## Surface-Enhanced Micro-Raman Detection and Characterization of Calix[4]Arene–Polycyclic Aromatic Hydrocarbon Host–Guest Complexes

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Surface-enhanced micro-Raman spectroscopy (micro-SERS) was used to detect traces of the hazardous pollutant polycyclic aromatic hydrocarbons (PAHs) pyrene and benzo[c]phenanthrene deposited onto a calix[4]arene-functionalized Ag colloidal surface. High spectral reproducibility and very low molecular detection limits (10<sup>-8</sup> M) were obtained by using 25,27-carboethoxy-26,28-hidroxy-p-tertbutylcalix[4]arene as host molecule. Films of immobilized aggregated Ag nanoparticles, obtained by chemical reduction with hydroxylamine, were prepared by direct adhesion on a glass surface. The influence of the aggregation degree of the initial Ag nanoparticles on the micro-SERS detection effectiveness was checked. Different relative concentrations of the host (calixarene receptor) and the guest (PAHs) were attempted in order to optimize detection of the pollutant. The obtained results indicated that the detection limit is much lower in the case of benzo[c]phenanthrene than in pyrene when exciting with the 785 nm line of a diode laser. A detailed interpretation of the Raman spectra was accomplished in order to obtain more information about the interaction mechanism of the host-guest complex, which could be useful in the future for the design of powerful detection systems.

Index Headings: Surface-enhanced micro-Raman spectroscopy; Micro-SERS; Calixarenes; Polycyclic aromatic hydrocarbons; PAHs; Host-guest complexes; Detection of pollutants.

#### **INTRODUCTION**

Molecular recognition with calixarenes capable of sizeselective molecular encapsulation is a topic of current interest in supramolecular chemistry with promising applications in sensor design.<sup>1–3</sup>

No surface-enhanced Raman (SERS) spectra of PAHs can be obtained in the absence of a host molecule due to the low affinity of these molecules for adsorbtion on a metallic surface. However, the situation is different in functionalized PAHs, such as nitro-PAHs, which can be attached to the metal surface through the nitro group.<sup>4–6</sup> For non-functionalized PAHs another strategy is necessary to bring the analyte to the surface and obtain a SERS spectrum. One of these strategies is surface functionalization with host molecules such as calixarenes.

Up to now, few published works have been devoted to the application of calixarene molecules in the detection of pollutants through Raman techniques.<sup>7,8</sup> In a recent work, we selectively detected PAH molecules at trace concentrations by using surface-enhanced Raman spectroscopy (SERS).<sup>9</sup> To accomplish that, we used calix[4]arene derivatives as self-assembled molecules, adsorbed on Ag nanoparticles. Among a large series of calix[4]arene derivatives, the 25,27-dicarboethoxy-26,28dihidroxy-p-*tert*-butylcalix[4]arene host molecule (DCEC) (Fig. 1a) displayed a significant selectivity for interaction with and detection of PAH molecules bearing four benzene rings, mainly pyrene (PYR) (Fig. 1b) and benzo[c]phenanthrene (BcP) (Fig. 1c). Moreover, a host– guest interaction mechanism based on a  $\pi$ – $\pi$  stacking interaction was deduced, leading to a charge transfer between the complex and the metallic surface, which also induces a notable influence on the surface charge of the metallic nanoparticle.

Furthermore, in this previous work we carried out macro- and micro-SERS measurements on Ag colloidal nanoparticles and on immobilized Ag nanoparticles on glass surfaces, respectively. Since a small surface area is studied by micro-Raman, the sensitivity of micro-SERS is much higher than in macro experiments.<sup>10</sup> Therefore, the aim of the present work is to systematize the use of the micro-Raman technique combined with SERS experiments (micro-SERS) to decrease the molecular detection limits of PYR and BcP as guest molecular systems and DCEC as a host molecule. Our ultimate goal is to understand the structural changes occurring in the molecular recognition phenomena involved in the interaction of calixarene derivatives with PAHs, in order to develop a reproducible measurement tool for single molecule studies.

### **EXPERIMENTAL**

**Materials.** *Calix[4]Arene.* The calixarene employed for this study was DCEC, since this molecule afforded the maximum SERS intensification, which was synthesized by us according to described procedures.<sup>11</sup> The precursor, p-*tert*-butylcalix[4]arene, was synthesized in the following manner. A mixture of p-*tert*-butyl phenol, 37% formaldehyde, and an amount of KOH corresponding to 0.045 mols with respect to the phenol is heated for 2 h at 110–120 °C to produce a light yellow, taffy-like precursor, which is then added to xylene and refluxed for 1.5–2 h. Filtration of the cooled reaction mixture yields a crude product that is neutralized and then recrystallized from chloroform–methanol.

The lower functionalization is achieved by addition of BrCH<sub>2</sub>COOEt in alkaline medium afforded by K<sub>2</sub>CO<sub>3</sub>.

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Fig. 1. (a) 25,27-dicarboethoxy-26,28-dihidroxy-p-*tert*-butylca-lix[4]arene (DCEC), (b) pyrene (PYR), and (c) benzo[c]phenanthrene (BcP).

First, 9.25 g of the precursor (8 mmol) were dissolved in 50 cm<sup>3</sup> of diphenylether, then 15 g (96 mmol) of BrCH<sub>2</sub>COOEt and 13.90 g (96 mmol) of potassium carbonate were added to the precursor solution. The DCEC product was extracted by adding ethyl acetate to the mixture. The precipitate was washed with distilled water and reprecipitated with acetone.

**Polycyclic Aromatic Hydrocarbons.** Pyrene (PYR) and BcP were purchased from Aldrich and Merck and used as received. Solutions of these compounds in acetone (99%) were prepared to a final concentration of  $10^{-2}$  M.

Preparation of the Metal Surfaces and Samples for Surface-Enhanced Micro-Raman Spectroscopy. Colloidal silver nanoparticles were prepared by means of a novel procedure based on the chemical reduction of Ag<sup>+</sup> using hydroxylamine as the reducing agent.<sup>12</sup> These nanoparticles have the advantage of a more uniform distribution of size and shape together with the absence of the reducing agent (citrate or borohydride) excess and their oxidation products,<sup>13</sup> which could interfere with the SERS measurements.<sup>14</sup> In addition, this colloid could have better electrical conditions on the surface for the detection of PAHs, since the number of negative charges, mainly due to the residual chloride ions, should be much lower than in the case of citrate and borohydride colloids. On the other hand, the adherence properties of these chloride-covered nanoparticles seems to be better, as revealed by their effective immobilization on glass giving rise to films by a direct deposition on a glass surface.

Metal films of Ag nanoparticles for micro-SERS measurements were prepared by immobilizing the colloidal nanoparticles. Previous to this immobilization, an aliquot of the calixarene in acetone was added to 500  $\mu$ L of silver colloid up to the desired concentration. In the case of the calixarene/PAH complexes, an aliquot of the PAH solution, also in acetone, was then added to reach the final desired host–guest concentrations. Afterwards, the colloid was activated by addition of 0.5 M aqueous potassium nitrate up to a final concentration of  $4 \times 10^{-2}$  M. This activation is needed in order to increase the nanoparticle SERS activity by properly modifying the morphology of the particles.<sup>15</sup> Then, 20  $\mu$ L of the final suspension was deposited onto a glass cover slide and dried at room temperature.

The immobilization of the Ag nanoparticles already having the host–guest complex afforded a more effective result, as concerns the SERS signal intensification, than the *a posteriori* addition of host and analyte. This is probably due to the better organization of adsorbates on the metal surface. An aliquot of the original non-activated colloid was placed on a glass slide with a shallow groove (2 cm in diameter and 380  $\mu$ m deep), and then the cover glass slide containing the dried activated Ag nanoparticles was placed on the groove with the side containing the dried nanoparticles facing downwards so that the suspension is placed in the groove, as depicted in Fig. 2.

A scanning electron micrograph of an Ag film obtained by the procedure above is also shown in Fig. 2. As can be seen, the resulting Ag aggregates have an average diameter of  $1-2 \mu m$  and are separated by a distance of several micrometers (1–10  $\mu$ m). This distribution is uniform throughout the whole immobilized surface. A detail of an aggregate is also displayed in Fig. 2, showing that they are integrated with 50–60 nm diameter Ag nanoparticles giving rise to a morphology that is much appropriate for the SERS enhancement.

**Spectral Reproducibility.** The SERS spectra obtained from different aggregates are reproducible in what concerns the SERS profiles, although the intensities varied due to the dependence on the aggregate morphology. This reproducibility was maintained from batch to batch.

**Preparation of Samples for Scanning Electron Microscopy.** The samples obtained by immobilization of nanoaggregates on glass cover slides were also employed for SEM observation. All samples were coated at room temperature with a 3–4 nm layer of gold–palladium (Au/ Pd) using a high-resolution magnetron sputter coater operated at 800 V and 5 mA plasma current to obtain a coating rate of 0.5 nm/min.

**Instrumentation.** The micro-SERS spectra were recorded with a Renishaw Raman Microscope System RM2000 equipped with a diode laser (providing a line at 785 nm), a Leica microscope, an electrically refrigerated charge-coupled device (CCD) camera, and a notch filter to eliminate the elastic scattering. The spectra shown here were obtained by using a  $100 \times$  objective. The output laser power was in the range of 2.0 mW. Spectral resolution was 2 cm<sup>-1</sup>. A scheme of the Raman system employed is depicted in Fig. 2.

Scanning electron micrographs were taken in an Environmental Scanning Electron Microscope, (ESEM) PHILIPS XL30, with tungsten filament operating under high vacuum mode. The acceleration voltage was 25 KV. For secondary electrons, the standard Everhard–Thornley detector was used. Sample coating was accomplished using a high-resolution magnetron sputter coater Polaron SC 7640.

#### **RESULTS AND DISCUSSION**

**Colloidal Aggregation.** Since the Ag nanoparticles were activated with KNO<sub>3</sub>, the aggregation effect of the



Fig. 2. Raman instrument and sampling device employed for micro-SERS measurements. See text for further details regarding the SEM images.



Fig. 3. Relative Raman intensities of the most intense SERS bands of PYR (1234 cm<sup>-1</sup>) and BcP (1376 cm<sup>-1</sup>) at different potassium nitrate concentrations. The relative intensities were calculated by dividing all the SERS intensities by the SERS intensity observed at the nitrate concentration at which the maximum SERS intensity was obtained ( $10^{-2}$  M).

salt was studied in order to optimize the immobilized Ag film rendering the most intense micro-Raman signal in the surface-enhanced Raman spectra. In Fig. 3 the SERS relative intensity of the most intense bands of PYR (1234 cm<sup>-1</sup>) and BcP (1376 cm<sup>-1</sup>) are plotted against the nitrate concentration. A maximum SERS intensity obtained when using a  $2 \times 10^{-2}$  M concentration of KNO<sub>3</sub> was the most adequate final concentration, since it induced the formation of Ag aggregates with optimal morphological properties. Thus, this concentration was used to carry out the micro-SERS experiments.

Below and above that optimal nitrate concentration the Ag immobilized aggregates do not have as good a morphology due to either a poor aggregation leading to string aggregates at lower concentrations, or globular-like aggregates at higher concentrations.<sup>16</sup>

Surface-Enhanced Micro-Raman Spectroscopy of the Complexes at Different DCEC Concentrations. It is important to note that no SERS spectra of PAHs can be obtained in the absence of calixarene. Since the presence of the host molecule is absolutely necessary for the observation of any SERS signal coming from the PAHs, we have obtained the SERS spectra of the DCEC/PAH complexes by varying both the concentrations of the host and the guest in order to study the spectral modifications induced on the calixarene and the PAH molecule as a consequence of the interaction.

The DCEC/PYR and DCEC/BcP complexes were studied with the DCEC concentrations ranging from  $10^{-6}$ 



Fig. 4. Raman spectra of PYR in the solid state (*a*) and micro-SERS spectra of DCEC/PYR complexes at the following concentrations:  $10^{-12}/10^{-5}$  M (*b*) and  $10^{-6}/10^{-5}$  M (*c*). (Inset) SERS intensity of the PYR 1234 cm<sup>-1</sup> band at different DCEC concentrations. The intensity measurements were carried out by averaging the values found for the PYR 1234 cm<sup>-1</sup> band at each DCEC concentration in four different immobilized aggregates. In the figure the average value as well as the quadratic standard deviation are displayed.

M to  $10^{-12}$  M while keeping the PAH concentration at  $10^{-5}$  M. Figures 4 and 5 show the SERS spectra corresponding to the extreme calixarene concentration, i.e., at  $10^{-6}$  and  $10^{-12}$  M. In the inset figures the SERS intensities of the most intense bands (1234 and 1376 cm<sup>-1</sup>, for PYR and BcP, respectively) are plotted against the DCEC concentration. As can be observed, the PAH signal is still observed at low calixarene concentration (Figs. 4b and 5b). Taking into account the analyzed area (approximately 1  $\mu$ m<sup>2</sup>) and the analyte concentration of the added solution, we have calculated that the total amount of analyzed molecules is about 50, which is in the vicinity of the single molecule.

We also note the fact that BcP rendered a higher SERS intensity than PYR at all the calixarene concentrations analyzed. In a previous work<sup>9</sup> we have seen that the SERS signal of PYR is higher in macro-sampling experiments exciting at 1064 nm. However, the fact that at 785 nm BcP afforded a higher SERS signal could be related to a resonance effect for the BcP/DCEC complex, which indicates that the interaction with the calixarene is in principle different for PYR and BcP. This also points out the importance of the experimental conditions on the study of these complex systems. On the other hand, the SERS intensity of PYR increases on lowering the concentration of DCEC from  $10^{-6}$  to  $10^{-8}$  M (see the inset



Fig. 5. Raman spectra of BcP in the solid state (*a*) and micro-SERS spectra of DCEC/BcP complexes at the following concentrations:  $10^{-12/}$   $10^{-5}$  M (*b*) and  $10^{-6/}10^{-5}$  M (*c*). (**Inset**) SERS intensity of the 1376 cm<sup>-1</sup> band at different DCEC concentrations. The intensity measurements were carried out by averaging the values found for the BcP 1376 cm<sup>-1</sup> band at each DCEC concentration in four different immobilized aggregates. In the figure the average value as well as the quadratic standard deviation are displayed.

figure in Fig. 4). Below the latter concentration the SERS intensity decreases. In the case of BcP, a progressive intensity increase was seen on lowering the calixarene concentration such that the SERS intensity at a DCEC concentration of  $10^{-12}$  M is much higher than at  $10^{-6}$  M (see inset of Fig. 5). This trend could be due to a multilayer effect of the calixarene when adsorbed on the metal, which at high DCEC concentrations may avoid the adsorption of the PAH molecule leading to a decrease in the SERS signal.

The analysis of the PYR SERS bands (Fig. 4) in the complex also reveals interesting differences with respect to the solid compound (Fig. 4a) due to the complexation with the host calixarene, with the trend being similar at low and high calixarene concentrations (Fig. 4b and 4c, respectively). In general, there is a significant  $6-10 \text{ cm}^{-1}$ shift downwards of the SERS bands above 1000 cm<sup>-1</sup>, even larger than that observed in our previous work,9 probably because of the lower PYR concentration employed here. The enhancement of in-plane ring bands such as those at 1616 and 590 cm<sup>-1</sup> indicates a perpendicular orientation of PYR with respect to the surface. The band at 1400 cm<sup>-1</sup> decreases in the spectrum of Fig. 4c, but in other spectra of complexed PYR shown here this trend is not observed; thus, we suggest that this is a local effect of the analyzed area.

The BcP SERS spectra also display a significant shift



Fig. 6. Raman of DCEC in the solid state (*a*); micro-SERS spectra of DCEC ( $10^{-4}$  M) (*b*); DCEC/PYR complexes at the following concentrations (M/M):  $10^{-4}/10^{-6}$  (*c*) and  $10^{-4}/10^{-4}$  M (*d*); and micro-Raman spectra of PYR in solid state (*e*).

downwards for the most intense in-plane ring stretching bands at 1600, 1497, and 1384 cm<sup>-1</sup>, which is stronger as the calixarene concentration is lowered (Fig. 5b). In particular, the band at 1600 cm<sup>-1</sup> shifts towards 1574 cm<sup>-1</sup> when DCEC is at a concentration of 10<sup>-12</sup> M. However, the relative intensity of the bands does not change as strongly as in the case of PYR.

Surface-Enhanced Micro-Raman Spectroscopy of the Complexes at Different Polycyclic Hydrocarbon Concentrations. In order to verify the detection limits imposed by the calixarene concentration, we have obtained the spectra of the PAHs at different concentrations by keeping constant the calixarene concentration at  $10^{-4}$ M (Figs. 6 and 7 for PYR and BcP, respectively). We have employed this relatively high concentration of calixarene in order to investigate its structural modification when interacting with the analyte. In this case the bands ascribed to the PAHs are observed up to concentrations of 10<sup>-6</sup> M in the case of PYR and 10<sup>-8</sup> M in the case of BcP. We suggest that the detection limit is not as low at a relatively high concentration of DCEC ( $10^{-4}$  M) due to the larger amount of calixarene molecules existing on the surface, invoking the multilayer effect described above.

Figure 8 displays the SERS spectra of DCEC (Fig. 8b) and its complexes with PAHs in the region where the most important changes were observed, the 1350-600 cm<sup>-1</sup> region. Many of the changed bands correspond to



Fig. 7. Micro-SERS spectra of DCEC ( $10^{-4}$  M) (*a*); DCEC/BcP complexes at the following concentrations (M/M):  $10^{-4}/10^{-8}$  (*b*),  $10^{-4}/10^{-6}$  M (*c*), and  $10^{-4}/10^{-4}$  M (*d*); and micro-Raman spectra of BcP in solid state (*e*).

the calixarene carboethoxy moiety, such as those observed in the Raman of the solid at 1243 and 1202 cm<sup>-1</sup>, which are markedly enhanced and shifted downwards in the complex (Figs. 8c–8e). In particular, the band at 1202 cm<sup>-1</sup> is very intense in the IR (result not shown here), thus indicating that it is due to C–O stretching vibrations in the ester moiety. Other bands that are also sensitive to the complexation are those seen at 1300, 1122, 1029, 924, 907, 867, and 749 cm<sup>-1</sup>, which are also related to the ester group and the benzene rings. This suggests that the spectral modifications induced by PAHs are due to changes in the carboethoxy side chain and to conformational changes occurring in the four-benzene calixarene cycle.

The DCEC ester carbonyl band also undergoes important variations upon adsorption and interaction with the guest, which were commented on extensively in our previous work.<sup>9</sup> In general, the relative intensity of the carbonyl band markedly weakens in the complex and is inversely proportional to the PAH concentration. This indicates that the interaction strength of DCEC with the surface increases in the complex.



Fig. 8. Effect on DCEC of the interaction with PAHs in the 1350– 600 cm<sup>-1</sup> region: Raman of DCEC in the solid state (*a*); micro-SERS spectra of DCEC ( $10^{-4}$  M) (*b*); DCEC/PYR complex ( $10^{-4}/10^{-6}$ ) (*c*); and DCEC/BcP complexes at the following concentrations (M/M):  $10^{-4}/10^{-8}$  (*d*) and  $10^{-4}/10^{-6}$  M (*e*). (*f*) The micro-Raman spectra of BcP in the solid state.

When comparing the effect on the calixarene spectrum of PYR and BcP at a 10<sup>-6</sup> M concentration (Figs. 8c and 8e, respectively) a stronger influence was deduced for BcP. The differences noted between both PAHs in the complexation with DCEC are probably related to the different stereochemistry of the analytes. In fact, PYR and BcP exhibit structural differences based on the existence of a bay-like structure in BcP (Fig. 1).

The steric hindrance between H atoms existing in this bay moiety induces a non-planar structure in BcP, which could be in part responsible for the remarkable differences seen in the distinct interaction of PYR and BcP with the calixarene host. This non-planar structure could induce stronger structural changes in the DCEC. Thus, the accommodation of each adsorbed analyte on the host molecule is not equivalent. On this basis one can infer that the observed detection limits, different for each analyte, should be a consequence of the analyte's own stereochemistry. Since PAHs containing bay-like regions have been demonstrated to be potent carcinogens,<sup>17,18</sup> the use of calixarene of the DCEC type opens a promising perspective in the selective calixarene-based detection of these important pollutants.

#### CONCLUSION

The micro-SERS technique has been employed in the detection and characterization of guest-host supramolecular systems at very low concentrations. By using calix[4]arenes functionalized with a carboethoxy group in the lower rim under a 1,3 substitution pattern, the detection limits of PYR and BcP are in the neighborhood of single molecule detection.

Silver films prepared by immobilizing hydroxylaminereduced Ag nanoparticles were demonstrated to be very sensitive when applied in micro-SERS detection, giving rise to very reproducible results. The morphological properties of the Ag nanoparticle aggregates, and thus, the effectiveness of the enhancement, can be modulated by changing the amount of potassium nitrate added to the suspension. The measurements are very reproducible in terms of spectral pattern, but not in what concerns the overall intensity, which strongly depends on the optical properties of the immobilized Ag aggregates.

The SERS spectra of the calixarene/PAH complexes obtained at different host and guest concentrations indicate that at conditions of high host concentrations the PAH signal can be dramatically lowered due to a massive adsorption and probable multilayer formation onto the surface of the metal. Thus, it is concluded that for analytical purposes the best micro-SERS spectrum of the analyte should be obtained at relatively low concentrations of the host molecule rather than the opposite.

The interaction of the PAH with the calixarene host induces a marked structural change in the analyte and the host molecule, which seems to depend on the analyte stereochemistry. While PYR is more affected by the complexation, BcP seems to induce a stronger effect on the calixarene adsorbed molecule because of its non-planar structure induced by the existence of bay-like moieties. Many of the changes induced on the calixarene are related to the carboethoxy moieties, which are responsible for the molecule anchorage to the metal surface. Furthermore, the interaction of the PAH molecule with the calixarene also induces a marked strengthening of the complex interaction with the metal surface.

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