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SERS SPECTRA OF MONO AND BISPHTHALOCYANINE COMPLEXES DEPOSITED ON Ag AND Au SUPPORTS

Key words: phthalocyanine complexes, surface-enhanced Raman spectroscopy, magnesium, lutetium

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ABSTRACT

In this letter, we present a study of surface-enhanced Raman spectra of thin layers of phthalocyanine (Pc) complexes deposited on Ag and Au rough surfaces. The materials of this work are MgPc (monophthalocyanine) and the asymmetrical lutetium bisphthalocyanine $(tBu)_4PcLuPcCl_8$ (Pc'LuPc") under three oxidation states. Enhancement of specific bands is observed depending on the surface and the oxidation state. SERS signatures of neutral, oxidised and reduced $Pc'LuPc''$ are identified.

INTRODUCTION

Surface-enhanced Raman scattering (SERS) is a spectroscopic method used to intensify the Raman spectra of molecules and polymers adsorbed at metallic surfaces. The enhancement effect is strongly dependent on the metal, the surface roughness, and the π -electron polarisability. Minute amounts of substances can be analysed that way, and also weak vibrational modes may be considerably enhanced [1]. In the past, Raman spectra of porphyrins [2,3] and phthalocyanines [4-7] were presented in the literature but few studies have been carried out using SERS [8]. In this paper we present SERS results on a monophthalocyanine MgPc and a lutetium asymmetrical bisphthalocyanine under different oxidation states.

These compounds were deposited on silver and gold surfaces. In MgPc, the Mg cation sits in the plane of the macrocycle and the molecule is centrosymmetrical (D_{4h}). In $\text{Pc}'\text{LuPc}''$ the lutetium cation is sandwiched between two differently substituted unplanar macrocycles. This results in a molecular symmetry loss (C_s) increasing the number of Raman active modes. The average distance between the macrocycles is less than the van der Waals radius of an aromatic carbon and therefore, a π - π interaction occurs. It is, nevertheless, limited by a 45° twist of the macrocycles. In $\text{Pc}'\text{LuPc}''$ each of the benzene rings of the first macrocycle Pc' is substituted with a tertiobutyl ammonium group (tBu). The benzene units of the second macrocycle Pc'' are substituted with two chlorine atoms. We have tried to link qualitatively the changes occurring in SERS spectra to the electron affinity of these systems. We find that the spectra differ considerably depending on the supporting metal. This allows identifying the oxidation states and getting more insight on the electronic delocalisation.

EXPERIMENTAL

The magnesium phthalocyanine was synthesised using a classical approach [9]. The asymmetrical bisphthalocyanine $\text{Pc}'\text{LuPc}''$ has been prepared following a method already published [10]. The oxidised bisphthalocyanine $[\text{Pc}'\text{LuPc}'']\text{SbCl}_6$ was prepared by a reaction of the neutral compound with phenoxathiinum

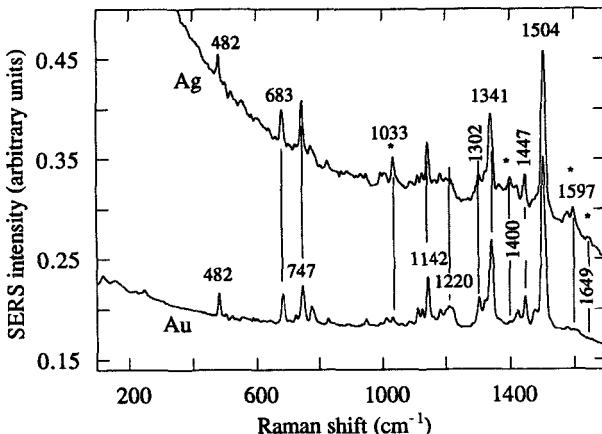


FIG. 1. SERS spectra of the MgPc monophthalocyanine recorded on silver and gold supports. Stars indicate enhanced lines on the Ag support.

hexachloroantimonate, in CH_2Cl_2 ; the reduced form $[\text{Pc}'\text{LuPc}"]\text{NBu}_4$ was obtained by addition of a 40% aqueous solution of Bu_4NOH . The redox reactions were followed by UV-visible spectrophotometry. Solutions of MgPc and $(t\text{Bu})_4\text{PcLuPcCl}_8$ in dichloromethane (0.1 and 0.2 percent in weight) were uniformly spread on 1 cm^2 rough silver and gold surfaces, and the solvent was evaporated. Raman spectra were recorded using a Fourier-transform spectrometer operating with a 1064 nm laser line. This near-IR wavelength eliminates any fluorescence that might occur with other excitation energies.

RESULTS

1-MgPc

In this compound, the SERS spectra on silver and gold differ slightly and are in fact very similar (Fig. 1). However, the Ag surface reveals enhanced bands at $1033, 1400, 1597, 1649\text{ cm}^{-1}$. Common bands occur at $482, 683, 747, 1142, 1220, 1302, 1341, 1447$ and 1504 cm^{-1} . We note that SERS spectra are able to enhance

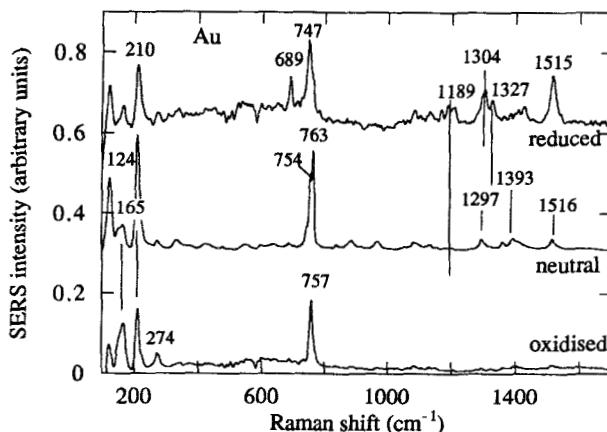


FIG. 2. SERS spectra of the asymmetrical bisphthalocyanine $(tBu)_4PcLuPcCl_8$ recorded on the gold surface.

bands, which were masked by fluorescence or hardly detectable in conventional Raman spectroscopy (at 1302, 1341, 1447 and 1597 cm^{-1}) [11,12].

2- $(tBu)_4PcLuPcCl_8$

Figs. 2-3 displays six SERS spectra on the two metal supports, corresponding to the three possible oxidation states of the bisphthalocyanine. In the reduced form, the best spectrum has been recorded on gold (Fig. 2). Strong enhancement of the lines at 689, 1189, 1304, 1515 cm^{-1} is observed. The main line at 747 cm^{-1} on the Au surface is shifted towards higher wavenumbers when the compound is on the Ag surface: 756 cm^{-1} . In the neutral form, the spectrum recorded on the Ag surface (Fig. 3) is of better quality although very similar to that taken on the Au surface.

In the oxidised form, the spectrum from the Ag surface reveals numerous lines above 800 cm^{-1} that are absent in the Au surface. There are additional drastic differences: the line at 757 cm^{-1} on Au corresponds to a doublet at 755-763 cm^{-1}

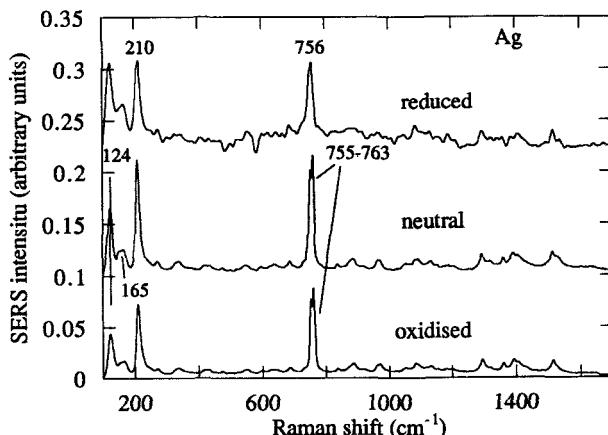


FIG. 3. SERS spectra of the asymmetrical bisphthalocyanine $(t\text{Bu})_4\text{PcLuPcCl}_8$ recorded on the silver surface.

on Ag and the lines at 165 and 274 cm^{-1} are considerably enhanced at the Au surface.

The SERS spectra of asymmetrical $(t\text{Bu})_4\text{PcLuPcCl}_8\text{MgPc}$ differs completely from that of MgPc. High frequency bands between 1000 and 1600 cm^{-1} are enhanced in MgPc whereas in $(t\text{Bu})_4\text{PcLuPcCl}_8$ enhanced lines lie in the low frequency region (between 100 and 800 cm^{-1}).

DISCUSSION AND CONCLUSION

The experiments above described show strong spectral discrepancies when the materials are deposited onto two different metallic surfaces. The experimental set of data obtained with a specific support also helps to discriminate the different oxidation states of the bisphthalocyanine. The data may be discussed as follows. On the one hand, it is well known that phthalocyanines are high-density π -electrons macrocycle systems. Since the macrocycle can either be a donor or an acceptor of electrons, this electronic density may be modulated by substituting a

functionalised group at the isoindole units. For instance, in our case, $(t\text{Bu})_4$ groups for the donor, and 8 Cl for the acceptor. On the other hand, lanthanide bisphthalocyanine sandwiched complexes ($\text{Pc}'\text{LuPc}''$) are known to exhibit π - π interactions between the two macrocycles. These properties are for example responsible of the luminescence quenching. The most interesting chemical character of $\text{Pc}'\text{LuPc}''$ is the presence of a single electron delocalised on the whole molecule which leads to the actual formula $\text{Pc}^2\text{Lu}^{\text{III}}\text{Pc}^{\bullet-}$ [13]. In the asymmetrical bisphthalocyanine $(t\text{Bu})_4\text{PcLuPcCl}_8$ we expect that a localisation of the electron might take place on one of the macrocycles. In principle, this electron affinity can be probed by Raman spectroscopy.

The distinction between neutral, reduced, and oxidised forms in $(t\text{Bu})_4\text{PcLuPcCl}_8$ is easily achieved using intrinsic spectral tracers obtained from the SERS spectra on gold (Fig. 2). In fact every Raman-active line of this data set provides a criterion for ascertaining the oxidation state. The frequency of the more intense line is shifted from 747 cm^{-1} in the reduced form to 757 cm^{-1} in the oxidised form. Note that in the neutral form, this line splits into two bands at 754 - 763 cm^{-1} . This particular line is supposed to stem from the chlorine-substituted macrocycle. We may interpret this result as an internal redox process where one of the macrocycles ($(t\text{Bu})_4\text{Pc}$) donates an electron to the other macrocycle (PcCl_8), thus inducing stiffening of a characteristic bond in PcCl_8 . During this electron transfer, we note the enhancement of the lines at 689 cm^{-1} and above 1300 cm^{-1} for the reduced compound and an increase of the lines at 165 and 274 cm^{-1} in the oxidised system. These lines may therefore be ascribed to the acceptor and to the donor, respectively. Moreover, the unshifted low-frequency lines at 124 , 165 , and 210 cm^{-1} undergo drastic intensity changes connected to the electron transfer. The intensity ratio $I(165)/I(210)$ increases in the oxidised material, whereas the ratio $I(124)/I(210)$ decreases. In summary, we find that asymmetrical bisphthalocyanine complexes are extremely amenable to SERS spectroscopy. In this case, detection of weak vibrational lines and occurrence of specific tracers to

discriminate the oxidation state of the macrocycles are the main advantages of SERS spectroscopy over conventional Raman techniques [12]. The main result is that selective SERS enhancements are drastically dependent on the metal surfaces and oxidation states of these systems.

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