

# Surface-enhanced Raman Scattering Detection of Polycyclic Aromatic Hydrocarbons (PAHs) by Nanostructured Ag particles Functionalised with Cationic Self-Assembled Monolayers

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Surface-enhanced Raman scattering (SERS) combines extremely high sensitivity, due to enhanced Raman cross-sections, comparable or even better than fluorescence, with the observation of vibrational spectra of adsorbed species, providing one of the most incisive analytical methods for chemical and biochemical detection and analysis [1]. SERS spectra requires nanostructured metal surfaces to be very intense and, moreover, the scattering molecule must be close enough to the surface as to undergo an enhancement of its vibrational spectrum [2]. Thus, the molecule-nanostructure combination is very important to ensure a giant intensification of the Raman signal. The symbiosis molecule-nanostructure is a fertile ground for theoretical developments and a realm of applications from single molecule detection [3,4] to biomedical diagnostic and techniques for nanostructure characterization. However, there is not always a good affinity between the molecule-adsorbate and the metal-substrate as to induce the formation of the necessary adsorbate-metal systems. Unfortunately, this is the case of many hazardous pollutants. Between this kind of molecules the polycyclic aromatic hydrocarbons (PAHs) represents an important group of compounds which cannot approach the metal surface to be detected by neither SERS nor surface-enhanced IR Absorption (SEIRA).

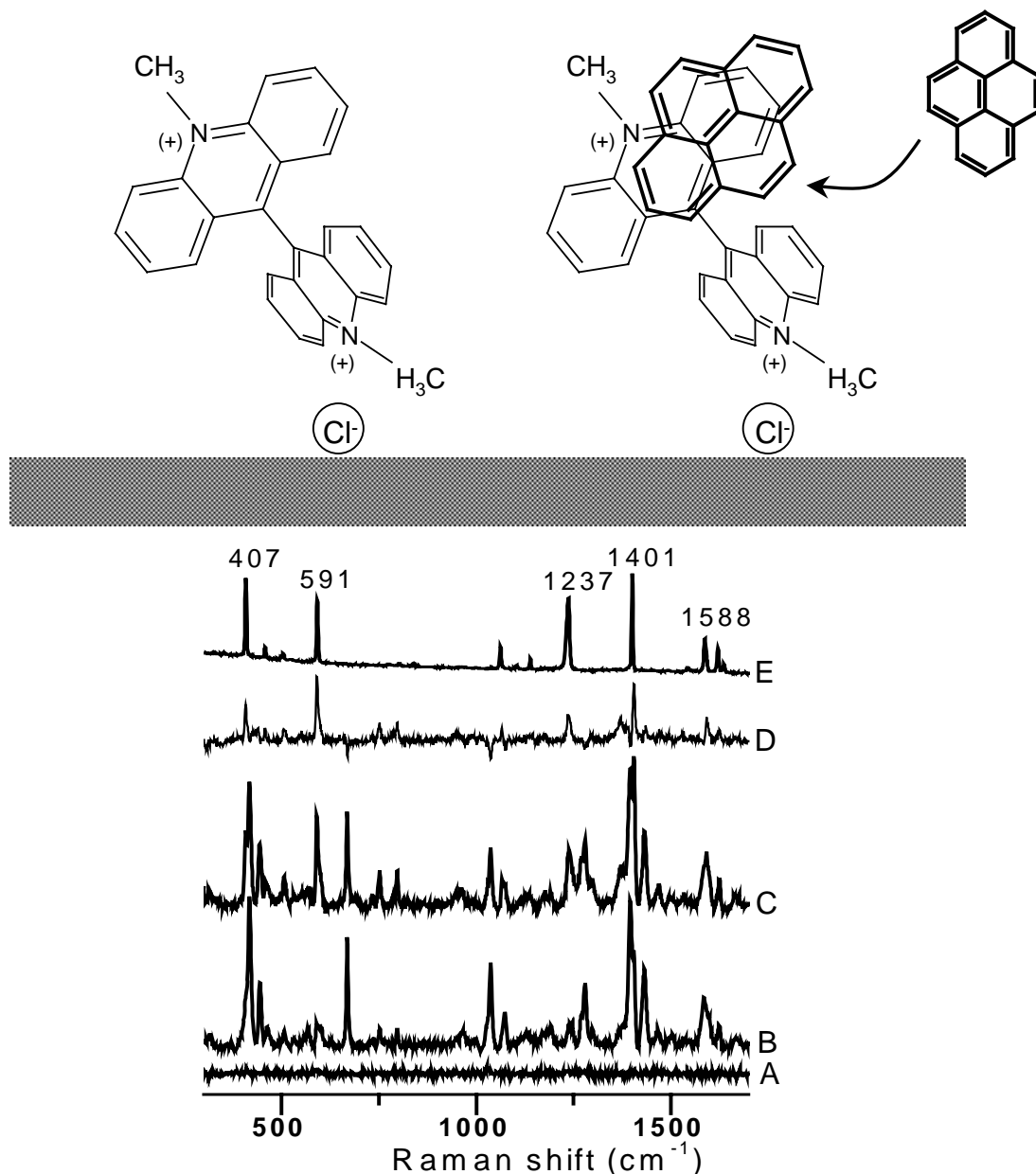
The low affinity of these pollutants can be overcome by a correct functionalisation of the metal surface. The formation of self-assembled monolayers of bifunctional molecular adsorbates is a good procedure to enhance the spectroscopic sensitivity and the molecular selectivity [5]. These characteristic are, indeed, very important in the design of chemical sensors.

In this work we show the preliminary results obtained by surface functionalisation of Ag nanoparticles, prepared by chemical reduction in suspension by *quat* molecules (Fig. 1). These molecules include in this structure a positively charged quaternary nitrogen (*quat*) and an aromatic moiety. The *quat* moiety is tightly attached to the surface via a ionic pair formation with addition of chloride ions [6,7], and can interact with aromatic ligands such as the PAHs pyrene (PYR) and benzo[c]phenanthrene (BcP) (Fig. 1).

Intense SERS spectra can be obtained from highly diluted PYR solutions ( $10^{-7}$  M) (Fig. 1). In absence of host molecule (A) no signal is obtained, but in presence of the *quat* molecule Lucigenine (C) strong PYR bands are detected together to those coming from the host molecule. The difference spectrum (D) corresponds to the PYR SERS spectrum which is compared to the Raman spectrum of the solid PYR (E). Other host molecules employed to functionalise the Ag surface were the well known pesticides paraquat and diquat. Furthermore, in this study the optimal conditions for the detection of PAHs on the functionalised surfaces were found.

## Acknowledgements

Authors acknowledge project FIS2004-00108 from *Dirección General de Investigación, Ministerio de Educación y Ciencia* and *Comunidad Autónoma de Madrid* project number GR/MAT/0439/2004 for financial support. L.G. acknowledges CSIC for a I3P grant.



**Fig.1** SERS spectra of (A) PYR  $10^{-7} M$ , (B) Lucigenine  $10^{-5} M$ , (C) Lucigenine  $10^{-5} M + PYR 10^{-7} M$ , (D) C-B difference spectrum and (E) Raman spectrum of Pyrene in solid state. All SERS spectra registered on Ag nanoparticles prepared by reduction with citrate and aggregated after the addition of  $60 \mu L$  of a NaCl (0.5M). Lase excitation at 785nm

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