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Functionalization of Ag Nanoparticles with Dithiocarbamate Calix[4]arene As an Effective Supramolecular Host for the Surface-Enhanced Raman Scattering Detection of Polycyclic Aromatic Hydrocarbons

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We report the use of 25,27-diethyl-dithiocarbamic-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene in the functionalization of Ag nanoparticles for pyrene detection by surface-enhanced Raman scattering (SERS). SERS spectra provided information about the calixarene orientation on the metal surface and the interaction mechanism with pyrene. Thus, in this work, we have combined a powerful spectroscopy technique such as SERS, the electronic plasmon-based properties of nanostructured metals, the molecular size-selective recognition of calixarene, and the strong chelating properties of the dithiocarbamate group toward the metal surface in the detection of polycyclic aromatic hydrocarbons.

Calixarenes (CXs) 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 toward the guest and the metal surface.¹ Surface-enhanced Raman spectroscopy (SERS) is an extremely highly sensitive analytical technique based on the giant electromagnetic enhancement induced by nanostructured metal surfaces via plasmon resonance. This technique has been extensively used in the identification and orientation of adsorbates on a surface.² The combination of the physical properties of nanostructured metal and the advanced chemical properties of self-assembled CXs is a subject of great interest in supramolecular science, with promising applications in different fields such as nanotechnology, environment, chemical sensing, and so forth.

Polycyclic aromatic hydrocarbons (PAHs) are a group of pollutants with condensed benzene rings formed during the incomplete combustion of coal, oil, and gas or other organic substances such as tobacco or charbroiled meat. Many of them have been reported to be strong carcinogens.³ These molecules show very low affinity for adsorption on a metallic surface, thus limiting the use of surface-enhanced techniques in their detection. However, in recent works,^{4,5} CXs with carboethoxy groups in the lower rim have been successfully applied in the detection of PAHs by using the SERS technique.^{4,5}

The strong interaction of dithiocarbamates (DTs) with metals has been known for quite some time, and it is related to the ability of the molecules to form chelate complexes.⁶ DT is able to strongly interact with the surface of metals, as demonstrated in previous studies on the adsorption of DT containing fungicides on nanostructured metal surfaces.^{7–9} Thus, the combination of

the good host properties of CX and the high affinity of the DT group in the same molecule, self-assembled on a nanostructured metal, should be a good strategy to design new sensitive and selective surfaces for the detection of PAHs.

In this work, we report the use of DTCX-functionalized Ag nanoparticles, prepared by the chemical reduction of AgNO₃ by hydroxylamine, in the pyrene detection by SERS spectroscopy. The synthesis of the 25,27-diethyl-dithiocarbamic-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene (DTCX) was carried out from the corresponding amino calixarene (AmCX) following the method described by Zhao et al.¹⁰ (Figure 1, inset) (see Supporting Information for experimental details). DTCX metal functionalization represents a remarkable improvement in the detection limit of pyrene in relation to carboethoxy CX.^{4,5}

In Figure 1, the Raman and IR spectra of AmCX and DTCX in the solid state are compared. The IR spectrum of DTCX (Figure 1d) shows new bands at 1522, 1034, 967, 678, and 485 cm⁻¹, corresponding to the DT group. The Raman spectrum of DTCX (Figure 1b) shows less differences with respect to AmCX, due to the polar character of DT. In fact, only an intensity decrease in the band at 1236 cm⁻¹ (assigned to a C–N stretching mode or a twisting of the CH₂ group close to the NH₂ one¹¹), the new band at 963 cm⁻¹ (assigned to the ν (C–S) mode), and the changes observed in the bands at 698 and 668 cm⁻¹ are observed. The latter bands are actually due to the DT group and other groups already existing in AmCX, since two bands at approximately the same wavenumber appear in the solid of AmCX (Figure 1a). Thus they were not considered to evaluate the adsorption of DTCX on the Ag surface.

The SERS spectrum of DTCX (Figure 2c) is much more intense than that of AmCX (spectrum not shown), thus indicating the existence of a stronger interaction of DTCX with the metal. This interaction takes place through the S atoms, as indicated by the band at 198 cm⁻¹ (Figure 2, inset), attributed to the Ag–S stretching motion.⁸ A consequence of the strong interaction of

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(1) Houk, K. N.; Leach, G. L.; Kim, S. P.; Zhang, X. *Angew. Chem., Int. Ed.* **2003**, *42*, 4872.

(2) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.

(3) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; John Wiley & Sons: New York, 1997.

(4) Leyton, P.; Domingo, C.; Sanchez-Cortes, S.; Campos-Vallette, M.; García-Ramos, J. V. *Langmuir* **2005**, *21*, 11814.

(5) Leyton, P.; Sanchez-Cortes, S.; Campos-Vallette, M.; Domingo, C.; García-Ramos, J. V.; Saitz, C. *Appl. Spectrosc.* **2005**, *59*, 1009.

(6) Thorn, G. D.; Ludwig, R. A. *The Dithiocarbamates And Related Compounds*; Elsevier Monographs: New York, 1962.

(7) Sanchez-Cortes, S.; Vasina, M.; Francioso, O.; García-Ramos, J. V. *Vib. Spectrosc.* **1998**, *17*, 133.

(8) Sanchez-Cortes, S.; Domingo, C.; García-Ramos, J. V.; Aznarez, J. A. *Langmuir* **2001**, *17*, 1157.

(9) Morf, P.; Raimondi, F.; Nothofer, H. G.; Schnyder, B.; Yasuda, A.; Wessels, J. M.; Jung, T. A. *Langmuir* **2006**, *22*, 658.

(10) Zhao, Y.; Perez-Segarra, W.; Shi, Q.; Wei, A. *J. Am. Chem. Soc.* **2005**, *127*, 20, 7328.

(11) Socrates, G. *Infrared and Raman Characteristic Group Frequencies*; John Wiley & Sons, Ltd.: New York, 2004.

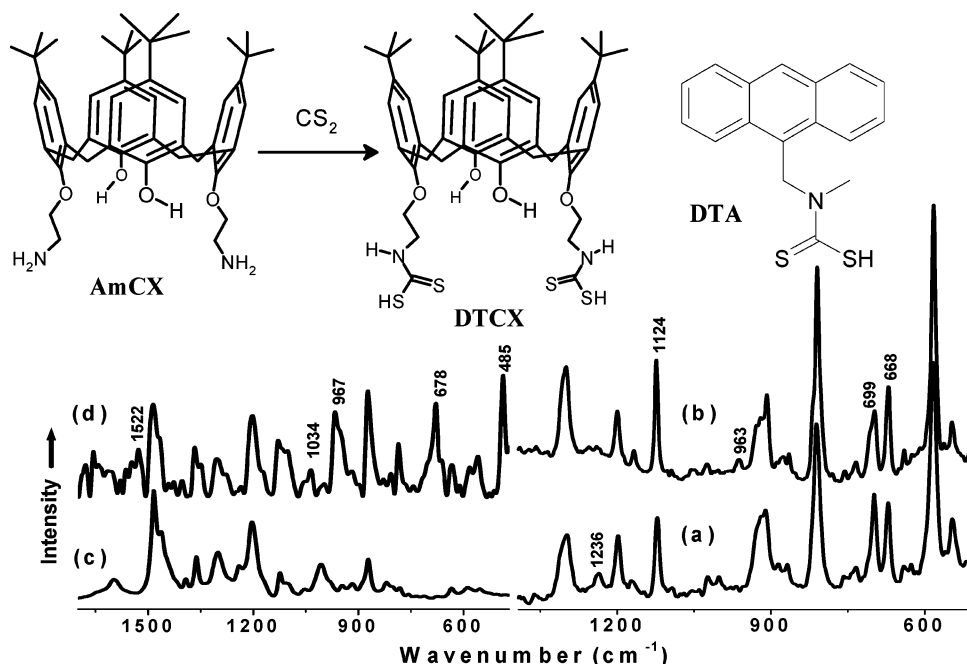


Figure 1. Raman Spectra of AmCX (a) and DTCX (b) exciting at 785 nm, and the IR spectra of AmCX (c) and DTCX (d) in KBr. Inset: scheme of the DTCX synthesis from AmCX and the DTA structure.

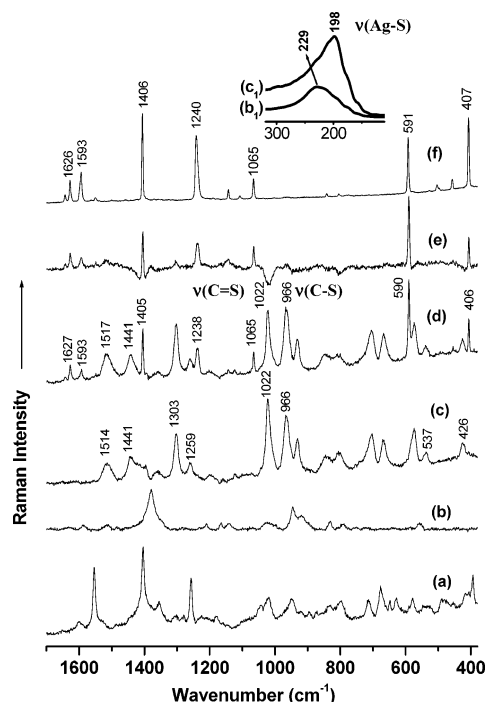


Figure 2. SERS spectra of (a) DTA/PYR (10^{-4} M/ 10^{-6} M), (b) PYR (10^{-6} M), (c) DTCX (5×10^{-4} M), (d) DTCX/PYR (5×10^{-4} M/ 10^{-7} M) complex. (e) Difference spectra of d-c. (f) Raman spectrum of solid PYR. Inset: b_1 and c_1 spectra; detail of the 320–100 cm^{-1} region of b and c spectra.

DTCX with Ag is the band at 1514 cm^{-1} , attributed to the partial C–N double bond induced by the transformation of the DT group (Figure 3a) into the corresponding thioureide form^{6–8} (Figure 3b), due to the lone pair electron attraction of the nitrogen by the complexation with the metal. The DTCX SERS spectrum is dominated by the DT bands seen at 1022 cm^{-1} and 966 cm^{-1} that have been ascribed to the $\nu(\text{C}=\text{S})$ and to $\nu(\text{C}-\text{S})$ motions, respectively, which are characteristic of a thioureide monodentate complex with the metal surface.^{7,8} These bands undergo a shift and subsequent broadening in the presence of Ag nanoparticles

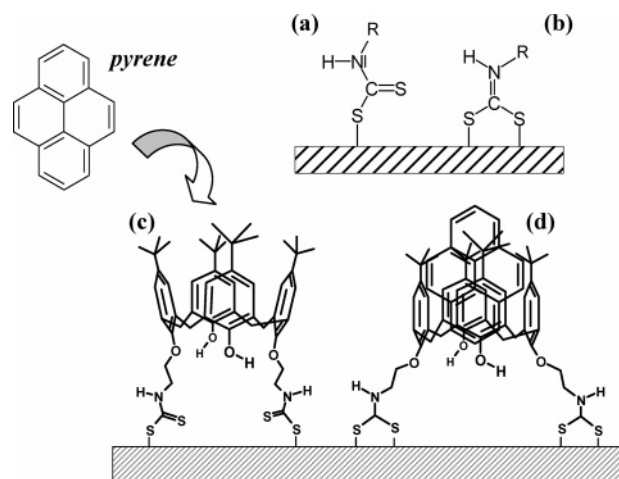


Figure 3. Structural changes occurring on DTCX upon complexation with PYR as deduced from SERS spectra: (a) monodentate DTC; (b) bidentate thioureide; (c) monodentate and (d) bidentate adsorption of DTCX induced by the interaction with PYR.

as compared to the corresponding band appearing at 1027 and 963 in the Raman of the solid DTCX (Figure 1b). Furthermore, the bands at 537 cm^{-1} and 426 cm^{-1} can be assigned to the C–S stretching and *N*-alkyl symmetric bending coupled modes, respectively, of DT linked to the metal,¹⁰ while the strong band at 1259 cm^{-1} has been attributed to $\delta(\text{CCH})$ and $\delta(\text{SCS})$ modes.¹² All these results indicate that DTCX is adsorbed onto the metal through the DT group, leading to a predominant monodentate interaction forced by the DTCX structure (Figure 3c).

This orientation should lead to a general intensity decrease in the Raman bands corresponding to the aromatic central and *tert*-butyl upper rim moieties of the CX,^{13–16} which are placed further

(12) Bauer, G.; Nikolov, G. St.; Trendafilova, N. *J. Mol. Struct.* **1997**, *415*, 123.

(13) Marengo, C.; Stirling, C. J. M.; Yarwood, J. *J. Raman Spectrosc.* **2001**, *32*, 183.

(14) Kondyurin, A.; Rautenberg, C.; Steiner, G.; Habicher, W. D.; Salzer, R. *J. Mol. Struct.* **2001**, *503*, 563.

(15) Moreira, W. C.; Dutton, P.; Aroca, R. *Langmuir* **1995**, *11*, 3137.

from the metal surface, in agreement with the short-range effect of SERS.² In fact the bands appearing in the Raman spectrum of the solid at 1601 cm^{-1} (which correspond to the benzene $\nu(\text{C}=\text{C})$ vibrations), at 1459 cm^{-1} (attributed to the $\delta(\text{CH})$ of the *tert*-butyl groups), at 1124 cm^{-1} (ascribed to the $\delta(\text{CCH})$ motions in the *tert*-butyl groups), and that at 810 cm^{-1} (due to the $\rho(\text{CH})$ ring motion) almost disappeared or strongly decreased in the SERS spectrum (Figure 2c). The band at 1441 cm^{-1} , which has a high percentage of contribution from the $\delta(\text{CH})$ mode of the ethyl portion linked directly to the nitrogen atom, is still observable in the SERS spectra due to the relative proximity of this group to the surface.

No SERS spectrum was obtained from PYR neither in the free colloid (Figure 2b), even at concentrations of PAHs higher than 10^{-7} M, nor when PYR was added to Ag nanoparticles functionalized with 9-ethylanthracene-methyl-dithiocarbamate (DTA; Figure 1, inset), used as the control in this experiment (Figure 2a). The spurious bands observed in Figure 2b correspond to the residual citrate, while the band at 229 cm^{-1} is due to the different ionic species that may be adsorbed on the surface.¹⁷ On the contrary, when the PYR solution was added to the DTCX-functionalized Ag nanoparticles (Figure 2d), intense Raman bands of PYR can be seen because of the formation of the DTCX/PYR complex. The analysis of the SERS bands in the complex reveals strong changes in both the host and the ligand Raman spectra. For instance, the DTCX band at 966 cm^{-1} becomes more intense than that at 1022 cm^{-1} , while the thioureide band shifts from 1514 cm^{-1} to 1517 cm^{-1} . These changes are attributed to a relative increase of bidentate DTCX-metal complexes (Figure 3d) induced by the interaction with PYR, leading to a higher

double bond of C–N (Figure 3b) and a subsequent strengthening of the host–metal interaction in the presence of the ligand.

The pyrene bands in the complex with DTCX, which are better seen in the difference spectrum of Figure 2e, only displayed changes in the relative intensity of the bands in comparison to the Raman spectrum of solid pyrene (Figure 2f). For instance, an increase of the in-plane bands at 1627 and 590 cm^{-1} was seen. Thus, from this result, we have deduced that the most probable host–guest interaction mechanism is based on a π – π stacking interaction where PYR adopts a perpendicular orientation with respect to the surface.

In conclusion, the self-assembling monolayer functionalization of metal SERS surface by using DTCX derivatives is a very promising research line in the detection of pollutants at trace concentrations. This work made possible a proper combination of interesting technological applications: a powerful spectroscopy technique such as SERS, the electronic properties of nanostructured metals, the molecular size-selective recognition of CX, and the strong chelating properties of the DT group toward the metal surface in the detection of PAHs.

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Supporting Information Available: Synthesis of DTCX. This material is available free of charge via the Internet at <http://pubs.acs.org>. LA062266A

(16) Leyton, P.; Domingo, C.; Sanchez-Cortes, S.; Campos-Valette, M.; Diaz, G.; García-Ramos, J. V. *Vib. Spectrosc.*, in press.

(17) Sanchez-Cortes, S.; García-Ramos, J. V. *J. Raman Spectrosc.* **1998**, *29*, 365.