SURFACE-ENHANCED RAMAN SCATTERING DETECTION OF PAHs: DITHIOCARBAMATE CALIX[4]ARENE DERIVATIVE AS AN EFFECTIVE SUPRAMOLECULAR HOST

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Surface enhanced-Raman spectroscopy (SERS) is an extremely high sensitive analytical technique mainly based on the giant electromagnetic enhancement induced by nanostructured metal surfaces via plasmon resonances. This technique has been extensively used in the identification and the orientation of adsorbates on a surface [1].

Polycyclic aromatic hydrocarbons (PAHs) are a group of pollutants with a condensed benzene rings structure. These molecules show very low affinity for the adsorption on a metallic surface, thus limiting the use of surface-enhanced techniques in their detection [2].

Calixarenes (CX) are synthetic cyclooligomers with a “cup-like” shape, capable of size-selective molecular encapsulation. By changing the chemical groups of the upper and/or lower rim, it is possible to modify their affinity towards the guest and the metal surface [3].

In this work we present a proper combination of interesting physical and chemical properties to technological applications in the detection of pollutants at trace concentration: the powerful spectroscopy technique SERS, the electronic properties of nanostructured metals, the molecular size-selective recognition of calixarene and the strong chelating properties of the dithiocarbamate group toward the metal surface.

The self-assembling monolayer functionalization of metal SERS surface was done by using the calixarene 25,27-diethyl-dithiocarbamic-26,28-dihidroxy-p-*tert*-butylcalix[4]arene (DTCX, fig. 1) synthetized from an amino calixarene precursor, and which allowed the selective recognition of large PAHs molecules such as: pyrene (PYR), benzo[*c*]phenantrene (BcP), triphenylene (TP) and coronene (COR). The DTCX host molecule adsorbed onto the metal surface captures the PAH molecule close enough to the surface for the SERS detection.

ACKNOWLEDGMENT. We acknowledge project FIS2004-00108 from *Dirección General de Investigación, Ministerio de Educación y Ciencia* and *Comunidad Autonoma de Madrid* project number S-0505/TIC/0191 MICROSERES for financial support.

References:

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Figures:

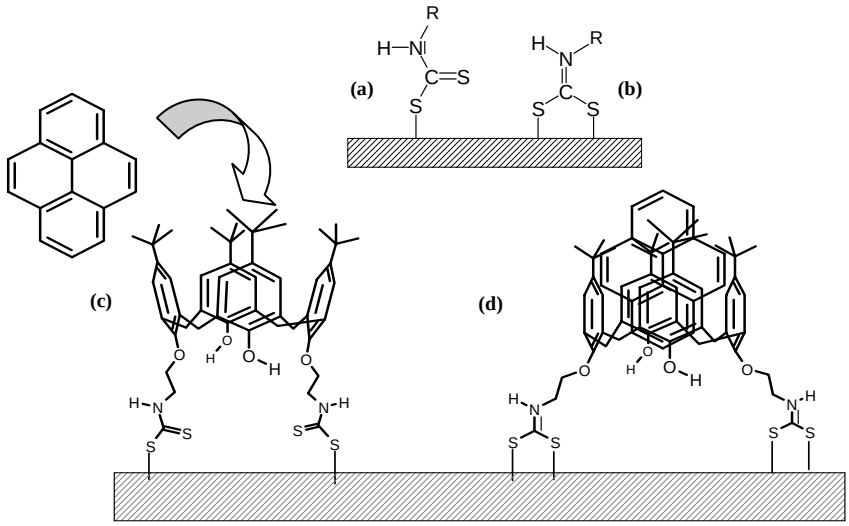

Figure 1. *Structural changes occurring on DTCX upon complexation with PYR as deduced from SERS spectra: (a) monodentate DTC; (b) bidentate thioureide; (c) monodentate and (d) bidentate adsorption of DTCX induced by the interaction with PYR.*