pared according to modifications of the published procedures and exhibited melting or boiling points and spectral data that agreed satisfactorily with those reported in each case. The chlorosilanes employed in these syntheses were used as received from Petrarch Systems or Aldrich.

Nanosecond laser flash photolysis experiments were carried out using the pulses from a Lumonics TE-861M excimer laser filled with F_2/Kr/He (248 nm, ca. 12 ns, 80–120 mJ) or N_2/He (337 nm, 6 ns, ca. 3 mJ) and a microcomputer-controlled detection system that has been described elsewhere.[14] All laser samples were continuously deoxygenated with bubbling nitrogen. Solutions of **1** and **7** were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was 0.8 ($1.7-2 \times 10^{-4}$ M for **1**; ca. 0.002 M for **7**). The disilane solutions were flowed continuously through a 3 × 7 mm quartz flow cell, supplied by a calibrated 100-mL-capacity reservoir. Quenchers were added to the reservoir by microliter syringe as aliquots of standard solutions in dry acetonitrile. Oxygen quenching studies were carried out using a Matheson 600 gas proportioner to regulate the composition of oxygen/nitrogen mixtures, which were then bubbled continuously through the solution contained in the reservoir. A value of 3.18×10^{-3} M for the concentration of oxygen in air-saturated isooctane[21b] was used to calculate the oxygen concentration for the various mixtures in this solvent.

Samples for laser flash photolysis of solutions of methyldiphenylsilane and triphenylsilane in 1:4 di-*tert*-butyl peroxide/isooctane were contained in 7 × 7 mm quartz cells. The concentrations of the two silanes were 0.125 and 0.068 M for Ph_2MeSiH and Ph_3SiH, respectively.

Steady-state photolyses of deoxygenated 0.005 M solutions of **1** in cyclohexane containing 0.1 M methanol were carried out using a Rayonet photochemical reactor equipped with 254-nm lamps and the unfocused pulses of the KrF excimer laser (248 nm) as excitation sources. Photoproducts were identified by GC/MS and by coinjection of the photolysates with authentic samples.

Acknowledgment. We thank Mr. F. Villella for technical assistance in the early stages of this work and the McMaster University Regional Centre for Mass Spectrometry for mass spectral determinations. We gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada.

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Reversible Adsorption on a Single Langmuir–Blodgett Monolayer

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Abstract: The reversibility of the adsorption of NO_2/N_2O_4 (NO_x) on a single Langmuir–Blodgett monolayer of phthalocyanine (Pc) complexes is demonstrated using surface-enhanced Raman scattering on Au island films. The effect of the adsorbate on the relative Raman intensity of characteristic vibrational fundamentals of the Pc molecule permits the monitoring of the kinetics and the nature of the small molecule–macrocycle interaction. The localization and strength of the interaction can be correlated with patterns observed in the change of the electronic and resonant Raman spectra in the series of Pc molecules. The approach presented in this work allows one to study, at a molecular level, the properties that control the adsorption of small molecules on Pc monolayers. The results are relevant to the general understanding of an adsorption process that has been demonstrated to have applications in the development of phthalocyanine-based gas sensors, and the use of Pc as a catalyst.

Introduction

It is known that the surface of crystals and thin solid films of phthalocyanine (Pc) and other organic macrocycles adsorb small gaseous molecules which strongly alter the electrical properties of the material.[1,2] The changes in the semiconducting and photoconducting properties of Pc materials due to adsorption are so dramatic that they may be the basis for the development of these materials as chemical sensors for gases.[3,4] For instance, Honeybourne and Ewen[1] have studied the effect of NO_2/N_2O_4 on CuPc and reported an increase of 6 orders of magnitude in conductance upon gas adsorption. Recently, Zhu and Petty[5] have reported a potential optical sensor for nitrogen dioxide based on copper tetra-*tert*-butylphthalocyanine (CuTTPc) using surface plasmon resonance on Ag. However, in the adsorption process the nature of the interaction between gas and phthalocyanine is not well known, and there is a need for experimental techniques that would permit the characterization of the Pc adduct. It should be pointed out that the problem of metalated Pc–small molecule interaction is also central to the electrocatalytic activity of Pc complexes[6] or the use of Pc complexes as catalysts.[7] Surface-enhanced (resonant) Raman scattering (SERS or SERRS[8]) and electronic absorption spectroscopy are powerful analytical techniques that contribute to characterize and monitor the nature of the interaction between an electron acceptor molecule and Pc derivatives laid down in the form of a single Langmuir-Blodgett (LB) monolayer. In the present report the reversible adsorption of NO_x on a single LB monolayer of H_2TTPc (metal-free tetra-*tert*-butylphthalocyanine), CuTTPc, and $YbPc_2$ (ytterbium bisphthalocyanine) monitored by SERRS is presented. The observations are rationalized in terms of effect of the NO_x–Pc interaction on the molecular properties of the Pc monolayer: the large delocalized π system (and changes in the electronic spectrum), the presence of pyrrole and azomethine groups in the macrocycle (and changes in the vibrational spectrum), and the electronic structure of the central metal atom.

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Experimental Section

Metal island films of Au, suitable for SERS, were prepared by the evaporation of 4 nm of Au at a rate of 0.05 nm/s onto a glass substrate held at 220 °C. The thicknesses were monitored by a XTC Inficon crystal oscillator. Glass slides (Corning 7059) were cleaned in hot chromosulfuric acid and made hydrophilic by treatment with sodium hydroxide or hydrophobic with dichlorodimethylsilane, respectively, as described by Mobius et al.,[9] and used as the substrate for monolayer transfer to bare glass. Stable LB monolayers of H_2TTPc were transferred to hydrophobic glass slides by Y deposition. Mixed monolayers of CuTTPc and $YbPc_2$ with arachidic acid (Pc:arachidic acid = 3:1) were transferred by X and Y deposition, respectively, on the hydrophilic treated slides. The arachidic acid acts as a lubricant for the monolayer on water subphase and improves the transfer ratio to near unity for these materials.[10] A single LB monolayer of mixed Pc (3:1 ratio) was transferred to a SERS active substrate by Z deposition. The monolayers were prepared in a Lauda Langmuir film balance equipped with an electronically controlled dipping device, Lauda Filmlift FL-1. The molecules were spread from a chloroform solution onto aqueous subphase maintained at 15 °C. Monolayers were compressed to 15 mN/m and transferred at a constant rate of 6 mm/min.

Films were treated with NO_x (Matheson Co. lecture bottle) by placing the samples in the reaction vessel and evacuating to a pressure of 300 Pa. The gas was then admitted until 600 Pa, and the sample was exposed to gas for 1 min before reevacuation. Desorption studies consisted of evacuating the exposed film at 3 Pa for 3 h.

Spectra Physics Model 2020 Kr^+ was used. Typical spectral bandpass and laser power were 4 cm^{-1} and 50 mW, respectively. A rotating cell was used in all Raman measurements to prevent laser damage of the LB sample. Raman shifts were measured with a Spex-1403 double spectrometer. Electronic absorption spectra were recorded on a Response UV–vis spectrophotometer interfaced with and IBM PC microcomputer.

Results and Discussion

The spectral characterization of H_2TTPc and $YbPc_2$ has been previously reported.[10–12] The CuTTPc sample was kindly provided by Prof. Luk'yanets from the Organic, Intermediates and Dyes Institute of the Academy of Sciences of the USSR in Moscow, and its spectroscopic characterization will be reported separately. In a preliminary report[13] we have shown that LB monolayers of $YbPc_2$ were prepared and transferred to a SERS active substrate containing Ag-coated Sn spheres. Rough Ag surfaces produce an electromagnetic enhancement of the inelastic scattering in the region of plasmon absorption[14] that included the 514.5- and 488-nm laser lines. However, silver reacts with the NO_x and the rough Ag film was tarnished, and thereby adsorption studies could be carried out only on thick Ag films. In contrast, the structure and plasmon absorption of gold island films were not affected by the NO_x gas. Therefore, Au films provided a SERS active substrate with a plasmon absorption in resonance with the Q electronic band of the Pc macrocycle. Three SERRS experiments were carried out for each Pc monolayer. First, a vibrational characterization of the LB monolayer using the 647.1-nm laser line which is in resonance with the Q-band and the plasmon absorption of the Au film were carried out. Second, SERRS of the same sample was recorded after being exposed to NO_x gas, and finally the recovery of the monolayer was monitored. Adsorption–desorption studies were also carried out by electronic absorption spectroscopy on LB monolayers deposited on glass. In the latter experiment five LB monolayers of CuTTPc, three LB monolayers of $YbPc_2$, and a multilayer assembly (8 LB monolayers) of metal-free H_2TTPc were used. In order to correlate structure with NO_x–Pc interaction it is important to remember that the absorption spectrum of crystals and films of Pc derivatives has shown to be very sensitive to small changes in structure that may also be induced by solvents.[15]

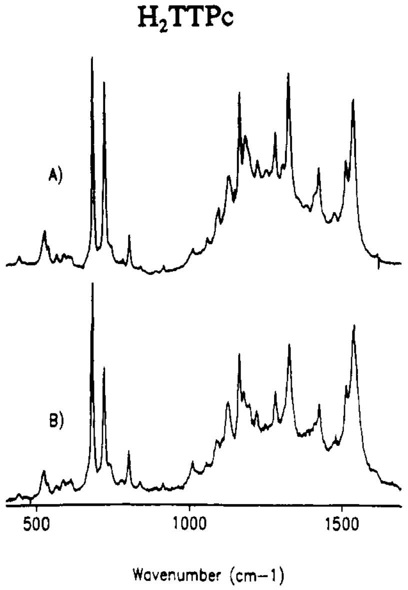

Figure 1. SERRS spectra of one mixed LB of H_2TTPc on a Au island film (A) and after exposure to NO_x gas (B).

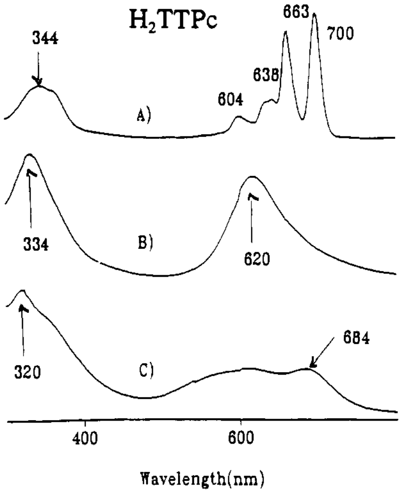

Figure 2. Electronic spectra of H_2TTPc in solution (A), eight LB monolayers on glass (B), and eight monolayers exposed to NO_x (C).

The results for H_2TTPc are illustrated in Figure 1. The SERRS reference spectrum of one LB monolayer (mixed with arachidic acid in a 3:1 ratio) on Au is only slightly different from that of the same monolayer exposed to NO_x. Frequencies were observed with the same value in both spectra, and only minor changes in Raman relative intensities can be seen in Figure 1. The electronic spectra are shown in Figure 2, where the Q-band of the H_2TTPc in solution was included for comparison. The absorption spectrum of eight LB layers gave the unique single peak for the Q-band of H_2TTPc unlike the double peaks seen in solution and crystals.[10] The spectrum may be considered typical of ordered domains of transferred Pc monolayers consisting of stacks of cofacially oriented molecules due to π–π aromatic interactions. However, the absorption spectrum of the latter sample exposed to NO_x showed two bands. The first maximum was in correspondence with the original LB spectrum, and the second with the maximum of the solution spectrum. The change in the electronic structure would decrease the overall intensity of the SERRS spectrum but would not cause major changes in the relative intensities of the observed fundamentals. The observation may be explained by physisorption of the NO_2 molecule near the

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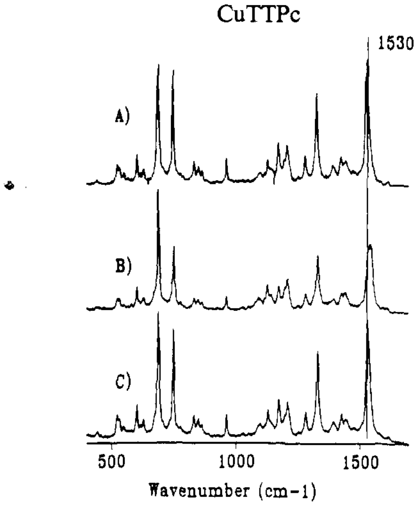

Figure 3. SERRS spectra of one mixed LB of CuTTPc on a Au island film (A), after exposure to NO_x (B), and after desorption of NO_x (C).

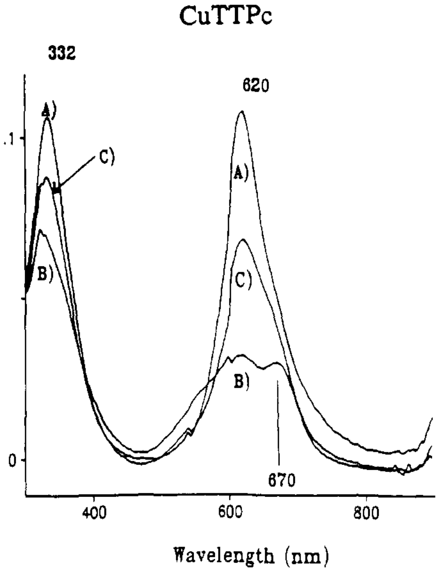

Figure 4. Electronic spectra of five LB monolayers of CuTTPc (A), after adsorption (B) and desorption (C).

center of the macrocycle with enough binding energy to cause disruption of the π–π aromatic interactions. The NO_2 self-desorbs at room temperature and normal pressure, and the Pc electronic spectrum of stacks is recovered.

The reversible adsorption of NO_x on mixed LB monolayers of CuTTPc is shown in Figure 3. The top spectrum (A) is the SERRS of one LB monolayer of CuTTPc on a 4-nm Au film. The middle spectrum (B) corresponds to the same LB monolayer on Au exposed to NO_x gas, and the Raman spectrum at the bottom (C) is the LB monolayer on Au after being evacuated. It is known that the observed Raman spectrum, and particularly resonance Raman scattering (RRS) of Pc molecules owe their simplicity to the large relative intensity with which macrocycle vibrations are detected. For instance, in Figure 3 the band at 1530 cm^{-1} can be assigned to a stretching vibration with a strong contribution from the pyrrole moiety. The NO_x–Pc interaction decreases the relative intensity of this Raman band. Since Raman intensities are the results of the change in the polarizability with the corresponding normal mode, a polarization (or loss) of the electronic density about the nuclei involved in the vibration should result in a loss of scattering intensity. The spectral evidence may be interpreted as a polarization of the pyrrole moieties by the NO_x acting as an electron acceptor. However, the interaction is not strong enough to cause a shift of the observed vibrational frequencies, as is usually observed for direct intermolecular complexes. It is, thereby, possible to postulate an indirect interaction of the adsorbate with the Pc macrocycle through the metal. The latter qualitative interpretation is also supported by the electronic spectra of monolayers presented in Figure 4. The NO_x adsorption seems to break the π–π aromatic interactions that formed the Pc stacks. Desorption of the gas at room temperature for 3 h allowed a complete recovery of the electronic properties of the CuTTPc monolayers. A close comparison of the results for H_2TTPc and CuTTPc seems to indicate that the pyrrole groups are better protected from the NO_x attack by the protons than the Cu^{2+} cation. Conversely, the adsorption of NO_x would occur more readily in metalated Pc than in metal-free Pc. A diagram of the proposed intermolecular interaction for CuTTPc with the NO_2 molecule is given in Figure 5. Indirect support for the proposed adduct structure was provided by EPR measurements in toluene solution. In the experiment the EPR signal of the CuTTPc solution became silent after addition of NO_x gas. The latter result suggests a direct NO_2–metal interaction.

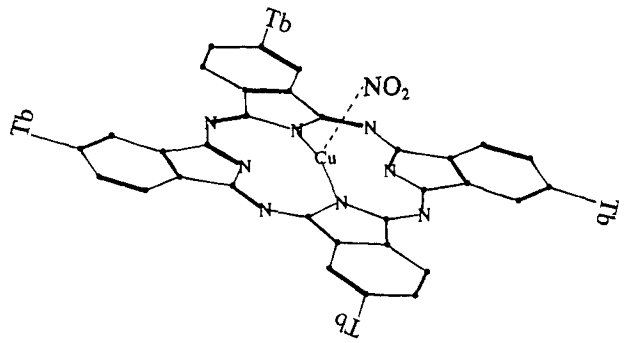

Figure 5. Molecular diagram for the CuTTPc interaction with one molecule of NO_2 gas. The tetra-*tert*-butyl group is represented by Tb.

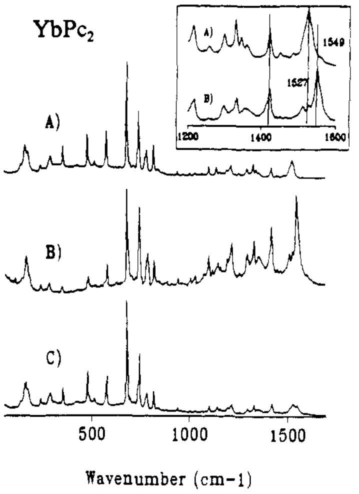

Figure 6. SERRS spectra of one LB monolayer of $YbPc_2$ on Au (A), after adsorption of NO_x (B), and recovery after gas desorption (C). Pyrrole frequency region is expanded in the inset.

The third material was a bis-Pc where one central atom is coordinated to two Pc macrocycles. From a simple description of energy levels,[16] the monoelectronic energies of the Pc aromatic system would be of higher energy than the corresponding orbitals of the Yb central atom, which may allow a flow of electron density from the Pc to the metal. The "molecular semiconductor"[16] could then transfer charge to an external electron acceptor (NO_2) that could be attached to the central metal atom (Yb). The SERRS spectra are shown in Figure 6. It can be seen that the NO_x produces a much more pronounced change in the relative intensities of the stretching frequencies of the macrocycle than in the previous two cases. Moreover, a weak band at 1549 cm^{-1} becomes the most prominent Raman band after the adsorption of NO_x. In Pc molecules of the C_{4v} symmetry, the pyrrole- and the aza-

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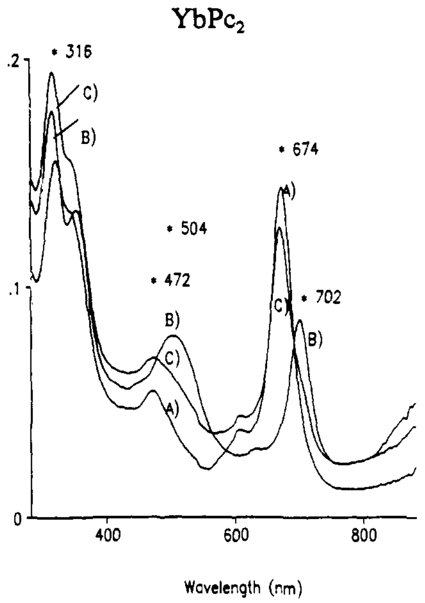

Figure 7. Electronic spectra of three LB monolayers of YbPc$_2$ on glass (A), after NO$_x$ adsorption (B), and gas desorption (C).

stretching vibrations are clearly observed with slightly different frequencies in the 1500-cm^{-1} region.[17] The latter is also observed in bis-Pc compound.[11] After the adsorption of NO$_x$ on the single Langmuir-Blodgett monolayer of YbPc$_2$, the relative intensity of the pyrrole stretching (1527 cm^{-1}) and the characteristic macrocycle vibrations was strongly decreased by the gas–Pc interaction. Conversely, the stretching vibration at 1549 cm^{-1} appears strong in the SERRS spectrum. The observations may be rationalized in terms of a highly localized NO$_x$–metal–macrocycle interaction which allows a decoupling of the aza-stretching vibration or bridging nitrogen atom. Notably, the resonant Raman effect enhances the intensity of molecular vibrations of the chomophore. Therefore, for π–π^* transitions the macrocycle vibrations are enhanced in the RRS as can be seen in Figure 5A. However, if the absorption has a large contribution from the N P_σ–π^* (a transition that according to various molecular orbital treatments is expected in the same spectral region), the vibrations of the bridge nitrogen group will be enhanced similar to what is seen in Figure 6B. The electronic spectra shown in Figure 7 suggest a charge-transfer interaction with enough loss of electronic charge in the macrocycle to cause the appearance of a second maximum in the Q-band spectral region. The latter absorption band has been identified in the literature as the oxidized form of the macrocycle.[18] Clearly, the NO$_x$–YbPc$_2$ interaction in the LB monolayer is the strongest in the series presented here. Similar preliminary results have been obtained in our laboratory for a series of lanthanide bis-Pc complexes. Nevertheless, the adsorption of NO$_x$ is reversible (see Figure 6) and the Pc$_2$ complexes may have potential applications as gas sensors. The work will continue in order to find a correlation between the molecular interactions of adsorption and changes in the electrical and photoelectrical properties of LB films.

Conclusions

Reversible adsorption of NO$_x$ on a LB monolayer of Pc molecules can be monitored by SERRS on Au island films, a technique that would allow quantitative kinetic studies. The polarization of the π-electronic system by the electron acceptor gas seems to depend on the central metal atom and particularly affects the intensity of the vibrations localized at the pyrrole moieties. In the case of the YbPc$_2$ molecule, the changes in the Raman intensities of the stretching frequencies of the pyrrole and aza groups were parallel by the appearance of a new band in the electronic spectrum, indicating the formation of a complex where charge has been transferred from the macrocycle to the electron acceptor molecule. It was concluded that the strength of the NO$_x$–Pc interaction increases from H$_2$TTPc to CuTTPc to YbPc$_2$. The role of the electronic structure of the metal in the charge-transfer complex formation in a series of MPc$_2$ complexes is presently under investigation.

Acknowledgment. Financial support from NSERC, Canada, is gratefully acknowledged.

Registry No. H$_2$TTPc, 35984-93-1; CuTTPc, 39001-64-4; YbPc$_2$, 83534-87-6; NO$_x$, 11104-93-1; Au, 7440-57-5.

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