SURFACE-ENHANCED RAMAN SCATTERING OF QUINACRIDONE QUINONE PIGMENT EMPLOYING CALIXARENES AS DISPERSIVE CAVITANDS

E. del Puerto, S. Sánchez-Cortés, J.V. García-Ramos and C. Domingo

1Instituto de Estructura de la Materia, CSIC, Serrano 121, 28006 Madrid, SPAIN, elena@iem.cfmac.csic.es

Surface-enhanced Raman spectroscopy (SERS) is an extremely high sensitive analytical technique, which has recently began to be used in the detection and characterization of natural organic pigments employed in Artworks since antiquity \cite{1}. On the other side, synthetic organic pigments -predominantly azo pigments, phthalocyanines and quinacridones \cite{2}- have been mostly used as artist’s materials since the 1950s. They have frequently eluded consistent identification in the museum laboratory, and confident high sensitive and selective analytical methods for their detection are required. Fresh results report the application of Laser Desorption Mass Spectrometry (LDMS), complemented with FTIR and EDS, to identifying several synthetic pigments in artworks of the collection of the Philadelphia Museum of Art \cite{3}. Aiming to add effective new detection methods for such elusive organic pigments, we are investigating the capabilities of SERS spectroscopy. In this sense, preliminary studies of the SERS characterization of Quinacridone quinone QAQ (CI 73920), are here presented.

QAQ is a molecule integrated by five condensed rings with amine and carbonyl groups which originate hydrogen bond intermolecular interactions. Such interactions are responsible of its insolubility, then, these pigments are usually dispersed, for example, in ionic liquids. In this work we have tested calixarenes as dispersing agents of QAQ, with two goals referred to its SERS detection: 1) the dispersion of the pigment in aqueous colloidal system and 2) the approach of QAQ to the metal surface employed in SERS. Calixarenes are synthetic cyclooligomers which have a cup like shape with a defined upper and lower rim and a central ring \cite{4}. They are used as cavitand molecules to host/disperse the ligand, and we have previously reported their successful application to the SERS detection of traces of Polycyclic Aromatic Hydrocarbons, PAHs \cite{5}.

Raman spectrum of the solid QAQ is shown in Fig. 2a, together with the SERS spectrum of QAQ solved in concentrate sulphuric acid, using hydroxylamine silver colloids as Raman-enhancer substrate (Fig.2.b.). The disappearance in SERS of bands at 1667 and 1589 cm\(^{-1}\) in the Raman spectrum of the solid sample (carbonyl group stretching vibrations) and the appearance of bands at 1274 cm\(^{-1}\) and 1147 cm\(^{-1}\) (aromatic \(\delta\) COH and \(\delta\) OH coupled to aromatic \(\nu\)CO), suggest that an enolization of the carbonyl groups occurs at these extreme acidic conditions, thus changing the chemical structure of the original pigment.

We have developed a different approach to get SERS spectra of QAQ in silver colloids using calixarenes, and avoiding the chemical changes induced by acidic solution. The host ability towards QAQ of a series of calixarenes with different sizes of the central ring (eight and four aryl moieties) and different upper and lower rims (Fig. 1) has been evaluated. Main test point in the evaluation is the relation R= I(SERS band of
QAQ at 1519 cm⁻¹ / (νAg-Cl band of the colloid at 230 cm⁻¹). R can be related to the capability of the calixarenes in approaching the QAQ to the metal surface.

The SERS spectra of QAQ dispersed in calixarenes, normalized to the νAg-Cl band of the colloid (not displayed in the spectra), are given in Fig. 2 c-e. They show similar spectral profiles although changes in intensities are observed. Figure 3 compares the R value for the different calixarenes employed, which follows: Calix8 > DCEC > TCEC > CE-NO₂ > TOHC. This means that the SERS intensity depends on the affinity of QAQ towards the calixarene host, as well as on the binding strength of the host towards the metal surface. Therefore, the structure of the upper and the lower rims, and the size of the cavity are both important to determine the above affinities.

Figure 1. Chemical structures of the calixarenes employed in this work. Upper substitution: p-tert-butyl groups, unless other given. CE: carboxethoxy group. D: di. T: tetra.

Figure 2. a) Raman spectrum of QAQ in the solid state (b) QAQ SERS spectrum in sulphuric solution. SERS spectra of QAQ with (c) CE-NO₂ (d) TCEC (e) Calix8 (f) TOHC (g) DCEC. Excitation at 514 nm. *Contribution of SERS bands of calix.

Figure 3. R (1519 cm⁻¹ band) value (see text for definition) for the different calixarenes.


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