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Langmuir−Blodgett Films of Bis(octakispropyloxy) Samarium Bisphthalocyanine. Spectroscopic and Gas-Sensing Properties

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In this work, the synthesis of a novel substituted bisphthalocyanine, the bis[octakis(propyloxy)-phthalocyaninato] samarium(III) complex, is reported. Langmuir−Blodgett (LB) films of this compound have been prepared. The influence of the propyloxy groups in the structure of the LB films and in their spectroscopic, chemical, electrochromic, and gas-sensing properties has been evaluated. The $\pi-A$ isotherms exhibit greater monolayer stability than that observed in the unsubstituted analogue. The compressed monolayers are easily transferred by Y-type deposition resulting in red films instead of the expected green monolayers. The LB films have been characterized spectroscopically using UV−vis, near-IR, and FTIR techniques. The UV−vis spectra show that the Q-band splits into two peaks on passing from the chloroform solution to the LB films. This is the first example of a Davydov splitting in a bisphthalocyanine compound. The Davydov splitting, which is responsible for the red color of the LB films, is characteristic of crystalline order. The FTIR spectra also indicate the presence of long-range order in the LB films. Electrochromism is clearly observed in cast films but appears attenuated in LB films due to the coincidence of the electronic absorption bands of the blue and red forms with the bands corresponding to the Davydov splitting. Finally, LB films deposited onto ITO microelectrodes (spacing of 75 microns) show an appreciable conductivity. The resistance of the devices varies reversibly when they are exposed to several volatile organic compounds. Although the resistance of the LB films is higher than that observed in similar gas sensors prepared from unsubstituted or tertbutyl-substituted bisphthalocyanines, the response toward the vapors is more intense.

Introduction

During the past decade, phthalocyanines (Pc) have attracted considerable interest owing to their unique optical and electrical properties.[1−3] Attention has been increasingly focused on exploiting these properties in a range of applications that include gas sensors, photovoltaic cells, electrochromic displays, and so forth.[4−7] The possibility of preparing ultrathin films of Pc molecules is the basis of their potential applications in molecular devices. Phthalocyanine thin films can be produced by a variety of techniques including the Langmuir−Blodgett (LB) technique that plays a crucial role providing ordered arrays of Pc molecules with well-expressed surfaces.[8]

The possibility of changing the ordering and the electrooptical properties of the LB films by using new phthalocyanine derivatives has brought several groups to explore the feasibility of using substituted phthalocyanines as LB materials. Most of these works have been carried out using monophthalocyanine compounds (MPcs).[1−7,9−13] Nevertheless, a comparatively small number of studies have focused their attention toward bisphthalocyanines (LnPc$_2$). The LnPc$_2$ are sandwich complexes where a lanthanide is coordinated with two phthalocyanine rings. These molecules have a particularly rich electrochromism,[14−19] and their conductivity is higher than that observed in MPcs molecules.[20−23] The high conductivity of the LnPc$_2$ favors the use of these molecules as the sensing material in chemical resistive sensors.[24−30]

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During the last years, our own interests have been centered on the synthesis of new bisphthalocyanine derivatives (LnPc$_2$R),[31] on the preparation of their LB films, and on the study of their chemical and spectroscopic properties.[26,27] In addition, our group has paid attention to the evaluation of the potential applications of these LB films in electrochromic and gas-sensing devices.[26-32]

In this paper, the new bis[octakis(propyloxy)phthalocyaninate] samarium(III) complex ((4,5-OC$_3$H$_7$)$_{16}$Pc$_2$Sm) in which eight propyloxy groups were introduced into each phthalocyanine ring has been synthesized. Unlike the tetra-substituted compounds, which are normally formed as a mixture of isomers and used as such, the octa-substituted derivatives can be synthesized isomerically pure, a feature which should encourage molecular ordering. The influence of these groups in the LB film structure and in the spectroscopic, electrochromic, and gas-sensing properties of the films has been evaluated.

Experimental Section

All chemical and solvents (Aldrich Chemical Ltd.) were of reagent grade and used as supplied.

The synthesis was performed by mixing samarium acetate and 4,5-propyloxyphthalonitrile (molar ratio 1:8) in *n*-hexanol in the presence of DBU. It has been established[17,18] that the LnPc$_2$ are obtained via the corresponding monophthalocyanines (PcLnX) that subsequently are transformed into the bisphthalocyanine neutral stable free radical form [Pc^{2-}Ln^{3+}Pc$^{-\bullet}$]^0. The purification of the obtained bisphthalocyanines was carried out by column chromatography on alumina followed by a thin-layer chromatography on Silufol plates (yield, 72%).

The electronic absorption spectra were recorded with a Shimadzu UV-1603. The infrared and near-infrared spectra were recorded in a Nicolet Magna 760.

Isotherms and LB films were prepared in a KSV 5000 Langmuir–Blodgett trough equipped with a Wilhelmy plate to measure the surface pressure. The (4,5-OC$_3$H$_7$)$_{16}$Pc$_2$Sm molecules were dissolved in chloroform (5 × 10^{-5} mol L^{-1}) and spread onto ultrapure water (Millipore MilliQ), which was kept at a constant temperature (18 °C). The experiments at basic pH were carried out by solving NaOH 0.1 mol L^{-1} in the water subphase until a pH of 8 was reached.

The surface–area isotherms were measured by compressing the floating molecules at a speed of 5 mm/min. At a surface pressure of 30 mN/m, the Langmuir–Blodgett films were deposited onto different types of substrates (glass substrates, ZnS, and ITO glass) with a substrate speed of 3 mm/min. Films of 10 or 25 layers were built by Y-type deposition with a transfer ratio close to 1. The films thus prepared were stored in a vacuum desiccator until use and returned to the desiccator after every experiment.

Cast films were prepared by casting a drop of a 10^{-4} mol L^{-1} chloroform solution of (4,5-OC$_3$H$_7$)$_{16}$Pc$_2$Sm onto a glass substrate.

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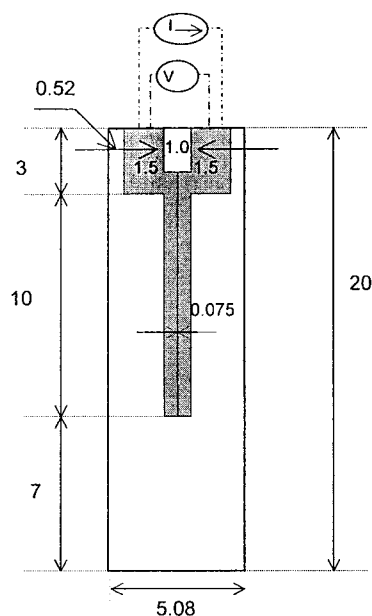

Figure 1. Layout of the electrodes used in this work. All dimensions are in mm.

Electrochemistry was carried out in a PAR model 263A potentiostat galvanostat using a conventional three-electrode cell. LB films deposited on ITO glass were used as the working electrode, Pt wire was the counter electrode, and a Ag/AgCl electrode was the reference electrode. KClO$_4$ (0.1 mol L^{-1}) or KCl (0.1 mol L^{-1}) was used as electrolyte. A two-window cuvette was used to obtain the in situ electronic absorption spectra.

The gas sensors were prepared by transferring 25 monolayers onto ITO microelectrodes with electrode spacing of 75 microns (Figure 1). The changes in voltage were measured as follows. The sensors were mounted in a test box with a volume of 15 mL. An air flow of 100 mL per minute was passed through the chamber where the sensors were placed until the stabilization of the signal. A Dynamic Headspace sampler (Hewlett-Packard model HP 7694E) was used for the injection of the headspace above the sample to the test box. The samples (100 μL of hexanol, hexanal, acetic acid, or HNO$_3$) were placed in 10 mL vials that were kept at a constant temperature (50 °C) for 9 min in order to obtain a homogeneous headspace. Each vial was pressurized for 8 s at 1.5 bar. The pressure gradient that builds up permits filling of a 3 mL loop in 9 s, and its content is then injected to the charge carrier gas that drives the volatiles to the sensor chamber. An injection of the content of the loop (1 s) was performed every 15 min.

The voltage drop across each one of the sensing units was monitored with a computer-controlled Keithley 2000-SCAN scanner card. The scan rate used to measure the changes of resistance of the sixteen sensors was 0.5 s. The data were monitored in real time, and the graphs could be followed using TestPoint software.

Results and Discussion

The molecular formula of the phthalocyanine dealt with in our study is illustrated in Figure 2.

Langmuir Monolayers and Langmuir–Blodgett Films. Isotherms were recorded by spreading a chloroform solution of (4,5-OC$_3$H$_7$)$_{16}$Pc$_2$Sm onto a deionized (MilliQ) water surface kept at a constant temperature. After solvent evaporation (10 min), the phthalocyanine molecules were compressed at a constant speed of 5 mm/min until the film pressure rose sharply, indicating that a continuous surface film was formed. The isotherm recorded at 18 °C and pH 5.5 is given in Figure 3a. Under these conditions, reproducible isotherms (surface pressure versus molecular area) were obtained. The limiting area calculated from the slope of the curve is 120 Å^2. The area is slightly larger
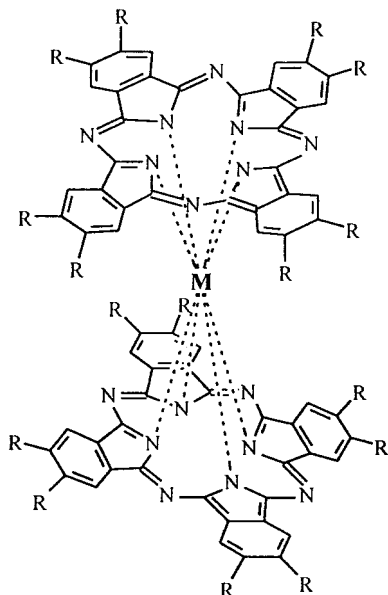
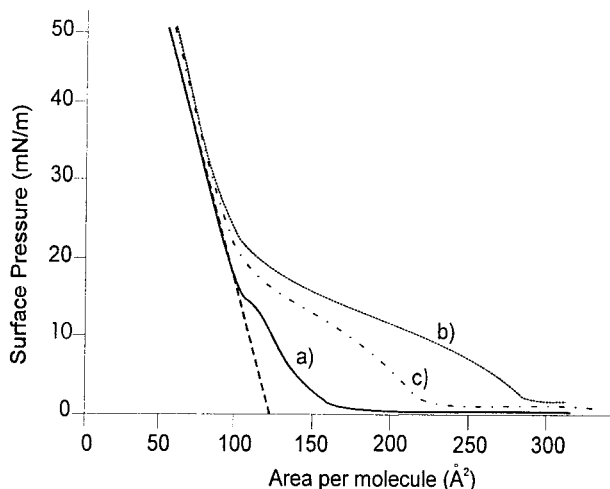**Figure 2.** Molecular formula of the bis[octakis(propyloxy)-phthalocyaninate] samarium(III) complex($(4,5\text{-}OC_3H_7)_{16}Pc_2$-Sm).

Figure 3. Surface pressure−area isotherms for $(4,5\text{-}OC_3H_7)_{16}$-$Pc_2Sm$ on water at 18 °C: (a) pH = 5.5, waiting time 10 min; (b) pH = 5.5, waiting time 30 min; (c) pH = 8, waiting time 10 min.

than that observed in unsubstituted bisphthalocyanines,[25,33] but it is smaller than the limiting areas of 170−180 Å^2 reported for Lu(III) or Er(III) tetrapropyloxy-substituted phthalocyanines (four groups per ring).[16] The limiting area obtained for the $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ suggests edge-on orientations with the Pc ring tilted and assembled with the main molecular axis parallel to the water subphase (lying flat, they should occupy an area approximately 20 Å × 20 Å). The monolayer shows a considerably higher stability than the unsubstituted bisphthalocyanines, and a collapse is not observed until a surface pressure of 65 mN/m is attained.

The behavior of the isotherms of the compound under study is rather complex. Nearby 140 Å^2, the curve shows a marked change of the slope indicative of a reorganization of the structure of the monolayer, the latter being characterized by a near-vertical region in the isotherms. Figure 3b shows the Langmuir isotherm obtained when
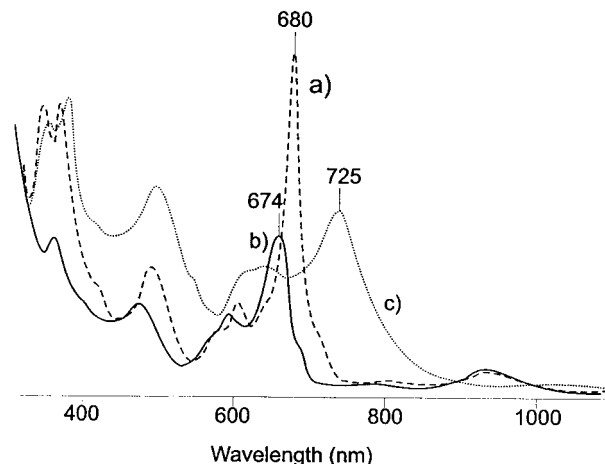

Figure 4. Electronic absorption spectra of $(4,5\text{-}OC_3H_7)_{16}Pc_2$-Sm in (a) 10^{-5} mol L^{-1} chloroform solution, (b) cast film, and (c) LB film (25 monolayers).

waiting 30 min for solvent evaporation. The shape of the plateau changes with the waiting time after spreading; as the waiting time increases, the plateau becomes more pronounced. This phase transition is not observed in the unsubstituted bisphthalocyanines nor in the tetratert-butyl- or tetrapropoxy-substituted derivatives previously reported.[16,33,34] Although a pronounced plateau has also been observed in a butoxy-substituted lutetium bisphthalocyanine,[33] the shape of the reported curves differs considerably from those obtained in this case.

Figure 3c shows the result of a similar experiment performed at pH 8. The basic pH favors the appearance of intermolecular interactions, and first rise begins at 225 Å^2. After changing to the solid phase, the slope raises sharply and shows a similar behavior to that at pH 5.5.

The floating monolayers formed at pH 5.5 or 8 were easily transferred to different substrates with Y-type deposition and a transfer ratio close to 1, resulting in red films.

UV−Vis−NIR Absorption Spectroscopy. The electronic absorption spectra for the green chloroform solution, the green cast films, and the red LB assemblies (25 monolayers) of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ deposited onto a glass substrate are shown in Figure 4.

The UV−vis spectrum of a 5×10^{-5} mol L^{-1} chloroform solution of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ shows the characteristic features of these macrocyclic compounds. The spectrum presents strong B and Q bands that have been assigned to $\pi \rightarrow \pi^*$ transitions.[35] The B band is split into two bands at 337 and 372 nm (a similar splitting has been observed in the octa-15-crown-5 lutetium bisphthalocyanine[28]). The Q band is centered at 680 nm. As observed, the presence of electron donor propyloxy groups cause all the bands present in the UV−vis region to be considerably red-shifted compared with those observed in the unsubstituted samarium bisphthalocyanine.[17,18]

The UV−vis spectrum of the green cast film is similar to that of the chloroform solution, but a hypsochromic shift of the Q band (674 nm) is observed in this case.

Instead of the expected green color, the LB films obtained either at pH 5.5 or 8 showed a distinct red color. Their UV−vis spectra presented noticeable differences when compared with those of the chloroform solutions and of the cast films.

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As observed in Figure 4, the electronic absorption spectrum of the LB film of the compound under study shows a broad absorption band with both red- and blue-shifted components of the Q band relative to that observed in the spectrum of the material in solution or in cast film. These bands appear at 668 and 725 nm, respectively. This behavior is characteristic of Davydov splitting and has been observed in certain MPcs: long-chained homologues of the $(OH)_2(C_9H_{19})_6$ HPc, $(OH_2C)_2(C_9H_{19})_6$ HPc series and their Cu^{II} derivatives.[36] It has also been observed in peripherally substituted octaalkyl phthalocyanines[36–39] that exhibit discotic mesophases at elevated temperatures. Nevertheless, although the UV–vis spectra of LB films of several substituted sandwich type bisphthalocyanines have been studied, this is the first time that the Davydov splitting has been observed in a bisphthalocyanine LB film. It has been established that the Davydov splitting is characteristic of crystalline order and suggests a different type of molecular packing that implies the presence of translationally nonequivalent molecules within the unit cell.[36] An example of such packing is the "herringbone" structure. In our case, the presence of eight propyloxy groups per ring encourages the ordering at the water surface and the monolayers can be deposited as highly ordered LB films.

The UV–vis spectra of the LB films recorded 3 months later show shifts in the absorption maxima that appear at 655 and 718 nm. Moreover, a modification of the relative intensities is observed, and after 3 months both bands show similar relative intensities. These changes are indicative of a certain degree of restructuration of the films.

The chloroform solution of the $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ shows two broad bands in the near-IR region (800–2000 nm): a band at 909 nm associated to the free radical structure of the bisphthalocyanine and a very intense band at 1754 nm associated with a charge transfer between the phthalocyanine rings. These spectral features are similar to those reported for other $LnPc_2$,[35,40] but the presence of the propyloxy groups causes a considerable red shift of the charge transfer band when compared with the position of the band in the unsubstituted samarium bisphthalocyanine.[40]

The near-IR of the cast film is similar to that obtained for the chloroform solution (Figure 5a). However, it is important to notice the marked blue shift of the charge transfer band that appears at 1667 nm due to solid-state interactions. In turn, the near-IR spectrum of a 25 monolayer LB film of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ differs considerably from the spectra registered for solutions and cast films. The near-IR charge transfer band disappears, and only a very small band at 1204 nm can be noticed. The differences in the spectrum can only be associated with the high degree of order induced by the propiloxy groups.

For comparison purposes, the near-IR of the 25 monolayer LB film of the unsubstituted $SmPc_2$ has also been recorded. The near-IR spectrum of the unsubstituted $SmPc_2$ does not differ significantly from the spectrum of
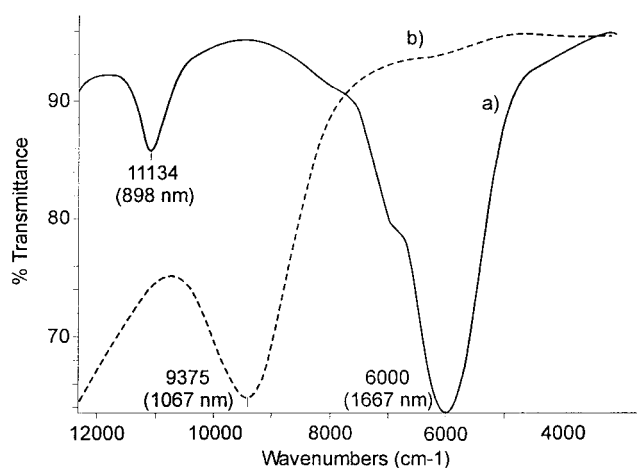
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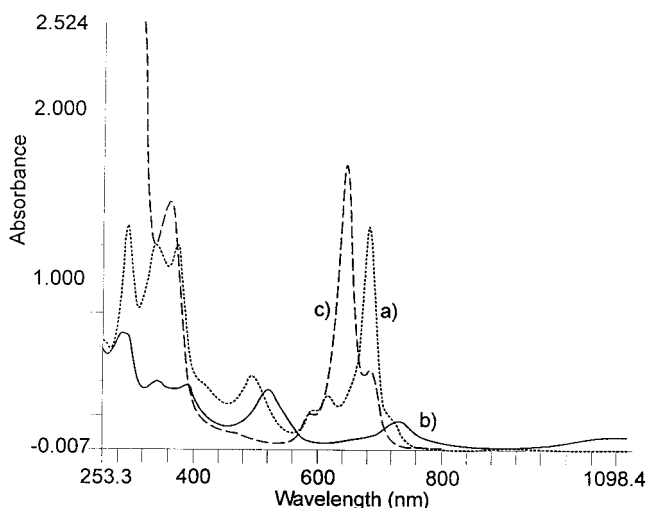**Figure 5.** Near-IR spectra of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ in (a) cast film and (b) cast film exposed to HNO_3.

Figure 6. UV–visible spectra: (a) 10^{-5} mol L^{-1} solution of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$; (b) after the addition of HNO_3; (c) after the addition of hydrazine.

the chloroform solution or the cast film, with the exception of the shifts due to the intermolecular interactions present in the solid state.

Chemical Reactivity. In common with other bisphthalocyanines, the addition of HNO_3 to the green $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ chloroform solution produces a spectrum characteristic of the oxidized form (red in color). This reaction can be followed by the shift of the Q band at 680 nm to longer wavelengths (729 nm). At the same time, the band at 520 nm that is related with the free radical structure of the phthalocyanine ring increases its intensity. The green color of the starting material in chloroform solution changes to blue when adding hydrazine. The spectrum of the blue reduced product has a maximum of the Q band at 642 nm, with a second absorption peak at 683 nm (Figure 6).

The cast films exposed to vapors of HNO_3 and hydrazine have shown the same reactivity as the solutions. For instance, the exposure of the cast films deposited on glass to the headspace of HNO_3 produces red films corresponding to the oxidation of the $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ molecules. This reaction can be followed by the shift of the Q band to longer wavelengths (732 nm). The interaction with hydrazine causes a blue shift to 640 nm. In both cases, the near-infrared charge transfer band disappears indicating that the charge transfer between both rings is no longer possible (Figure 5).
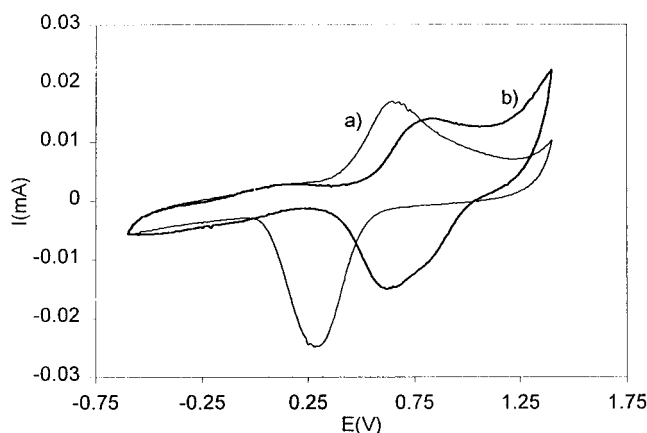
Figure 7. Cyclic voltammogram of an LB multilayer assembly of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ on an ITO working electode and Ag/AgCl reference electrode using (a) $KClO_4$ 0.1 mol L^{-1} and (b) KCl 0.1 mol L^{-1} as electrolytes.

Due to the splitting of Davydov that is responsible for the red color of the LB multilayers, the color changes produced in LB films by the interaction with electron donor or electron acceptor gases are less intense than in cast films. The oxidation produces a broadening of the band at 725 nm caused by the overlapping with the band of the oxidized form at 738 nm. Similarly, the reduction process produced only a small change in the color due to the overlapping of the band corresponding to the blue form at 668 nm and the blue-shifted band produced by the Davydov splitting at 670 nm. The band at 910 nm associated with the free radical structure of the phthalocyanine disappears; upon oxidation or reduction, no bands are observed in the near-infrared.

Electrochemistry and Electrochromism. Figure 7 shows the cyclic voltammograms (CV) of LB films (25 monolayers) of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ on ITO glass in contact with 0.1 mol L^{-1} $KClO_4$ and 0.1 mol L^{-1} KCl aqueous solutions. The experiments were carried out from -0.6 to $+1.4$ V at a scan rate of 100 mV/min. In good agreement with other $LnPc_2$,[17,18,32] one peak corresponding to the one-electron oxidation of the phthalocyanine ring can be observed in the CV of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$. The presence of electron donor propyloxy groups hinders the reduction of the Pc ring, and the peak corresponding to this process is not observed in the studied range.

The value of the half-potential $E_{1/2}$ for the oxidation peak is $E_{1/2} = 0.47$ V when using KCl as electrolyte, and $E_{1/2} = 0.70$ V when using $KClO_4$. The first scan is slightly different from the second cycle; subsequent scans were highly reproducible (the values reported above have been taken from the second scan). After 50 scans, the only noticeable change has been a decrease of the intensity of the peaks of 10%. A linear dependence of the cathodic peak current on the scan rate from 100 to 10 mV/s could be observed. In contrast, no dependence was observed for the anodic peak.

When using $KClO_4$ as electrolyte, the peaks are broader and the splitting of the first oxidation potential due to the proximity of the Pc rings can be partially resolved in the voltammograms of LB films.[19]

To study the electrochromism of cast and LB films, the in situ visible spectra of the coated ITO transparent electrodes were recorded. The first reference spectrum was recorded in the absence of an external potential. After one cyclic scan, UV–vis spectra were taken at controlled potential values. The electronic absorption spectra of a 25 monolayer LB assembly measured in situ for a number of controlled electrode potentials are shown in Figure 8.
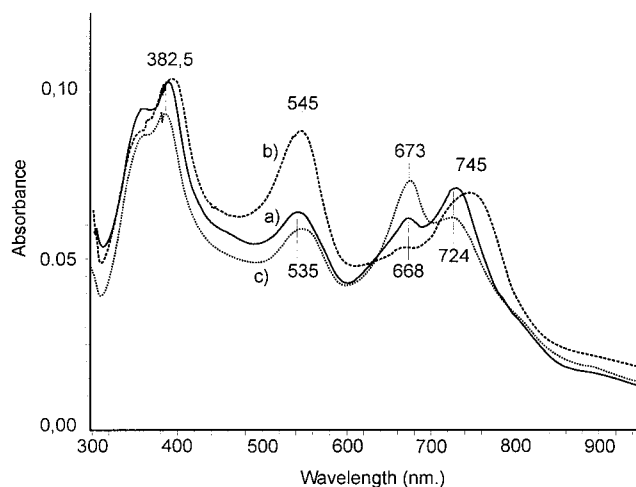

Figure 8. Electrochromism in the visible spectrum of an LB assembly of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ fabricated on an ITO electrode. Visible spectra were recorded at different applied potentials: (a) 0.0 V; (b) 1.4 V; (c) -1.2 V.

At positive potentials, the spectrum of a cast film of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ in the oxidized form is characterized by two absorption bands at 535 and 742 nm and the blue form is characterized by a shift of the Q band to lower wavelengths (640 nm).

In the case of the LB films, the spectral changes caused by the applied potential were less marked. The reason is that the band at 724 nm overlaps partially with the red-shifted band of the Davydov splitting at 745 nm. A similar phenomenon occurs at negative potentials where the band at 673 nm corresponding to the blue form overlaps with the blue-shifted band of the Davydov splitting at 668 nm. Nevertheless, in both cases the modification of the intensity of the original red color could be followed visually.

FTIR Spectroscopy. Transmission IR spectra of cast films and LB multilayers deposited on ZnS of the $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ were recorded (Figure 9 and Table 1). A partial assignment of the bands can be made by comparison with previous works.[33,41] The typical bands present in unsubstituted bisphthalocyanines at 728, 1114, and 1325 cm^{-1}, which are associated with C–H bending modes of the ring, do not have exact correspondence upon substitution. Nevertheless, characteristic vibrations of the macrocycle can be identified. For example, in cast films, the Pc ring vibration at 750 cm^{-1}, the pyrrole stretching at 1315, 1377, and 1542 cm^{-1}, or benzene stretching at 1599 cm^{-1} can be recognized easily.

The FTIR spectrum of a $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ cast film differs from the IR spectrum of the 10 monolayer LB film. For instance, the spectrum of the cast film, which is formed by aggregates of molecules, shows broad bands. These broad bands are well resolved in the LB film. As an example, the broad band observed in the cast film at 1496 cm^{-1} that is associated with the pyrrole stretching appears well resolved in three peaks at 1490, 1496, and 1506 cm^{-1} in the spectrum of the LB film. A similar behavior has been observed in the bands at 1377 and 1452 cm^{-1} that are resolved into two peaks in the spectrum of the LB film.

Some vibrations identified in the cast film are (a) absent or (b) split in the spectrum of the LB film. (a) The band at 754 cm^{-1} is strong in the transmission spectrum of the cast film and virtually absent in the spectrum of the LB film. This band is assigned to an out-of-plane vibration

(41) Battisti, D.; Tomilova, L.; Aroca, R. *Chem. Mater.* **1992**, *4*, 1323–1325.
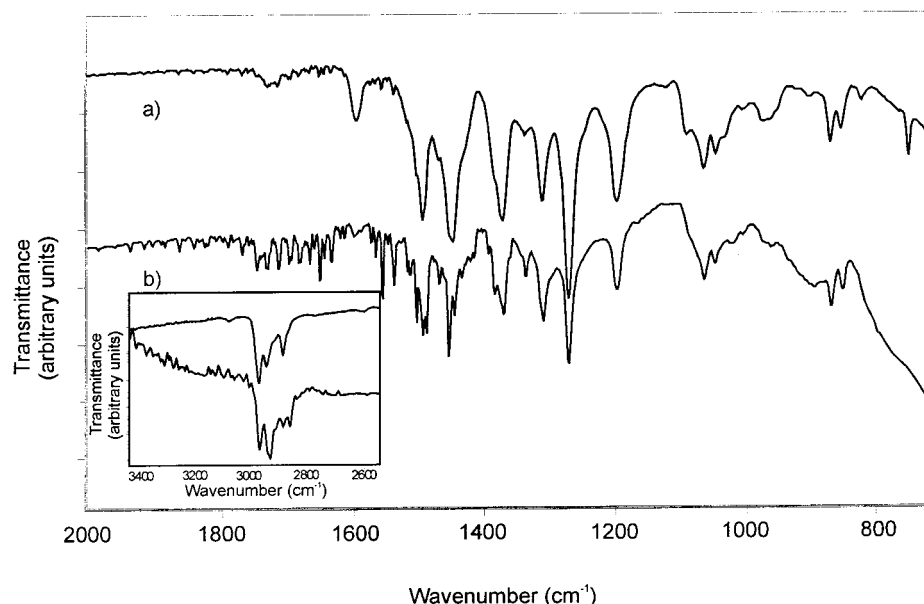
Figure 9. FTIR spectra of (a) cast film and (b) LB film. The inset shows the aliphatic C−H stretching modes.

Table 1. Observed FTIR Wavenumbers (cm^{-1}) for (4,5-OC$_3$H$_7$)$_{16}$Pc$_2$Sm

LB film	cast film	assignment
	754 (m)	Pc ring
	826	
855	856	CH$_2$-bend + benzene wag
873	873 m	
	906 vw	C−C stretch + CH$_2$-bend
	956 (sh) w	
979 vw	980	
1007	1007 vw	
1032	1037 sh	
1051	1049	benzene (C−H) wag
1068m	1068 m	C−C stretch
	1098	Pc ring
	1124 w	CH$_2$-bend
1200s	1200 s	C$_{ar}$-O−C stretch asym
1275vs	1275 vs	C$_{ar}$-O−C stretch sym
1313s	1313 s	CH$_2$-bend
1340 m	1340 w	pyrrole stretch
1376s	1377 s	isoindole stretch
1386		
1395		
1437		
1448	1448 vs	isoindole stretch
1457vs	1452 sh	
1473		
1490	1490 vs	pyrrole stretch
1496s	1496 sh	
1506 s		benzene stretch
1522		
1541s		
1550 w	1541 vw	
1559 s		
1570 m	1558 w	
1577 m−w	1570 w	
1591	1577 w	
1623	1597 m	
	2857	
2871		CH$_2$ stretch sym
	2879 w	CH$_2$ asym stret
2942	2942	CH$_3$ in-plane asym stret
2963	2963	

(arising from the macrocycle ring deformation), and therefore its dynamic dipole moment is polarized perpendicular to the plane of the macrocycle. (b) The band associated with the benzene stretching at 1597 cm^{-1} is split into two bands at 1590 and 1602 cm^{-1} in the LB film. Similarly, the bands associated with the side chain C−H

modes at 2871 and 2937 cm^{-1} are split into 2857 and 2879 cm^{-1} and 2925 and 2939 cm^{-1}, respectively.

This behavior can be associated with the high degree of order in the LB film. The existence of symmetry elements can result in an intermolecular coupling of the fundamental modes of vibration. The individual vibrations become a part of a collective movement. This coupling produces a splitting of the band in symmetrical and asymmetrical modes. When the selection rules favor the vibrational mode, the intensity of the band can be increased. Oppositely, if the vibration is not favored by the selection rules, the vibration disappears, which is the case of the vibration at 754 cm^{-1}. In summary, the changes observed in the spectra indicate the existence of long-range order in the LB film that favors the coupling of the vibrational modes.

This behavior has never been observed in the previously reported bisphthalocyanine LB films.

Gas-Sensing Properties. In previous works, several groups have demonstrated the possibility of using LB films of bisphthalocyanines as sensors for the detection of strong oxidizing or reducing gases.[24−28] Recently, our group has demonstrated the possibility of using LnPc$_2$ LB films deposited on ITO electrodes as sensors for the detection of volatile organic compounds (VOCs) such as aldehydes, esters, or alcohols, which are responsible for the aromas of foods and beverages.[29,30] It would be of great interest to find new sensors based on bisphthalocyanine molecules with improved sensibility or selectivity toward VOCs. It can be expected that the influence of the propyloxy donor groups in the properties and the morphology of the LB films described in the previous paragraphs has an effect on the sensing behavior of the LB films under study.

A few minutes after the preparation, the red (4,5-OC$_3$H$_7$)$_{16}$Pc$_2$Sm LB films (10 monolayers) deposited onto ITO microelectrodes (spacing of 75 microns) showed an appreciable conductivity. The resistance of the just-prepared films of (4,5-OC$_3$H$_7$)$_{16}$Pc$_2$Sm (600 kΩ) is higher than that observed in other LnPc$_2$ based sensors.[30] After the preparation, the resistance increases exponentially with time due to the drying process of the films.[29] After a few days, the resistance was so high (>100 MΩ) that it could not be measured accurately using our instrumental setup.
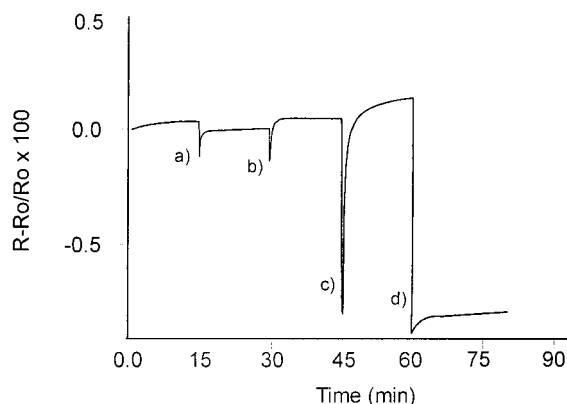
Figure 10. Response of a $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ LB film expressed as the fractional change in resistance $(\Delta R/R) \times 100$ toward (a) hexanol, (b) hexanal, (c) acetic acid, and (d) HNO_3.

The exponential increase of the resistance has also been observed in other bisphthalocyanine based sensors.[28,29] Nevertheless, in the case of the unsubstituted bisphthalocyanines the initial resistance is much lower, and even if initially the resistance increases exponentially, $10-15$ days after the preparation the resistance reaches a plateau and the conductivity is appreciable for several months. The low conductivity of the $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ sensors can be related with the decrease in the number of charge carriers produced by the presence of electron donor substituents in the phthalocyanine ring of these p-type semiconductors.[1,4,21]

This behavior limits the use of the $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ sensors to the next $4-6$ days following the preparation of the LB films. In addition, the presence of humidity can be the cause of a certain degree of irreproducibility and a slight drift of the baseline.

The response of the $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ sensors is shown in Figure 10. The exposure of the films toward VOCs including hexanol, hexanal, and acetic acid causes a sharp decrease of the resistance. The change is reversible, and a few minutes after the exposure the baseline is recovered completely.

The exposure to vapors of HNO_3 also leads to a fast decrease in the resistivity, but in this case, the reversibility is only partial and a few minutes after the gas flow is turned off a new baseline is reached.

The decrease in the resistance caused by HNO_3 vapors (rich in NOx) could be interpreted bearing in mind that phthalocyanines are p-type semiconductors and that electron acceptor molecules can oxidize the phthalocyanine molecules.[4] The change of the baseline can then be due to the film relaxing to a different oxidation state.

The interaction with VOCs (which are not strong oxidizing or reducing agents) is more difficult to explain. Two possible mechanisms have been proposed in the literature. One possibility is that VOCs would act as weak electron donors or acceptors.[4] The interaction of a certain VOC with the $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ LB film would allow the formation of a charge transfer complex, resulting in a partial oxidation of the phthalocyanine molecules and hence in a slight reduction of the number of charge carriers in the organic film.

The second mechanism proposed is related with the structure of the films.[12] The morphology must accom-

modate both the charge transfer interaction and charge carrier transport. In our case, the decrease of the resistance would be the result of the swelling effect caused by the adsorption of the VOCs, that would lead to a decrease of the mobility of the charge carriers.

The $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ LB films studied in this work showed a certain degree of selectivity toward the gases tested, hexanol, hexanal, and acetic acid, which are typical components of aromas. The response of the well-ordered $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ LB toward the studied VOCs is 3 times more intense than that observed in unsubstituted bisphthalocyanine based sensors. This result is in good agreement with previous observations that indicate that the higher the initial resistance of a sensor, the higher the intensity of the responses it produces.

The above results illustrate the importance of the presence of the substituent groups in the phthalocyanine ring to modulate the response of the sensors. The propyloxy groups (which have an electron donor character) not only influence the formation of the charge transfer complex between the phthalocyanine and the VOCs but also play an important role in the morphology of the films that, in turn, is closely related with the electrical response of the films to the gas exposures.[2]

Conclusions

The synthesis of a novel bisphthalocyanine $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ has been carried out. The introduction of propyloxy substituents enhances ordering at the water surface. The compound has shown to be an excellent material for LB deposition and gives highly ordered LB films. The molecular packing induced by the presence of the substituents differs from that shown by other bisphthalocyanine compounds and strongly affects the chemical, optical, and electrical properties of the films.

The electronic absorption spectrum of the LB film of the compound under study shows a broad absorption band with both red- and blue-shifted components of the Q band relative to that observed in the spectrum of the material in solution or in cast film. This Davydov splitting is characteristic of highly ordered LB films. The features observed in IR spectra also indicate a high degree of order inside the LB film.

The color change produced by redox or electrochemical processes in solutions or cast films is much less intense in LB films.

The presence of propyloxy groups and the new form of packing induced by the presence of the substituents influence the gas-sensing properties. The response of chemiresistors based on LB films of $(4,5\text{-}OC_3H_7)_{16}Pc_2Sm$ toward VOCs and HNO_3 has been found to be much more intense than that observed in unsubstituted derivatives. In contrast, the lifetime of the sensors is considerably reduced.

In summary, substituents on the Pc ring can tune some of the physical and chemical characteristics of the system and can lead to new forms of packing.