Supramolecular Architectures Formed by Hierarchical Self-Assembled PTM radicals

Francisco Vera,[a] Marta Mas-Torrent,[a] Concepció Rovira,[a] Jaume Veciana,[a] Yanfei Shen,[b] Takashi Nakanishi[b]
[a]Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitary de Bellaterra, 08193, Barcelona, Spain; [b]Max Planck Institute of Interfaces and Colloids, 14424, Potsdam, Germany.

fvera@icmab.es

The use of weak intermolecular forces can give rise to supramolecular architectures various morphologies and properties with potential applications in chemistry, materials science and nanotechnology.[1] Nowadays, the molecular self-assembly is a well-known field where many research efforts have been made,[2] but the self-organization of nano- and mesoscopic objects or systems from discrete molecules is not very predictable.

Polychlorotriphenylmethyl (PTM) radicals can be included in the molecular skeleton of the molecules in order to give different properties to the self-organized system. PTM radicals present a magnetic dipole moment and electrochemical activity, and the functionalization of these molecules have permitted to use these radicals to prepare new molecular materials that show specific properties, like in molecular switches in solution[3a] and on surface[3b], ONL systems,[4] porous magnets[5] and systems that shows intramolecular electronic transference phenomena.[6]

In previous works, PTM derivatives were covalently anchored to different surfaces by formation of self-assembled monolayers (SAMs).[3b,7] Another approach that has been employed is the study of the physisorption of a PTM-radical derivatives on HOPG. The functionalization of these PTMs consists in some attached alkyloxy chains (three, or two chains in metha or ortho positions) that dramatically changes the thermal properties of the molecules. Thus, compounds **1** and **2** are solid at room temperature, but **3** shows a liquid-like behaviour, as POM and DSC studies reveal. Some of those radicals organize on HOPG forming lamellar structures.[8]

The AFM studies of **1** and **2** on graphite shows this very well ordered structure (Figure 2), due to the fact that they have two crearly distinct regions that interact very differently between themselves (interactions between the PTM heads and between the aliphatic chains). This prompted us to study, following the work of T. Nakanishi *et al*.[9] with C_{60}, the formation of hierarchically organized supramolecular architectures using different solvents to precipitate the PTM radical. This investigation opened the possibility to study the multifunctional PTM-derivative molecules (Figure 1) as potential building blocks for preparing supramolecular materials with unique morphologies.

Indeed, we have found micro-objects with compounds **1** and **2** from a large variety of solvents, obtaining different sized objects between 2 and 40 micrometres, like desert-roses, particles, plates and fibers, as shown in a SEM image (Figure 3). The formation of hierarchically assembled PTM-micro-objects is an important step in the field of molecular magnetism because of they can present promising magnetic interactions between radicals compared with the non-structured bulk (as seen in EPR studies).

References:

[1] K. Sada, M. Takeuchi, N. Fujita, M. Numata, S. Shinkai, *Chem. Soc. Rev.*, **36** (2007) 514.

[2] J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.*, **27**, (1988) 89.

[3] a) I. Ratera, D. Ruiz-Molina, J. Vidal-Gancedo, K. Wurst, N. Daro, J. F. Létard, C. Rovira, J. Veciana, *Angew. Chem. Int. Ed.*, **40** (2001) 919; b) N. Crivillers, M. Mas-Torrent, S. Perruchas, N. Roques, J. Vidal-Gancedo, J. Veciana, C. Rovira, L. Basabe-Desmonts, B. Jan Ravoo, M. Crego-Calama, D. N. Reinhoudt, *Angew. Chem. Int. Ed.*, **46** (2007) 2215.

[4] I. Ratera, S. Marcen, S. Montant, D. Ruiz-Molina, C. Rovira, J. Veciana, J.-F. Létard, E. Freysz, *Chem. Phys. Lett.*, **363** (2002) 245.

[5] D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira, J. Veciana, *Nat. Mater.*, **2** (2003) 190.

[6] J. Bonvoisin, J. P. Launay, C. Rovira, J. Veciana, *Angew. Chem. Int. Ed. Engl.*, **33** (1994) 2106.

[7] N. Crivillers, M. Mas-Torrent, J. Vidal-Gancedo, J. Veciana, C. Rovira, *J. Am. Chem. Soc.*, **130** (2008) 5499.

[8] N. Crivillers, S. Furukawa, A. Minoia, A. Ver Heyen, M. Mas-Torrent, C. Sporer, M. Linares, A. Volodin, C. Van Haesendonk, M. Van der Auweraer, R. Lazzaroni, S. De Feyter, J. Veciana, C. Rovira, *J. Am. Chem. Soc.*, **131** (2009) 6246.

[9] a) T. Nakanishi, K. Ariga, T. Michinobu, K. Yoshida, H. Takahashi, T. Teranishi, H. Möhwald, D. G. Kurth, *Small*, **12** (2007) 2019; b) T. Nakanishi, Y. Shen, J. Wang, H. Li, P. Fernandes, K. Yoshida, S. Yagai, M. Takeuchi, K. Ariga, D. G. Kurth, H. Möhwald, *J. Mater. Chem.*, **20** (2010) 1253.

Figures:

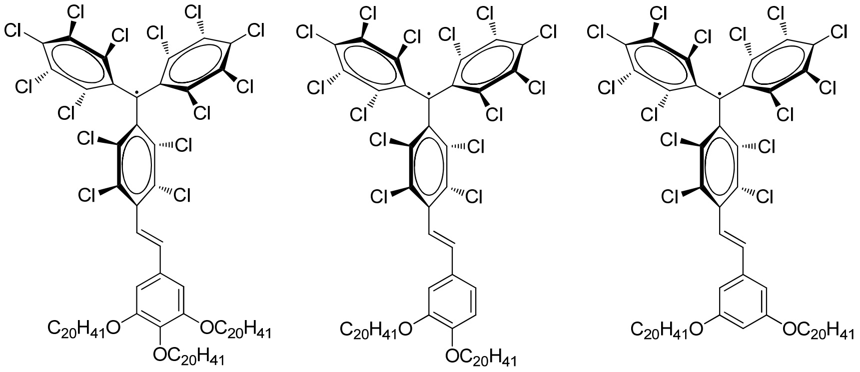
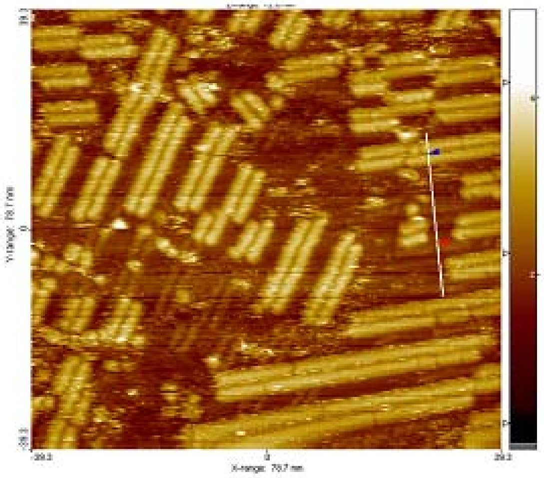


Figure 1. Molecules **1**, **2**, and **3**, PTM derivatives.



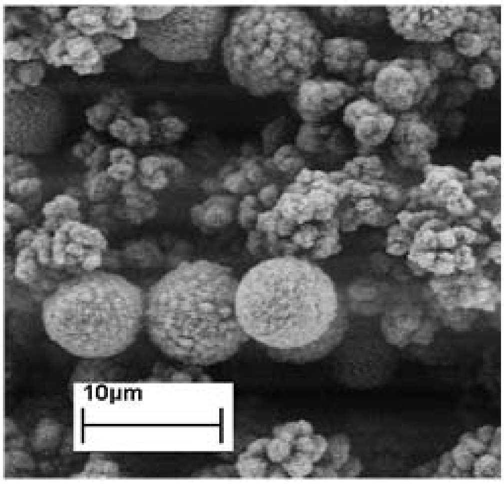


Figure 2. AFM image of **1** on HOPG. Figure 3. SEM image of **1** from a iPrOH solution.