# *Articles*

# Langmuir-Blodgett Films of Asymmetrically Phenyl-Substituted Lutetium Bisphthalocyanines. Spectroscopy and Gas-Sensing Properties

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Langmuir-Blodgett (LB) films of two new asymmetrically substituted phenylbisphthalocyanines, tetra-3,4,5,6-phenyllutetium bisphthalocyanine ($PcLuPc^{4Ph}$) and tetra-3,4,5,6-phenyl-tetra-3′,4′,5′,6′-phenyllutetium bisphthalocyanine ($Pc^{4Ph}LuPc^{4Ph}$) have been prepared. The spectroscopic studies include UV-vis, FTIR, and surface-enhanced Raman scattering (SERS) techniques. Electrochromism in LB films, formed on ITO glass, was observed with an electrode potential ranging from −0.4 to +1.2 V in 0.1 M $KClO_4$ aqueous solution. Similar color changes were observed after chemical oxidation-reduction and acid-base treatment. The presence of substituents and the lowering of the symmetry when compared to the parent compound $LuPc_2$, increases the number of IR-active modes particularly in the 600-780 $cm^{-1}$ region. The interaction of the LB films with $NO_x$ was followed using SERS on gold islands substrates.

## Introduction

The properties and applications of lanthanide bisphthalocyanines ($LnPc_2$), especially lutetium derivatives, have been studied extensively.[1] This is due to the fact of that these molecules can be used as catalysts,[2] in electrochromic devices,[3,4] and in photovoltaic materials.[5,6] These molecules also have a promising potential application in gas-sensing devices.[7]

It is well-known that thin films of $LuPc_2$ and their derivatives exhibit electrochromism with at least three distinct colors when a potential ranging from −1.5 to +1.5 V is applied.[8-10] Moreover, when these bisphthalocyanines are exposed to electron-donor or electron-acceptor gas molecules such as $NH_3$ or $NO_x$, respectively, they undergo changes in their spectroscopic properties. Shifts in the electronic absorption and Raman peak maxima are observed, and these changes are consistent with the shifts observed for electrochemically reduced and oxidized forms.[11-14] In a previous paper, our group described the spectroscopic and electrochromic behavior of Langmuir-Blodgett (LB) films of several lutetium bisphthalocyanine derivatives including the symmetrically substituted octa-3-bromo-octa-5-*tert*-butylbisphthalocyanine and the symmetrically substituted octa-4-phenylbisphthalocyanine. The presence of electron-withdrawing substituents in the macrocycle ring increased the rate of desorption for chemisorbed electron-acceptor molecules.[9] Until now few papers have reported the properties of asymmetrically substituted lanthanide bisphthalocyanine derivatives LB films.[10,15]

In the present work the spectroelectrochemistry of Langmuir-Blodgett films of asymmetrically substituted lutetium bisphthalocyanine molecules is studied. These complexes were the tetraphenyl-substituted derivative tetra-3,4,5,6-phenyllutetium bisphthalocyanine

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(1) *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1989, 1990, 1993; Vol. 1-3.

(2) Lever, A. B. P. *Adv. Inorg. Radiochem.* **1965**, *7*, 27.

(3) Besbes, S.; Plichon, V.; Simon, J.; Vaxiviere, J. *J. Electroanal. Chem.* **1987**, *237*, 61.

(4) Rodríguez-Méndez, M. L.; Aroca, R.; De Saja, J. A. *Chem. Mater.* **1993**, *4*, 1017.

(5) Tang, C. W. *Appl. Phys. Lett.* **1986**, *48*, 83.

(6) Perrier, G.; Dao, L. H. *J. Electrochem. Soc.* **1987**, *105*, 1148.

(7) Snow, W.; Barger, W. R. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1989; p 345.

(8) Aroca, R.; Clavijo, R. E.; Jennings, C. A.; Kovaks, G. J.; Duff, J. M.; Loufty, R. O. *Spectrochim. Acta* **1989**, *45A*, 957.

(9) Rodríguez-Méndez, M. L.; Aroca, R.; De Saja, J. A. *Chem. Mater.* **1993**, *5*, 933.

(10) Liu, Y.; Shigehara, K.; Hara, M.; Yamada, A. *J. Am. Chem. Soc.* **1991**, *113*, 440.

(11) Honeybourne, C. L.; Even, R. J. *J. Chem. Phys. Solids.* **1983**, *44*, 833.

(12) Battisti, D.; Aroca, R. *J. Am. Chem. Soc.* **1992**, *114*, 1201.

(13) M'Sadak, M.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1985**, *189*, 99.

(14) Pondaven, A.; Cozien, Y.; L'Her, M. *New. J. Chem.* **1991**, *15*, 515.

(15) Jennings, C. A.; Kovacs, G. J.; Aroca, R. *Langmuir* **1993**, *9*, 2151.

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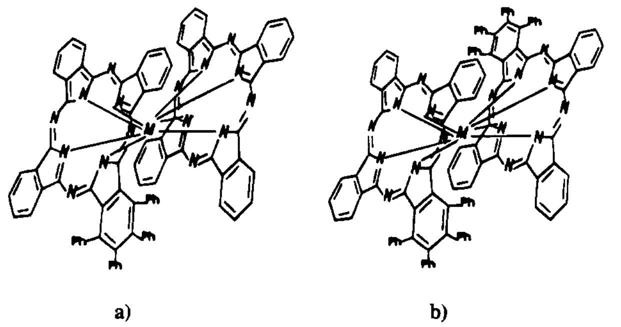

a) b)

**Figure 1.** (a) Structure of the asymmetrical tetraphenyl-substituted lutetium bisphthalocyanine PcLuPc$^{4\mathrm{Ph}}$. (b) Structure of the asymmetrical octaphenyl-substituted lutetium bisphthalocyanine Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$.

(PcLuPc$^{4\mathrm{Ph}}$, Figure 1a) and the octaphenyl-substituted tetra-3,4,5,6-phenyltetra-3′,4′,5′,6′-phenyllutetium bisphthalocyanine (Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$, Figure 1b). The electronic absorption spectra of solutions and LB films were recorded and the SERS spectra of LB films were obtained on Au island films. The electrochromic behavior of both complexes and the reversible adsorption of electron-acceptor molecules such as NO$_x$ by these bisphthalocyanine films were also investigated.

## Experimental Section

The synthesis involves heating a mixture of tetra-3,4,5,6-phenylphthalonitrile and unsubstituted phthalonitrile with lutetium acetate in relation 8:4:1 molar. The temperature was gradually raised from 100 to 270–280 °C, where it remained for 2.5 h. A mixture of different bisphthalocyanines was obtained and separated by column chromatography on aluminum oxide. Then, a purification by TLC using Silufol plates was performed. After a second TLC, the sample was further purified by sublimation. The complete synthesis and purification procedures for PcLuPc$^{4\mathrm{Ph}}$ and Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ materials have been recently described.[16]

Isotherms and LB films were prepared in a KSV 5000 Langmuir–Blodgett trough equipped with a Wilhelmy plate to measure the surface pressure. Monolayers were transferred with Z type deposition to 7059 Corning glass slides, ITO glass (sheet resistivity of 50 $\Omega$/cm$^2$) and glass slides covered with Au island films. Transfer was performed at a constant speed of 1 mm/min and at a constant surface pressure of 20 mN/m. Glass slides were pretreated with chromosulfuric acid in order to obtain a hydrophilic surface. Au island films were made by vacuum evaporation of 4 nm of Au onto glass slides kept at 200 °C. The mass thickness of these Au films was monitored by an XTC Inficon quartz crystal oscillator. Surface-enhanced Raman scattering (SERS) spectra were obtained using a Spectra Physics Series 2000 Ar$^+$ ion laser pumping a Spectra Physics 375 B rhodamine dye laser. The wavelength of the emitted laser light was 612.2 nm. Raman shifts were measured with a Dilor multichannel spectrophotometer. UV–vis spectra were recorded with a PU 8620 Philips UV–vis spectrophotometer. A Bomem Model MB155 FTIR spectrophotometer was used to obtain the IR spectra. Films were exposed to NO$_x$ in a chamber at 300 Pa and room temperature for 3 min. Desorption studies were carried out by comparing the spectrum recorded immediately after the exposure to another one recorded 24 h later. Electrochemistry was carried out in a PAR Model 263 potentiostat galvanostat using a conventional three-electrode cell. LB films on ITO glass were used as the working electrode, Pt wire as the counter electrode, and Ag/AgCl electrode as the reference electrode. KClO$_4$ (0.1 M) was used as electrolyte. A two-window cuvette was used to obtain the in situ UV–vis spectra for different applied voltages.

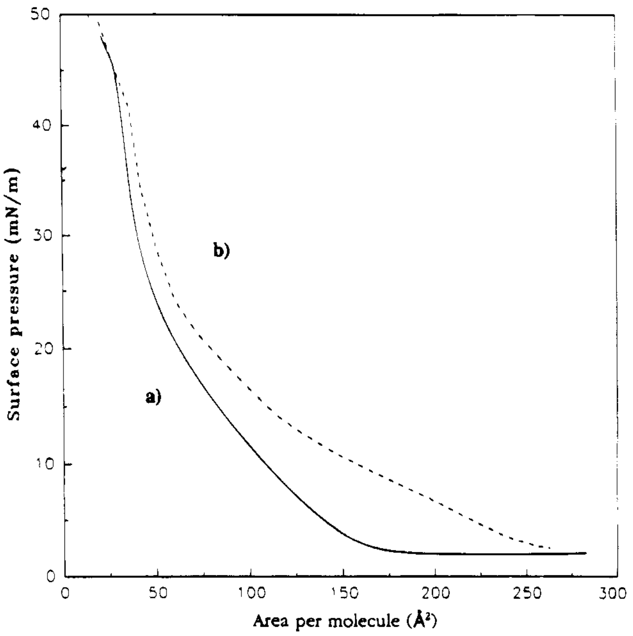

**Figure 2.** Surface pressure $\pi$ as a function of the molecular area Å per molecule for (a) PcLuPc$^{4\mathrm{Ph}}$ and (b) Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$.

## Results and Discussion

In LnPc$_2$, the structural data have shown that the cation is at the center of two Pc ligands facing each other in a staggered arrangement. It is reasonable to assume that a similar stable configuration would be found for the lutetium complexes under study (PcLuPc$^{\mathrm{Ph}}$ and Pc$^{\mathrm{Ph}}$LuPc$^{\mathrm{Ph}}$, Figure 1).

Isotherms were recorded by spreading chloroform solutions of PcLuPc$^{4\mathrm{Ph}}$ and Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ onto a deionized (MilliQ) water surface kept at 20 °C. After solvent evaporation, the phthalocyanine molecules were compressed by a barrier at a constant speed of 1 mm/min until the film pressure rose sharply, indicating that a continuous surface film was formed. Reproducible isotherms (surface pressure versus molecular area) were obtained for both molecules (Figure 2). In the case of the tetraphenyl substituted compound, the limiting area obtained from the slope of the curve was 70 Å$^2$; for Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ a limiting area of 87 Å$^2$ was found. The isotherms showed similar features to those described for other lanthanide bisphthalocyanine derivatives, especially those with bulky peripheral groups.[4,17] These results suggest a tilted edge-on configuration for the solid phase of the floating monolayer.

**UV–Visible Characterization.** The maxima corresponding to the electronic absorption peaks for the chloroform solutions and for LB assemblies of PcLuPc$^{4\mathrm{Ph}}$ and Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ are listed in Table 1.

The electronic spectra of the chloroform solutions of the samples under study presented two main absorption peaks; a band at 317 nm is seen for both PcLuPc$^{4\mathrm{Ph}}$ and for Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$, and a strong Q band is observed at 661 and 666 nm, respectively. For both complexes, the Q-band region was similar for LB films and for chloroform solutions. The Q bands in the solid-state spectra are broader than in solution, and they are red shifted. The band near 460 nm, which has been associated with

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(16) Tomilova, L. G.; Gorbunova, Y. G.; Rodríguez-Méndez, M. L.; De Saja, J. A. *Mendeleev Commun.* **1994**, *14*, 127.

(17) Bonosi, F.; Ricciardi, G.; Lelj, F. *Thin Solid Films* **1994**, *243*, 310.

**Table 1. Characteristic Electronic Absorption Wavelengths of PcLuPc$^{4Ph}$ and Pc$^{4Ph}$LuPc$^{4Ph}$ Phthalocyanines**

| PcLuPc$^{4Ph}$ | | Pc$^{4Ph}$LuPc$^{4Ph}$ | |
|---|---|---|---|
| solution | LB film | solution | LB film |
| 317 | 316 | 317 | 304 |
| 353 | 350 (sh) | 340 (sh) | 346 |
| 458 | 466 | 455 | 465 |
| 577 (sh) | | 581 (sh) | |
| 597 | 604 (sh) | 602 | 605 |
| 661 | 667 | 666 | 670 |

a free-radical structure of rare-earth bisphthalocyanines,[18] was present in both compounds.

As it has been previously reported, the chloroform solution of the symmetrically substituted eight phenyllutetium bisphthalocyanine has its absorption maximum at 676 nm.[9] The latter value should be compared with a Q-band maximum at 666 nm for Pc$^{4Ph}$LuPc$^{4Ph}$, 661 nm for PcLuPc$^{4Ph}$, and 658 nm for LuPc$_2$. The results indicate a small spectral shift directly connected with the substitution pattern. The symmetrical substitution of eight phenyl groups would slightly increase the aromaticity and, consequently, shifts the Q band to lower energy than in Pc$^{4Ph}$LuPc$^{4Ph}$. Similarly, Pc$^{4Ph}$-LuPc$^{4Ph}$ shows the transition at a lower energy than PcLuPc$^{4Ph}$.

A recent publication has studied the UV–vis spectroscopy of asymmetric monophthalocyanines and tetraazaporphyrins (TAP).[19] In accord with these results, if compared to the parent molecule (LuPc$_2$ with $C_{4v}$ symmetry), the lower symmetry of our compounds would give rise to a shift in the position and probably a small splitting of the Q band.

The changes observed in the position and shape of the Q bands obtained in our case are in accordance with the expected behavior for these molecules.

**Electrochromism, Redox Properties, and Acid–Base Behavior.** Cyclic voltammetry (CV) of PcLuPc$^{4Ph}$ and Pc$^{4Ph}$LuPc$^{4Ph}$ LB films (10–20 monolayers) on ITO glass in contact with 0.1 M KClO$_4$ aqueous solution was carried out, from −0.4 to +1.2 V at a scan rate of 20 mV/min. A cyclic voltammogram of a PcLuPc$^{4Ph}$ film is shown in Figure 3, where three peaks can be observed at $E_{1/2} = -0.05$ V, $E_{1/2} = 0.45$ V and $E_{1/2} = 0.92$ V. Pc$^{4Ph}$-LuPc$^{4Ph}$ showed two peaks, at $E_{1/2} = -0.06$ V and at $E_{1/2} = 0.46$ V. The values of the half-potentials obtained for the first oxidation peaks are similar to those previously reported for the symmetrically substituted eight phenylbisphthalocyanine (0.5 V for the first oxidation).[9] After 500 sweeps, reproducible voltammograms were obtained.

Absorption spectra were recorded in situ at different applied voltages. Figure 4 shows that the oxidized and reduced species of PcLuPc$^{4Ph}$ are clearly differentiated by a shift in the Q band. At 0.0 V, the unoxidized starting material shows a Q band at 667 nm, the oxidized material at 0.8 V presents two maxima at 690 and 505 nm and the reduced material at −0.2 V has a maximum at 618 nm. Similar results were found for Pc$^{4Ph}$LuPc$^{4Ph}$, where the starting material shows a Q band at 670 nm. At 1.2 V, the two characteristic bands at 714 and 490 nm of the oxidized form were observed. The blue form present at −0.3 V shows a maximum at 624 nm.

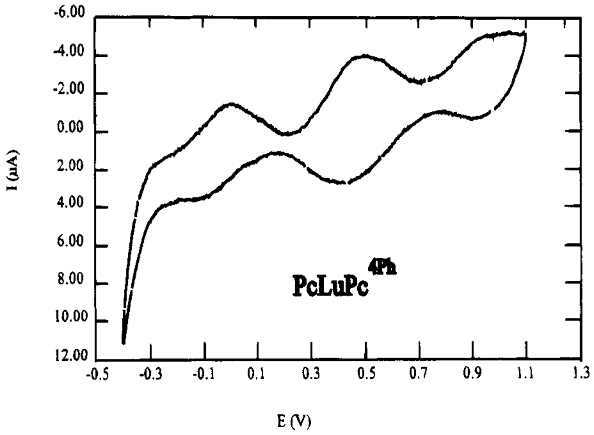

**Figure 3.** Voltammogram of a PcLuPc$^{4Ph}$ LB film (15 monolayers) on ITO glass in contact with 0.1 M KClO$_4$ aqueous solution.

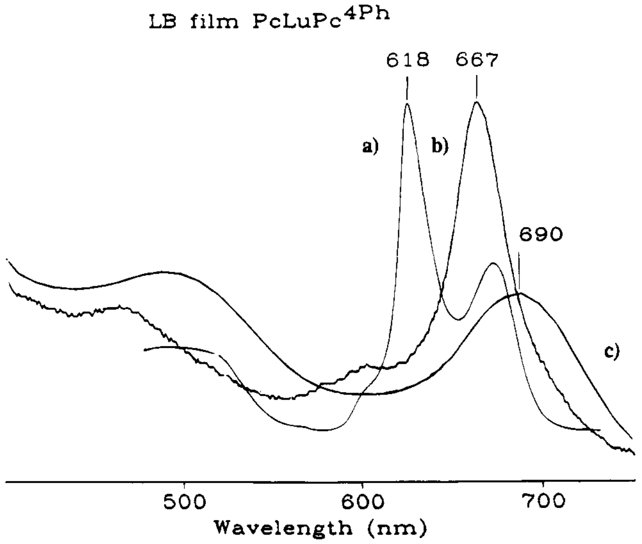

**Figure 4.** In situ UV–vis spectra of a PcLuPc$^{4Ph}$ LB film (15 monolayers) on ITO glass at different potentials: (a) −0.2, (b) 0.0, (c) 0.8 V.

For comparison purposes, the electrochromism was also studied in cast films. Similar results were found using cast films, but in this case, the peaks obtained were broader and few repeatable sweeps could be performed.

The UV–vis spectra of the red and blue forms could also be obtained by chemical oxidation and reduction. For example, when a typical oxidant such as Br$_2$ was added to PcLuPc$^{4Ph}$ and Pc$^{4Ph}$LuPc$^{4Ph}$ in chloroform solution, the Q bands of both complexes were shifted to longer wavelengths. Similarly, the effect of a typical reducing agent such as hydroquinone on PcLuPc$^{4Ph}$ and Pc$^{4Ph}$LuPc$^{4Ph}$ in chloroform solution was to reduce the starting green forms producing electronic absorption spectra in full agreement with the spectrochemical curves. These oxidation–reduction processes were fully reversible. For instance, upon the addition of hydroquinone to the oxidized red form, the blue form of the molecules was detected. It should be pointed out that color changes of the two compounds in chloroform solutions were also achieved by the addition of acids such as diluted HNO$_3$ or HCl or bases such as of

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(18) Markovitsi, D.; Trau-Thi, T.; Simon, J. *J. Chem. Phys. Lett.* **1987**, *137*, 107.

(19) Kobayashi, N.; Ashida, T.; Osa, T.; Konami, H. *Inorg. Chem.* **1994**, *33*, 1735 and references therein.

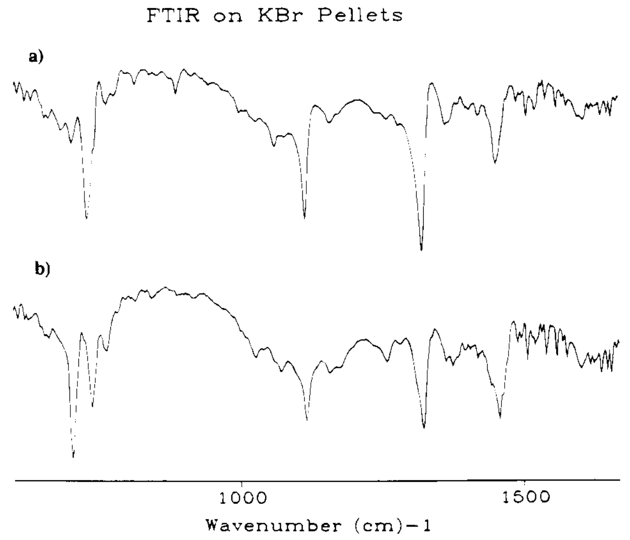

**Figure 5.** FTIR spectra of KBr pellets of (a) PcLuPc$^{4\mathrm{Ph}}$ and (b) Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$.

triethylamine.

**Vibrational Analysis of PcLuPc$^{4\mathrm{Ph}}$ and Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ LB Assemblies.** The infrared spectra of both materials were obtained in KBr pellets. The SERS spectra of single monolayers on a Au island was recorded to complete the vibrational characterization.

The SERS spectra of PcLuPc$^{4\mathrm{Ph}}$ and Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ monolayers on Au island films were obtained with the 612.2 nm line. A comparison between the spectra under study and those of the previously reported unsubstituted LuPc$_2$[8] and the symmetrical octaphenyl-substituted LuPc$_2^{\mathrm{Ph}}$ derivative,[9] permits the identification of characteristic vibrational frequencies of PcLuPc$^{4\mathrm{Ph}}$ and Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$, e.g., the macrocycle breathing vibration at 680 cm$^{-1}$, the phthalocyanine ring stretching at 744 cm$^{-1}$, pyrrole stretching at 1335 cm$^{-1}$, and the most intense band, corresponding to the pyrrole C−N stretching at 1530 cm$^{-1}$. The vibrational frequencies in the SERS spectra of PcLuPc$^{4\mathrm{Ph}}$ and Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ show similar wavenumbers when compared to that of the unsubstituted lutetium bisphthalocyanine and the symmetrical phenyl-substituted bisphthalocyanine.

The FTIR spectra of the PcLuPc$^{4\mathrm{Ph}}$ and Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ molecules showed the four characteristic molecular vibrations of the bisphthalocyanine molecules: 727, 1114, 1322, and 1452 cm$^{-1}$ for PcLuPc$^{4\mathrm{Ph}}$; and 734, 1114, 1322, and 1457 cm$^{-1}$ for Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ (Figure 5). The main differences between these spectra and the corresponding one for the unsubstituted LuPc$_2$ are in the 600−800 cm$^{-1}$ region. The PcLuPc$^{4\mathrm{Ph}}$ bisphthalocyanine showed six vibrational modes in the 600−800 cm$^{-1}$ region: 680, 690, 698, 727, 760, and 775 cm$^{-1}$, and the Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ showed five bands: 680, 699, 734, 761, and 779 cm$^{-1}$. In this region, unsubstituted LuPc$_2$ has only one intense band at 727 cm$^{-1}$ corresponding to the C−H out-of-plane mode. Additional bands in that region have been previously reported for the symmetrically substituted eight phenylbisphthalocyanine. This molecule shows four bands at 671, 695, 749, and 782 cm$^{-1}$. The increase in the number of IR active modes in the 600−800 cm$^{-1}$ region should be related to the presence of the phenyl groups, specially the band at 695 cm$^{-1}$ present in all the phenyl-substituted lutetium bisphthalocyanines studied, which is a characteristic benzene vibration.

**Table 2. Characteristic Vibrational Raman and IR Frequencies of PcLuPc$^{4\mathrm{Ph}}$ and Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ Phthalocyanines**[a]

| PcLuPc$^{4\mathrm{Ph}}$ | | Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ | | |
|---|---|---|---|---|
| IR | SERS | IR | SERS | description |
| | 480 (w) | | 481 (m) | |
| | | | 486 (m) | |
| | 580 (m) | | 578 (m) | |
| | | | 654 (m) | |
| | | | 667 (w) | |
| 680 (w) | 681 (s) | 680 (w) | 680 (s) | macrocycle breathing |
| 690 (w) | | | 687 (sh) | |
| 698 (w) | | 699 (s) | | phenyl groups |
| 727 (s) | 736 (sh) | 734 (s) | 736 (sh) | C−H wagging |
| 740 (sh) | 744 (s) | | 744 (s) | Pc ring |
| 760 (w) | | 761 (w) | | |
| 775 (w) | 777 (sh) | 779 (w) | | |
| | 784 (m) | | 784 (m) | |
| 811 (w) | 819 (m) | 809 (w) | 816 (m) | |
| 885 (m) | | | | C−H wagging |
| | 942 (w) | | 955 (w) | C−H bending |
| 998 (w) | | | | |
| 1027 (w) | | 1027 (w) | | |
| 1062 (w) | | | | C−H bending |
| 1079 (w) | | 1072 (w) | | C−H bending |
| 1114 (s) | 1106 (w) | 1114 (s) | 1108 (w) | C−H bending |
| | 1143 (w) | | 1140 (w) | |
| 1159 (w) | | 1157 (m) | | C−H bending |
| | | 1178 (sh) | | C−H bending |
| | 1198 (sh) | | | C−H bending |
| | 1217 (m) | | 1217 (m) | |
| 1261 (w) | | 1259 (m) | | C−H bending |
| 1281 (w) | | 1282 (w) | | C−H bending |
| | 1304 (w) | | 1304 (w) | |
| 1322 (s) | 1335 (m) | 1322 (s) | 1335 (w) | isoindol stretch |
| 1365 (m) | 1350 (w) | 1363 (m) | 1350 (w) | |
| 1369 (w) | | 1374 (m) | | isoindol stretch |
| 1384 (w) | | | | |
| 1405 (w) | 1410 (m) | | 1410 (m) | |
| 1423 (w) | 1426 (s) | 1419 (w) | 1426 (s) | isoindol stretch |
| | | 1442 (sh) | | isoindol stretch |
| 1452 (s) | | 1457 (s) | | isoindol stretch |
| | | | 1515 (sh) | |
| | 1530 (s) | | 1531 (s) | pyrrole stretch |
| 1606 | 1606 (w) | | 1602 (w) | benzene stretch |

[a] (s) strong; (m) medium; (w) weak; (sh) shoulder.

The PcLuPc$^{4\mathrm{Ph}}$ and the Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ IR spectra differ in the relative intensities of the two most intense vibrations; the band at 698 cm$^{-1}$ is the most intense band in the Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ bisphthalocyanine IR spectrum. However, for the PcLuPc$^{4\mathrm{Ph}}$ the most intense band is the C−H wagging at 727 cm$^{-1}$.

The asymmetry introduced in the eight phenyl Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ molecule introduced by the phenyl group substitution may be discussed by comparison with the previously reported symmetrically substituted eight phenyl bisphthalocyanine. The band at 749 cm$^{-1}$ present in the asymmetrically substituted molecule is shifted to 734 cm$^{-1}$ in Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$. A change in the relative intensities of the two most intense bands is also observed. Spectral differences are probably due to lower symmetry of the molecule and also ring distortions. A complete list of the observed fundamentals is given in Table 2.

**Adsorption of NO$_x$ on PcLuPc$^{4\mathrm{Ph}}$ and Pc$^{4\mathrm{Ph}}$LuPc$^{4\mathrm{Ph}}$ LB Films.** LB films on glass and on Au island films were exposed to NO$_x$ at a pressure of 300 Pa for 3 min. The changes due to the adsorption of the gas were monitored by both UV−vis and SERS spectroscopy.

In the UV−visible spectrum of the PcLuPc$^{4\mathrm{Ph}}$, the exposure to NO$_x$ caused a decrease in the intensity of the strong absorption at 667 nm, and the new spectrum

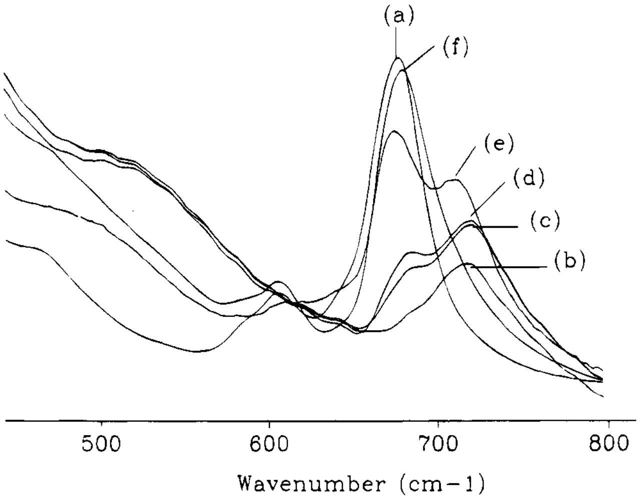

**Figure 6.** Electronic spectra of Pc$^{4Ph}$LuPc$^{4Ph}$ LB on glass (a) before NO$_x$ adsorption, (b) after NO$_x$ absorption, (c) 5 min later, (d) 10 min later, (e) 15 min later, (f) 20 min later.

is in correspondence with that of the electrochemical formation of the bisphthalocyanine oxidized form. Similarly, when the Pc$^{4Ph}$LuPc$^{4Ph}$ film is exposed to NO$_x$ the Q band is observed at 714 nm (red form) as can be seen in Figure 6b. In both cases the typical band of the red form at 495 nm for PcLuPc$^{4Ph}$ and 490 nm for Pc$^{4Ph}$LuPc$^{4Ph}$ was also recorded as shown in Figure 6b. The spectroscopic results clearly indicate a strong interaction of the adsorbate with the LB film (chemisorption), where the electron-acceptor molecule has decreased the electron density (oxidation) of the macrocycle.

The effects of gas adsorption in the SERS spectra of single monolayers of PcLuPc$^{4Ph}$ and Pc$^{4Ph}$LuPc$^{4Ph}$ LB were analogous and are illustrated in Figure 7 for Pc$^{4Ph}$LuPc$^{4Ph}$. The polarization caused by the electron-acceptor gas in the central macrocycle results in lower intensities for vibrations corresponding to the Pc ring. For example, as can be seen in Figure 7, the macrocycle breathing at 680 cm$^{-1}$ and Pc ring stretching at 744 cm$^{-1}$ were strongly affected by the NO$_x$ chemisorption. The adsorption of NO$_x$ also decreases the intensity of the pyrrole vibrations observed in the 1300–1500 cm$^{-1}$ region.

In summary, the electronic and the SERS spectra of LB films showed that chemisorption of NO$_x$ takes place where the electron-acceptor molecule strongly polarizes the macrocycle. UV–visible and SERS spectra also demonstrate that the chemisorption is reversible and that the total desorption time for the LB film is ca. 20 min (Figure 6).

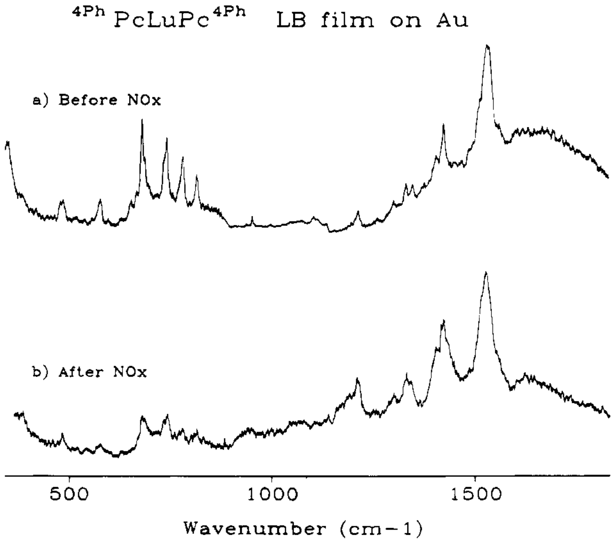

**Figure 7.** SERS spectra of one LB monolayer of Pc$^{4Ph}$LuPc$^{4Ph}$ on Au (a) before and (b) after adsorption of NO$_x$.

When cast films instead of LB films were exposed to the gas, the desorption rate decreased and at least 2 h was needed for the recovery of the film.

## Conclusions

Langmuir monolayers and LB films of asymmetrical phenyl-substituted bisphthalocyanines have been prepared. The electrochromic properties (blue-green-red forms) of both materials in LB films on ITO substrates have been demonstrated. The two peaks corresponding to oxidation reduction processes were clearly detected in the cyclic voltammograms of the LB films deposited on ITO glass and were stable under consecutive sweeps. The presence of phenyl groups and the reduced molecular symmetry produces shifts in the Q bands of the UV–vis spectra and an increase in the number of IR-active modes in the 600–800 cm$^{-1}$ spectral region. The chemisorption of the electron acceptor molecule polarizes the PC ring and decreases the Raman intensity of the Pc vibrations.

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