Functional Molecular Self-Assembled Monolayers

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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 device implementation the immobilisation of functional molecules on surfaces is also often required. Here, we describe the preparation of self-assembled monolayers (SAMs) of multifunctional polychorotriphenylmethyl (PTM) radicals on different substrates (SiO_2, Au and ITO) (Figure 1).[1-2]

The family of PTM radicals is highly 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. PTM radicals are also 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. Thus, the preparation of SAMs functionalised with PTM radicals on 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 and magnetic response (Figure 2).

Also, PTM SAMs can be employed as molecular wires. Very recently two different SAMs based on the closed and open-shell form of a PTM derivative were prepared and the conductivity through these SAMs was investigated by the 3D mode SFM.[4] These two systems exhibited small differences in their molecular structure but large differences in the electronic structure, which dramatically influenced the transport properties, being the radical SAMs much more conducting than the close-shell form.

The self-assembly by physisorption 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.[5]

In conclusion, the chemical flexibility and versatility of PTM radicals combined with their electrochemical and magnetic properties sheds lights on the huge potential of preparing surface self-assembled multifunctional molecular devices.

References:

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Figures:

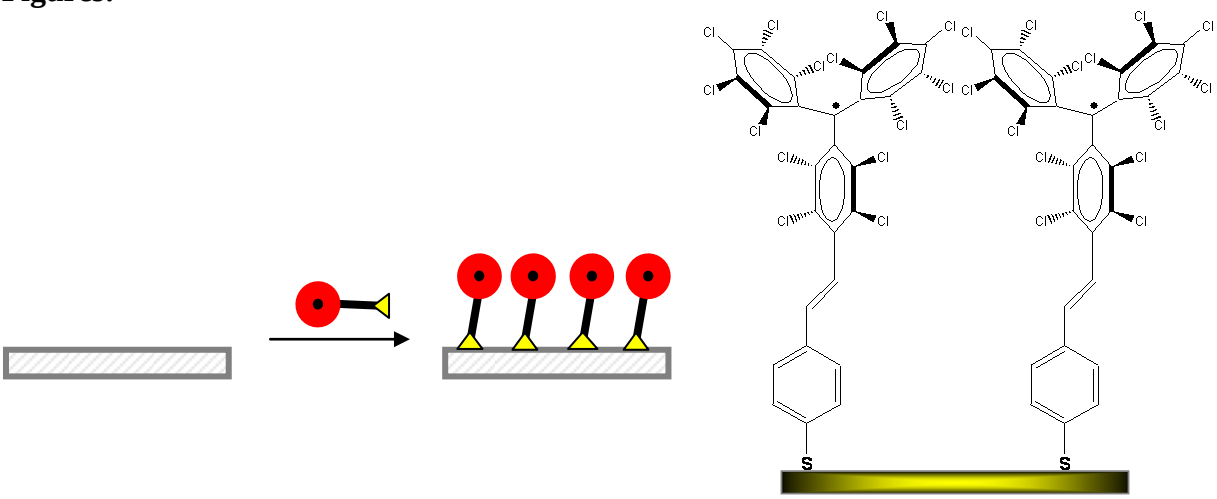

Figure 1. Scheme of a chemically-bonded PTM SAM.

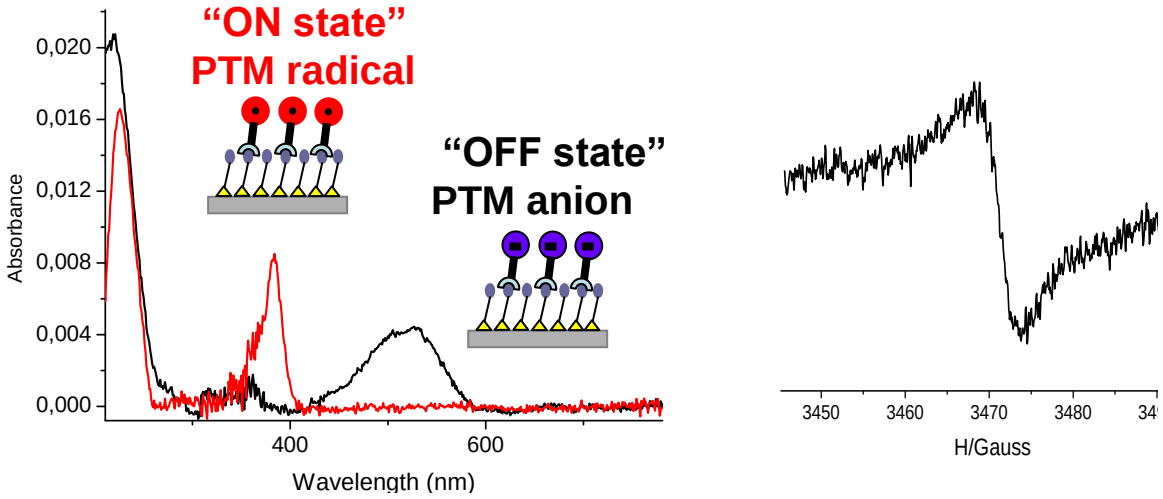

Figure 2. Left. Absorbance spectra of a PTM SAM that works as a molecular redox switch with optical and magnetic response. Right. EPR spectrum of a PTM SAM in the radical form demonstrating that the magnetic character is preserved on surface.