Electrochromic and Gas Adsorption Properties of Langmuir–Blodgett Films of Lutetium Bisphthalocyanine Complexes

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The electrochromic behaviour, spectroscopic properties and gas chemisorption of ultra thin films of lutetium octa-4-phenyldiphthalocyanine ($LuPc_2^{Ph}$), and the lutetium octa-3-bromo-octa-5-*tert*-butylphthalocyanine ($LuPc_2^{tBr}$) are reported. Electrochromism was observed for Langmuir–Blodgett (LB) and films cast onto indium tin oxide (ITO) coated glass electrodes in aqueous $KClO_4$ solution. Mixed LB films supported on ITO glass electrodes were more stable to repetitive cycling than cast films. Films of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ were sensitive to electron-acceptor gases as observed by the changes in the electronic absorption spectra and the surface-enhanced resonance Raman scattering (SERRS) spectra. The presence of electron-withdrawing bromine atoms in the phthalocyanine ring increased the rate of desorption for chemisorbed electron-acceptor molecules.

Introduction

The objective of the present work was to examine the effect of the macrocycle substituents on the electrochromic, spectroelectrochemical, and gas adsorption properties of substituted lutetium bisphthalocyanine complexes. The synthesis, elemental analysis and the electronic solution spectra of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ have been reported.[1] Our group has recently documented the reversible adsorption of nitrogen dioxide onto LB films of phthalocyanine derivatives and rare-earth bisphthalocyanines complexes.[2] The interaction between gas and phthalocyanine may find applications in the field of chemical sensors. In this respect, the rate of gas adsorption and desorption on LB films of bisphthalocyanines is an important issue. The present work is the first attempt to investigate the effect of an electron withdrawing substituent (Br) in the reversible adsorption of electron-acceptor molecules. LB films of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ were best formed by mixing the phthalocyanine (Pc) complex with arachidic acid. The addition of a small percentage of fatty acid to Pc lubricates the otherwise rigid Pc monolayer and facilitates the process of monolayer transfer to solid substrates. A parallel investigation of the spectroelectrochemistry of the LB films was also performed. In previous communications, the spectroscopic and the electrochromic behaviour of LB films in the series of lanthanide (Ln) bisphthalocyanine complexes with *tert*-butyl substituents ($LnPc^t_2$) were discussed.[3-5] Similar studies were conducted for films of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ with the perception that oxidation–reduction properties of both molecules could assist the understanding of the chemisorption mechanism.

Experimental Section

Samples of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ were kindly provided by Dr. L. Tomilova from the Institute of Organic Dyes and Intermediates in Moscow. Mixed LB films were prepared from chromatographically pure Pc samples and puriss grade arachidic acid (Fluka). Mixed monolayers were spread from chloroform or toluene solutions onto an aqueous subphase consisting of deionized and filtered water whose resistivity was 18.2 MΩ cm^{-1}. Monolayers and LB films were prepared in a Lauda Langmuir film balance equipped with the Lauda Filmlift FL-1 electronically controlled dipping device. The subphase was maintained at 15 °C and the monolayer was transferred at a constant surface pressure of 15 mN/m. Monolayers were transferred to Corning 7059 glass slides (previously cleaned with hot chromosulfuric acid), ITO conducting glass, and ZnS substrates. Monolayers were also deposited onto glass slides coated with 4 nm of gold (SERS substrate) and 110 nm of silver (RAIRS substrate).

Cyclic voltammetry (CV) was recorded in the conventional three electrode cell on an EG&G Princeton Applied Research Model 173 potentiostat galvanostat interfaced to an IBM-PC microcomputer. A platinum wire and Ag/AgCl electrode were used as the counter and reference electrodes respectively. A 0.1 M solution of $KClO_4$ was used as the electrolyte, and it was degassed with high-purity argon prior to all electrochemical measurements. A two window cuvette was used to obtain the *in situ* electronic absorption spectra. Electronic absorption spectra were recorded on a Response UV–visible spectrophotometer interfaced to an IBM-PC computer. Electrochromic experiments were conducted on LB films supported on ITO conducting glass.

LB films of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ were placed in a 0.4 dm^3 glass cell and exposed to Br_2 (Liquid Carbonic) and NO_x (Aldrich Chemical). The cell was first evacuated to 310 Pa, and then gas was admitted until 600 Pa. Films were exposed to gas for 1 min. Under the present conditions the ratio of NO_x to phthalocyanine was about 9000:1 assuming ideal gas law and 1 nm^2/molecule.

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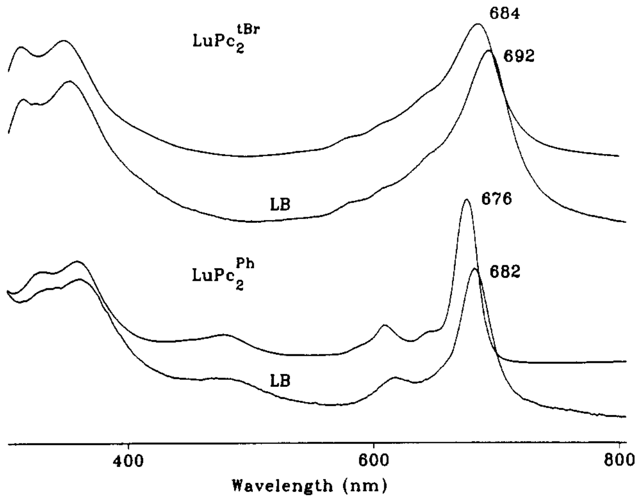

Figure 1. Electronic absorption spectra of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ in solution and LB film.

Table I

	solution	LB film	pellet
$LuPc_2^{Ph}$	330, 358, 480, 608, 646, 676	290, 360, 476, 618, 682	470, 618, 685
$LuPc_2^{tBr}$	313, 348, 684	314, 350, 692	312, 345, 691

A Spectra Physics Model 2020 Kr^+ ion laser operating at 647.1 nm was used for Raman excitation. Raman shifts were measured with a Spex-1403 double spectrometer and photon-counting electronics. Typical spectral bandpass and laser power were 4 cm^{-1} and 50 mW, respectively. Infrared spectra were measured in BOMEM DA3 FTIR spectrometer. EPR spectra of the solid material and solution (chloroform and toluene) were recorded at room and liquid nitrogen temperatures. The EPR spectra were recorded with Varian E-12 instrument. For data analysis, UV-vis, Raman, and IR files were imported to Spectra Calc software available from Galactic Industries Corp.

Results and Discussion

Sample Characterization. The EPR spectra confirmed the free-radical nature of the two Pc materials in this study. For instance the g value and the line width for $LuPc_2^{Ph}$(solid) measured at liquid nitrogen temperature were 2.004 and 6.0 G, respectively. Similarly, a $g = 2.000$ and a line width of 1.3 G was found for the solid sample of $LuPc_2^{tBr}$. Chloroform solutions of $LuPc_2^{tBr}$ produced $g = 2.005$ and a line width of 12.5 G at 298 K, and $g = 2.003$ with a line width of 6.5 G at temperatures near liquid nitrogen. In all cases, the g value for the phenyl derivative was slightly smaller than the g value for the bromine derivative. The intensity of the EPR signal in $LuPc_2^{Ph}$(solid) was almost three orders of magnitude stronger than that measured in the EPR spectrum of $LuPc_2^{tBr}$ (solid). The EPR data thus shows that both molecules have at least one unpaired electron in their structure, and they are free radicals as has been reported for a number of other bisphthalocyanines.

The absorption maxima (in nanometers) obtained from the electronic spectra of solution, of a KBr pellet and of LB films on glass for $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ are given in Table I. The spectra are illustrated in Figure 1.

The Q-band in the electronic spectrum of the LB film and KBr pellet of $LuPc_2^{Ph}$ was broadened and red shifted with respect to the toluene solution spectrum. $LuPc_2^{tBr}$ showed an asymmetric broad Q band at 684 nm which was also present in the solution spectra. Notably, the 480-nm band of $LuPc_2^{Ph}$, which was associated with a free radical structure of rare earth bisphthalocyanines,[6] was not observed in the spectra of $LuPc_2^{tBr}$. However, the EPR spectrum clearly demonstrated the existence of at least one unpaired electron in $LuPc_2^{tBr}$.

Table II

	E_a	E_c	ΔE	$E_{1/2}$
$LuPc_2^{Ph}$	0.44	0.67	0.23	0.55
$LuPc_2^{tBr}$	0.82	0.95	0.13	0.88
	0.98	1.17	0.19	1.07

Isotherms were obtained from chloroform solutions consisting of 2.38×10^{-5} M of $LuPc_2^{tBr}$ and 5.21×10^{-5} M of $LuPc_2^{Ph}$. Following the evaporation of the solvent, the insoluble monolayer for each of the two molecules was compressed at a rate of 0.3×10^{-2} nm^2 $molecule^{-1}$ s^{-1}. The surface pressure versus molecular area (π–A) isotherm of neat $LuPc_2^{Ph}$ material revealed the formation of a stable Langmuir monolayer with a limiting area of 0.65 nm^2/molecule. The limiting area would correspond to an edge-on organization of the molecules in the LB film. For $LuPc_2^{tBr}$, reproducible π–A isotherms were only obtained for the monolayer mixed with arachidic acid.

Electrochemistry and Electrochromism. LB films were prepared by transferring the floating layer to an ITO coated glass substrate. For electrochemical measurements, 10–20 mixed monolayers were transferred. Mixed layers (Pc:arachidic acid = 1:1 mole ratio) were used to achieve a near-unity transfer ratio for $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ monolayers. Cast films were prepared by spreading Pc solution onto the ITO surface followed by evaporation of the solvent. It is well-known that thin films of $LuPc_2$ exhibit electrochromism with five distinct colors (violet, blue, green, yellow-tan, and red) in the applied voltage range between −1.5 and 1.5 V.[7] Recently, Liu et al.[8] and Rodriguez-Mendez et al.[5] have described the electrochromic behaviour of LB films of rare earth metal bisphthalocyanine complexes. The CV for $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ in o-dichlorobenzene solutions showed two half-potentials at 0.12 and 0.61 V and 0.20 and 0.69 V, respectively. In solution, the two peaks in the CV were separated by 0.49 V. This separation value seems to be typical for rare-earth bisphthalocyanines.[8] The half potentials obtained for LB films of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ are listed in Table II.

$LuPc_2^{Ph}$ showed only one broad oxidation peak that was not resolved. However, the CV of $LuPc_2^{tBr}$ showed two well resolved peaks as illustrated in Figure 2. The LB film of $LuPc_2^{tBr}$ also showed an irreversible reduction peak at −1.08 V. As shown in Table II, the oxidation potential increases with the inductive effect of the bromine substituent. Similar CV curves were obtained for cast films, although the peaks were broader than in LB films. During the CV studies of cast films, differences were observed between the first and second CV. However, after several sweeps a reproducible CV was found. Both materials formed electrochemically stable mixed LB films. LB films of the neat $LuPc_2^{Ph}$ material were also stable to CV cycling.

For both materials, CV were obtained at different scan rates ranging from 5 to 500 mV/s. A linear relation between

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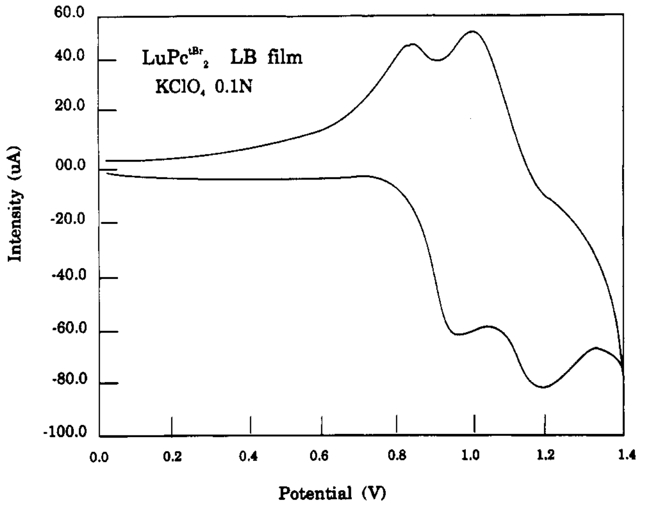

Figure 2. Cyclic voltammogram of an LB multilayer assembly of LuPc$_2$^{tBr} on ITO working electrode and Ag/AgCl reference electrode. The scan rate was 100 mV/s.

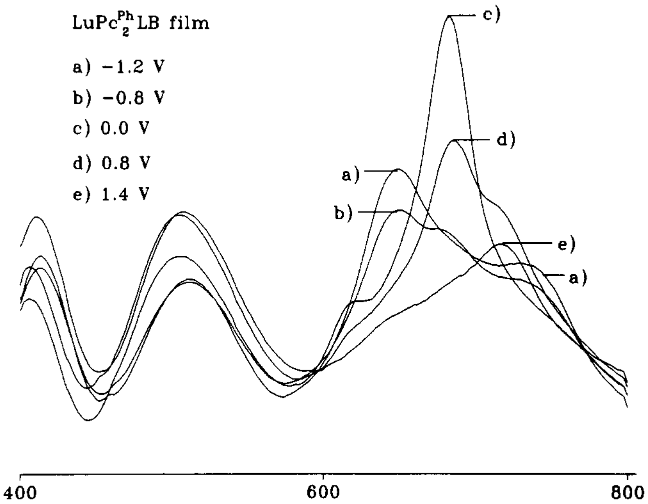

Figure 3. Electrochromism in the visible spectrum of an LB assembly of LuPc$_2$^{Ph} fabricated on an ITO electrode. (a) Reduced blue film. (d) Oxidized red film.

the intensity of the oxidation peak and the square root of the scan rate was observed for LB and cast films. At slow scan rates the separation between the anodic and the cathodic waves decreased and reached a constant value of 0.06 V, which corresponds to a one-electron process. To study the electrochromism (color changes) in LB films, the *in situ* electronic absorption spectra of the coated ITO transparent electrode were recorded. Both materials showed distinct color with the naked eye, and the films changed from blue to green, and green to red, when the applied potential was varied from −1.0 through 1.0 V. The *in situ* visible spectra recorded for LB films of both materials are shown in Figures 3 and 4. The stability of the electrochromic LB films was investigated by continuously monitoring the visible absorption spectrum and particularly the intensity of the Q band. After 150 cycles the absorbance value of the Q band showed a 5% reduction in the absorption maximum and no change to the band shape. In a similar experiment with cast films, a 7% decrease in the Q band absorbance maximum was observed between the first and the second scan.

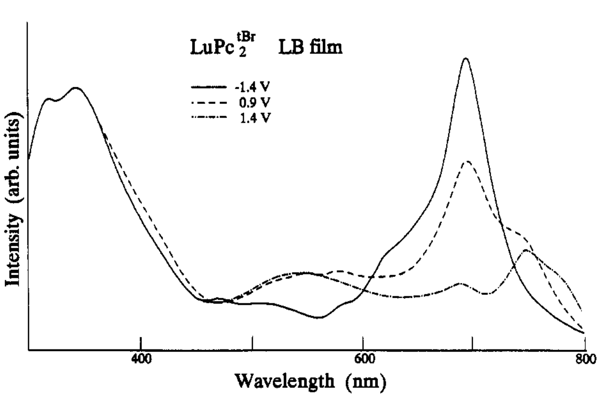

Figure 4. Visible spectra of an LB film of LuPc$_2$^{tBr} on ITO electrode recorded at different applied potentials.

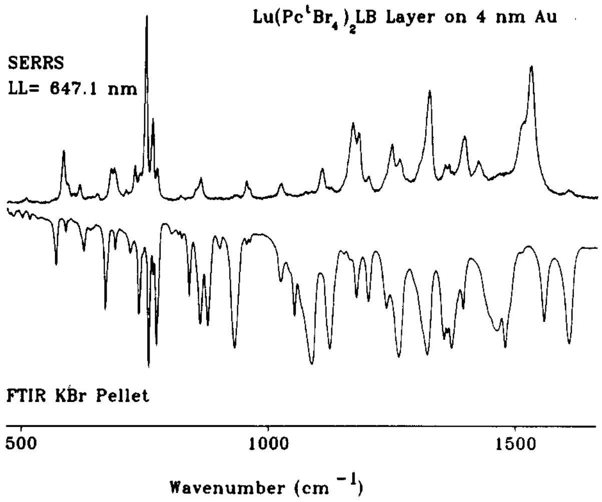

Figure 5. SERRS of a single mixed monolayer of LuPc$_2$^{tBr} on Au and transmission FTIR spectrum of a KBr pellet.

Infrared and Surface-Enhanced Raman Spectra. The vibrational characterization of both materials was carried out in KBr pellets and LB films. The transmission FTIR spectra of an LB film deposited on ZnS (10 monolayers on each face) was complemented with SERRS of a single monolayer on a Au island film. The infrared frequencies observed in the starting material (KBr pellet) were also observed in the LB film with only minor differences in relative intensities. To illustrate the results, the SERRS and transmission infrared spectra of LuPc$_2$^{tBr} are shown in Figure 5. The IR spectra of LuPc$_2$^{Ph} and LuPc$_2$^{tBr} differ considerably from the simple IR spectrum of the unsubstituted lutetium bisphthalocyanine.[10] The presence of substituents multiplies the number of infrared active modes due to lower symmetry and probably distortions in the Pc ring. The SERRS obtained for LuPc$_2$^{Ph} and LuPc$_2$^{tBr} were typical of a physisorbed monolayer. In an effort to determine the anisotropy in the LB film, reflection–absorption IR spectra (RAIRS) of LB films on 110 nm of smooth Ag were registered. There were no significant differences in the relative intensities seen in the transmission spectrum of LB films on ZnS and the corresponding RAIRS of the LB film on Ag. The LB films were therefore not anisotropic and the face-on or edge-on molecular alignments were not realized. Most likely, the organization consists of random molecular stacking with the molecular Pc ring forming a tilt angle with the substrate.

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Table III. Characteristic Vibrational Frequencies[a] of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$

$LuPc_2^{Ph}$		$LuPc_2^{tBr}$		interpretation
SERRS	IR	SERRS	IR	
583 m	585 w	583 m	588 w	benzene ring
	671 w	679 m	669 s	
686 vs		685 m	688 w	Pc breathing
	695 s			
			736 s	
744 s	749 vs	749 vs	756 vs	Pc ring
764 sh		762 s	764 sh	
781 m	782 m	772 m	772 s	
828 m	836 m		837 m	
		860 m	861 s	
	895 m		876 s	
	905 m		931 s	
		1025 w	1025 m	
			1053 m	
	1074 m		1087 s	Pc ring
1122 w	1114 m		1124 s	C–H bend(Pc)
		1168 s	1178 m	C–H bend(tb)
1203 w		1201 w	1202 m	
1248 vw		1248 m	1239 m	
1269 vw	1270 m	1263 m	1264 s	C–H bend(Pc)
1326 w	1320 s	1323 s	1322 s	pyrrole str
		1356 w	1355 s	C–H bend(tb)
			1370 s	C–H bend(tb)
	1407 m	1394 m	1394 m	isoindole str
	1451 m			phenyl str
	1463 s		1461 m	isoindole str
	1489 w		1479 s	isoindole str
1528 m		1528 s		pyrrole str
	1574 w		1558 m	benzene str
	1599 m			benzene str
	1608 m		1608 s	benzene str

[a] Strong (s), medium (m), weak (w), very (v), phthalocyanine (Pc), stretch (st), *tert*-butyl (tb).

Characteristic molecular vibrations of the Pc ring and substituent were clearly identified in both the FTIR and SERRS spectra. For instance, the most intense band in the SERRS spectrum of $LuPc_2^{Ph}$ at 686 cm^{-1} corresponds to the macrocycle breathing. Notably, the presence of the Br substituent decreases the electronic density of the macrocycle and overall intensity of the RRS spectrum. The macrocycle breathing was observed with middle relative intensity while the 749 cm^{-1} macrocycle ring vibration was the strongest Raman band (744 cm^{-1} in $LuPc_2^{Ph}$). Qualitatively, an increase in the dipole moment derivatives of $LuPc_2^{tBr}$ molecule is expected due to the Br groups. Correspondingly, a large number of the vibrational fundamentals showed infrared activity as shown in Figure 5. A list of the most characteristic vibrational frequencies, and their assignment is given in Table III.

Reversible Adsorption of Small Molecules by LB Films. In previous sections, the electrochromic properties of LB films of the new materials and their spectroscopic characterization were given. It was shown that the oxidation of the $LuPc_2^{tBr}$ and $LuPc_2^{ph}$ were characterized by a red shifted Q-band, which also produced red-colored films. In this section the interaction of the LB films with electron-acceptor molecules is described. First, it should be pointed out that the differences in electron density (at the center of the macrocycle) between $LuPc_2^{tBr}$ and $LuPc_2^{Ph}$, are mainly due to the presence of the Br groups. It was antcipated that a lower electron density in $LuPc_2^{tBr}$ would have limited the extent of charge transfer in the chemisorbed state with an electron-acceptor molecule. As a reference experiment, the EPR signal of $LuPc_2^{tBr}$ and $LuPc_2^{Ph}$ in toluene was monitored after adding nitrogen dioxide (NO_x). For both molecules the EPR signal disappeared following NO_x exposure.

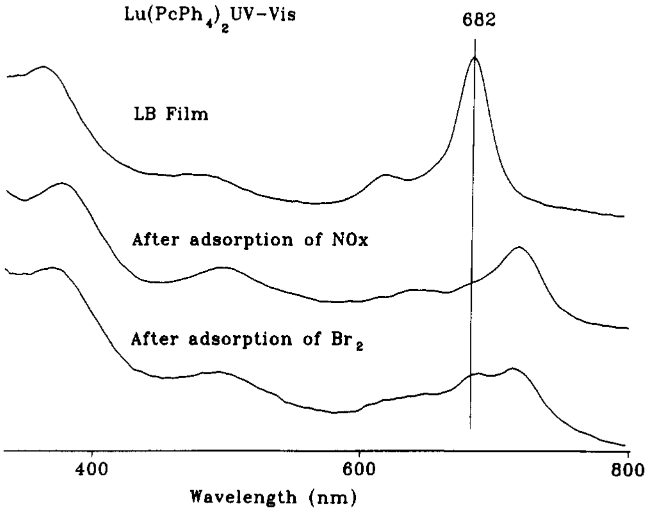

Figure 6. Electronic spectra of $LuPc_2^{Ph}$ LB on glass, after NO_x adsorption and after Br_2 adsorption.

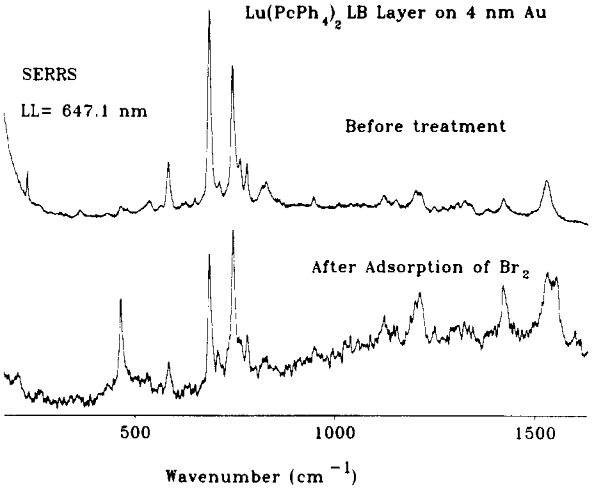

Figure 7. SERRS spectra of one LB monolayer of $LuPc_2^{Ph}$ on Au and SERRS after adsorption of Br_2.

The adsorption of NO_x and Br_2 on LB films was studied. As was previously reported,[2] chemisorption of electron-acceptor molecules can also be detected in the Raman spectrum. Typically, the relative intensity of the macrocycle vibrations are diminished (due to polarization of the macrocycle) and the intensity of the aza-group stretching vibration becomes prominent in the 1540-cm^{-1} region. The presence of two bands in this region can be seen in Figure 7, and deconvolution of the overlapping bands allowed complete fitting with two components of similar intensities. Surface-enhanced Raman spectroscopy and electronic absorption spectroscopy were used to characterize the interaction of the NO_x and Br_2 molecules with the LB films of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$. The effect of gas adsorption on the spectra of $LuPc_2^{Ph}$ LB films is illustrated in Figures 6 and 7. The electronic absorption spectra given in Figure 6 should be compared with the electrochromic properties given in Figure 3. The adsorption of NO_x and Br_2 gave rise to the spectrum of the oxidized $LuPc_2^{Ph}$ species which was characterized by a red-shifted Q-band. It can be argued that the electron-acceptor molecules were chemisorbed on the LB film, and the electron transfer between LB molecules and adsorbates

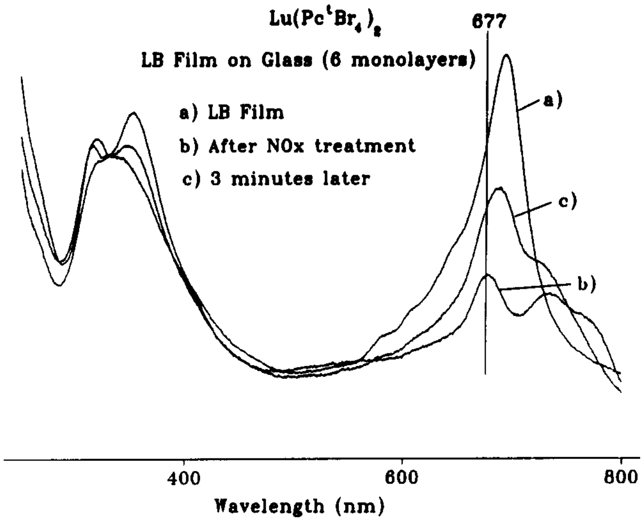

Figure 8. Electronic spectra of $LuPc_2^{tBr}$ LB on glass, after NO_x adsorption and desorption after 3 min.

was equivalent to oxidation of the Pc ring, according to the visible spectra. The SERRS spectra of a single monolayer of $LuPc_2^{Ph}$ on Au as shown in Figure 7, exhibit very clearly the predicted effect of Br_2 adsorption. Furthermore, the SERRS spectra for $LuPc_2^{Ph}$ LB monolayer were identical for both NO_x and Br_2 adsorption. It is also important to note that the optical evidence for gas adsorption was observed with a 9000-fold excess of NO_x. Under these conditions we can assume complete oxidation in the LB films of $LuPc_2^{Ph}$ and $LuPc_2^{tBR}$. Evidence of chemisorbed gas was observed several hours following the initial gas exposure.

The effect of NO_x adsorption on $LuPc_2^{tBr}$ is illustrated in Figure 8. The appearance of the "oxidized" spectrum was clearly identified, by comparison to the data presented in Figure 4. However, the desorption rate(in ambient) for $LuPc_2^{tBr}$ was higher than for $LuPc_2^{Ph}$ LB film. In fact, the absorption spectra of an LB film of $LuPc_2^{tBr}$ exposed to NO_x or Br_2 showed complete recovery at standard temperature and pressure within 3 min. Residual NO_x may also be present in the film even though the electronic spectra support the notion of a reversible reaction. Electrical conductivity studies of Pc films (transferred to an interdigital microelectrode) exposed to part per billion concentration of NO_x are currently in progress to further determine the reversibility of chemisorption. The latter study will address the use of bisphthalocyanine LB films for application as sensitive chemical sensors.

Conclusions

The reversible adsorption of NO_x and Br_2 by $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ LB films was demonstrated using visible spectroscopy and SERRS on Au island films. The most important conclusion of this work was the finding of a distinct rate of gas desorption in $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$. The results showed that the rate of desorption of small electron-acceptor molecules on bisphthalocyanine LB films can be controlled by introducing the appropriate substituent in the Pc ring. The electrochromic properties of mixed LB films of $LuPc_2^{Ph}$ and $LuPc_2^{tBr}$ and their electrochemical stability were confirmed.

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