GRAFTING OF MACROCYCLES AND ROTAXANES ONTO SELF-ASSEMBLED MONOLAYERS ON GOLD: XPS, RAIRS, AFM, ELECTROCHEMISTRY AND PHOTOPHYSICS RESULTS

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Self-assembled monolayer (SAM) technology provides a reproducible and powerful method of fabricating films of monolayer thickness of a wide range of molecular or supramolecular species, particularly where some control over the orientation and distribution of the molecules is needed. In this work we show some examples of attachment of potentially functional molecular architectures, such as benzylic amide macrocycles and rotaxanes on acid-terminated SAMs of alkanethiols on gold.

Rotaxanes are a class of molecules composed of a macrocycle which is locked onto a linear thread by stoppers at both end. The interest in rotaxanes is that the mechanical, as opposed to the chemical, bond between the components of the molecule is dynamic and can be used to modify the molecule's properties through external stimuli. Due to this ability, these structures are seen more and more as key elements in the development of nanoscale devices as molecular shuttles, switches and information storage system. However, the macrocycle units by itself exhibit the capacity to recognize and link specific chemical species and this property can involve them in the field of the chemical recognition.

There are two basic approaches to anchoring molecules on a SAM surface: either by forming a covalent bond between the molecule and the monolayer head, or by creating a non-covalent interaction between the two parts. We prepared films of macrocycles and rotaxanes onto acid-terminated SAMs by allowing for chemical or physical interactions, depending on the chemical func-tions in the molecules: in particular, the molecules studied contain two kinds of functionality, a hydroxyl function able to form an ester bond with the acid group of the SAM, or a pyridine moiety which can interact with the acid group by electrostatic or hydrogen bonding. The films were investigated by X-ray photoelectron spec-troscopy (XPS), reflection absorption infrared spectros-copy (RAIRS), atomic force microscopy (AFM), cyclic voltammetry, impedance spectroscopy and photophysics measurements, and these techniques together allowed a quite comprehensive characterisation of these surfaces and also showed their potential applications.

XPS analysis provides qualitative and quantitative information such as the evidence that the molecules are grafted on the SAM surfaces, or that the functionalisation yield depends on the reaction times and on the dimensions of the molecule investigated. RAIRS experiments and AFM measurements with modified tips have been carried out to gain information on the orientation of the grafted molecules with respect to the SAM surface. Cyclic voltammetry and impedance spectroscopy furnished both a structural and an electrical characterisation providing information on the films thickness, orientation and packaging, and on the insulating or conducting properties of these architectures by investigating the electron transfer processes through these organic layers. Photophysics experiments investigated the emission process from fluorescent molecules anchored on the SAMs demonstrating that the gold substrate does not affect dramatically the decay rate process and therefore that the intermediate SAM is sufficiently thick to moderate the quenching effect of the gold substrate.

This work was performed within the EU RT network "EMMMA" contract n. HPRN CT-2002-00168.