SELF-ASSEMBLY OF POLYCHLOROTRIPHENYLMETHYL ORGANIC RADICALS ON SURFACES

M. Mas-Torrent, [a] *N. Crivillers,* [a] *S. Perruchas,* [a] *N. Roques,* [a] *J. Vidal-Gancedo,* [a] *J. Veciana,* [a] *C. Rovira,* [a] *L. Basabe-Desmonts,* [b] *B-J Ravoo,* [b] *M. Crego-Calama,* [b] *D. Reinhoudt,* [b] *S. Furukawa,* [c] *A. Ver Heyen,* [c] *S. De Feyter,* [c] *A. Minoia ,* [d] *M. Linares* [d] *R. Lazzaroni* [d]

a) Laboratory of Molecular Nanoscience and Organic Materials, Institut de Ciència de Materials de Barcelona (CSIC), Bellaterra, Campus de la UAB E-08193, Spain

b) Laboratory of Supramolecular Chemistry and Technology MESA+ Research Institute, University of Twente, P.O. Box 217, NL-7500 AE Enschede, The Netherlands

c) Department of Chemistry, Katholieke UniVersiteit LeuVen, Celestijnenlaan 200-F, 3001 Heverlee, Belgium.

d) Service de Chimie des Matériaux Nouveaux, Université de Mons-Hainaut, 20, Place du Parc, B-7000 Mons, Belgium.

mmas@icmab.es

The ultimate goal of molecular bottom up approaches is to employ functional building blocks to construct nanometer scale devices addressed to specific applications. Furthermore, for practical device implementation the immobilisation of functional molecules on suitable surfaces is also often required. One powerful and versatile strategy for the modification of surfaces at the molecular level is via the preparation of self-assembled monolayers (SAMs). Here, we describe the functionalisation of SiO_2 and Au surfaces with poly-chorotriphenylmethyl (PTM) radicals via covalent and noncovalent interactions (Fig. 1). [1-2]

The family of PTM radicals is chemically and thermally stable due to the fact that their open-shell centres are shielded by six bulky chlorine atoms.[3] These radicals are colored and also exhibit fluorescence in the red region of the spectra. More interestingly, PTM radicals are electroactive and can be easily and reversibly reduced (or oxidized) to their anionic (or cationic) species. The oxidised and reduced states show different absorption spectra than the radical and are in addition non magnetic and non fluorescent. Therefore, the preparation of SAMs functionalised with PTM radicals (PTM SAMs) on solid substrates results in multifunctional surfaces which are electrochemically, optically and magnetically active. We also demonstrate that these SAMs can be used as chemical and electrochemical redox switches with optical (absorption and fluorescence) and magnetic responses. In addition, the fabrication of surface patterns of these radical molecules has also been achieved using microcontact printing and visualized by fluorescence microscopy (Fig 2).

The self-assembly of novel PTM radicals bearing long alkyl chains at the liquid-graphite interface was also investigated. We show that the PTM hierarchical self-assembles giving rise to 3-dimensional ordered nanostructures forming double rows composed by a magnetic core of radicals surrounded by alkyl chains.

The fabrication of ordered surface nanostructures of multifunctional organic radicals represents an important step forward in the field of molecular electronics and molecular magnetism.

References:

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Figures:

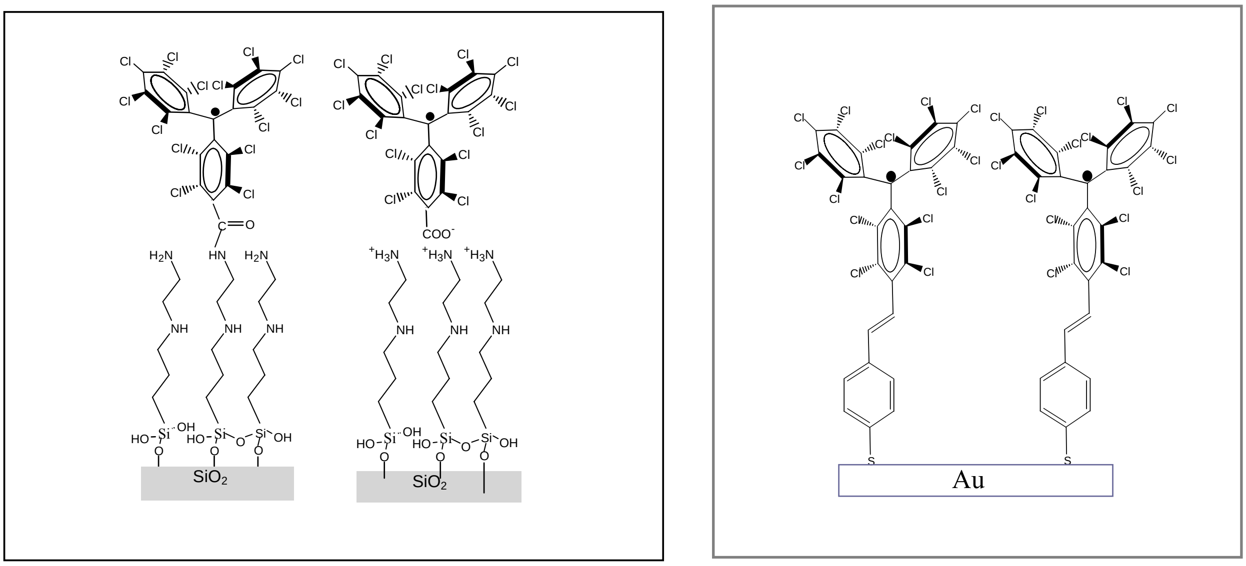

Fig. 1 Left: PTM SAMs on SiO_2 prepared via covalent and noncovalent interactions Right: PTM SAMs on Au(111).

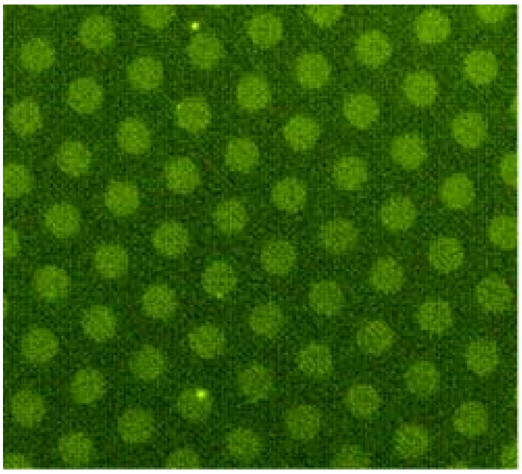

Fig. 2 Fluorescence microscopy image of a patterned PTM SAM by microcontact printing on glass (λ_{exc}=340-370 nm, spotsize of 10µm).