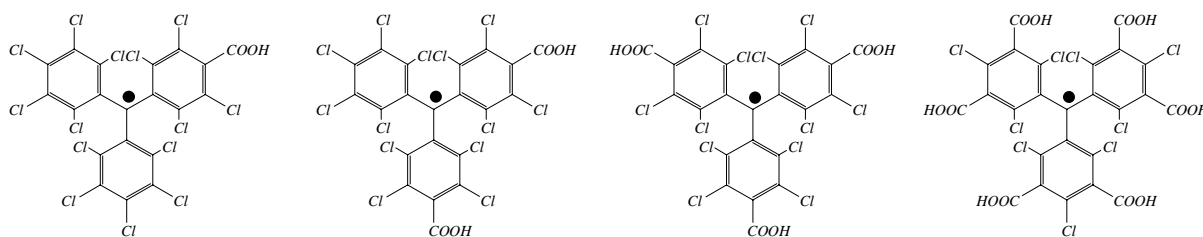


Figure 1. PTM radicals studied

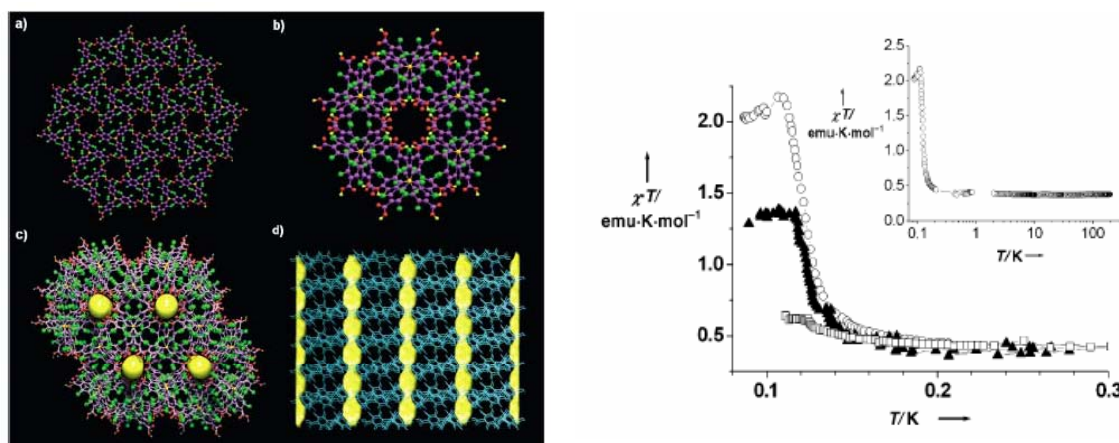


Figure 2. POROF-2: a robust and nanoporous organic magnet resulting from the self assembly of a PTM radical substituted by 3 carboxylic groups.