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# Langmuir-Blodgett Films of Rare-Earth Lanthanide Bisphthalocyanines. Applications as Sensors of Gases and Volatile Organic Compounds

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The Langmuir-Blodgett (LB) technique is a method of obtaining highly ordered thin films. The homogeneous nature of the surface and the large surface area per unit volume of this type of films are of key importance in the preparation of electronic gas sensors.

The phthalocyanines (Pc) are among the most interesting molecules in the fabrication of LB films for sensing applications. The bisphthalocyanine derivatives ($LnPc_2$) are of special interest due to their high intrinsic conductivities. LB films of $LnPc_2$ have been successfully used not only for the detection of strong electron donor or electron acceptor gases but also for the detection of Volatile Organic Compounds (VOCs), which are responsible of aromas. The response of the sensors is fast, reproducible and sensitivities down to a few parts per million are readily achieved.

By coupling an array of sensing elements based on $LnPc_2$ LB films (each with a different sensitivity) to signal processing methods based on pattern recognition or artificial neural networks, it has been possible to construct a prototype of electronic nose.

Keywords: *Phthalocyanines; bisphhalocyanines; Langmuir-Blodgett films; gas sensors; electronic nose*

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## 1. INTRODUCTION

Ultrathin organic films have attracted increasing interest for several reasons. They open the possibility of constructing designed molecular architectures which allow the study of physical phenomena at the molecular level. In addition, organic materials often exhibit interesting physical properties, and full advantage of these properties can only be taken in thin films of controlled structure and thickness. Interest also arises from the continuous trend of size reduction of electronic devices[1].

The Langmuir-Blodgett (LB) technique is a method of obtaining highly ordered thin films[2–3]. LB films are formed by spreading a solution of the film forming molecule (usually an amphiphilic molecule) onto the clean water surface contained in a Langmuir trough (Fig. 1). After the evaporation of the solvent, the molecules are compressed using a barrier. Upon compression, the molecules are oriented at the interface giving rise to an ordered monolayer. This floating monolayer can be transferred to a solid substrate by dipping the substrate perpendicularly to the water subphase. Repeated dippings allow to obtain multilayers where the thickness can be controlled by the number of dipping cycles.

This method, allow to obtain organized arrays of molecules with well-defined surfaces; the film architecture can be controlled at the molecular level, thus determining the macroscopic properties of the material.

Most of the interest of the work in the field of LB films lay in their possible applications. It can be expected that LB films play an important role in the development of new technologies for information storage and display media, printers, sensors and many others.

The applications are related to the high degree of control available with the LB process (control of the architecture at the nm level and uniformity of the LB films). The possible uses are also related to the physical and chemical properties of the LB forming molecules. There is an increasing number of film forming materials with conducting, semiconducting, photochemical and photothermic properties, non-linear optic activity, pyroelectricity, and electroactive properties such as redox activity or electrochromism[2,3].

The semiconducting nature of some LB films suggests possible uses in electronic devices. A much-studied electronic device using LB films is the gas sensors[2,4,5]. These devices exploit the change of resistance of

a semiconducting LB film on exposure to oxidizing or reducing gases. Most gas and vapour sensors have relied on measurement of the dc conductivity across the surface of a material fitted onto a planar electrode. In these sensors, the number of charge carriers is modified as a result of the interaction between the organic compound and the reaction gas.

The observation that semiconucting properties of phthalocyanines (Pc) are modulated by the absorption and desorption of gases has led to significant efforts to use them as the sensing material in chemical sensors[6,7]. Pc possesses other properties that make them suitable for sensing applications. These properties include a good thermal and chemical stability and manipulation as microelectronic compatible thin films, in particular Langmuir-Blodgett films[2,4,8–10]. The precise control of the organization and thickness of the films may enhance the performance of these devices.

Finally, the sensitivity and selectivity of such chemical sensors can be varied by changing the central metal atom and by substitutions in the periphery of the phthalocyanine molecule[11,12]. The selectivity can be enhanced by using an array of sensors, each with slightly different response, coupled with signal processing methods based on pattern recognition or artificial neural networks. These are the basis of the so-called electronic noses[13].

The concept of an artificial nose system was proposed in 1982[14]. Since then important advances have occurred in this field. The arrays of sensors are usually formed by metal oxide semiconductors or conducting polymers. Even if some commercial electronic noses already exist, further improvements in this field are necessary. In particular it is highly desirable the development of sensors working at room temperature, reproducible and insensitive to ambient fluctuations. The use of organic semiconductors (including phthalocyanines) as sensitive materials could open new perspectives in the development of arrays of sensors working at room temperature.

## 2. LANTHANIDE BISPHTHALOCYANINES ($LnPc_2$) AS GAS SENSORS

The semiconducting properties of phthalocyanines can be modulated by the absorption and desorption of gases. For this reason, these compounds have been proposed as sensitive materials in chemical sensors.

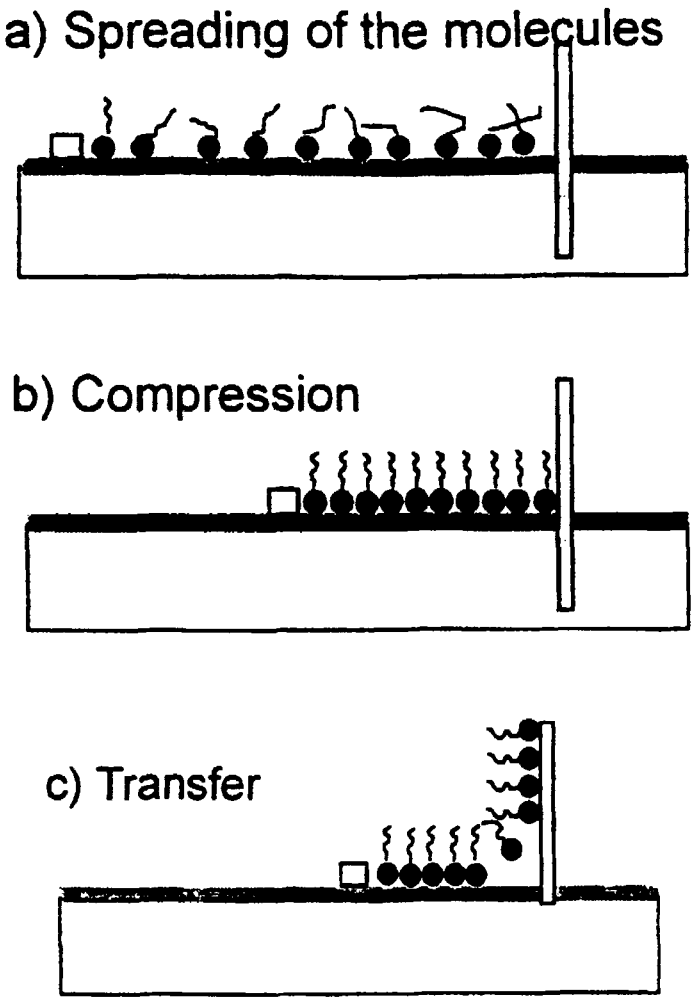



FIGURE 1 The Langmuir-Blodgett technique

Most of the studies on this field, have been carried out using monophthalocyanines (MPc)[7,8,10,12,15]. These molecules consist in a phthalocy-

anine ring coordinated with a transition metal (Fig. 2.a). They are p-type semiconductors with conductivities ranging from $10^{-10}$ to $10^{-12}$S/cm at 300K. The electronic conductivity of monophthalocyanine materials is altered dramatically by the presence of gases that behave as electron acceptors. Such oxidising gases include oxygen ($O_2$), the halogens ($Cl_2$, $Br_2$and $I_2$) and nitrogen oxides ($NO_x$) (Fig. 3). The increase in the conductivity has been interpreted as follows. A charge transfer complex is formed between the phthalocyanine and the acceptor gas, and the charge carriers are the holes produced in the phthalocyanine matrix.

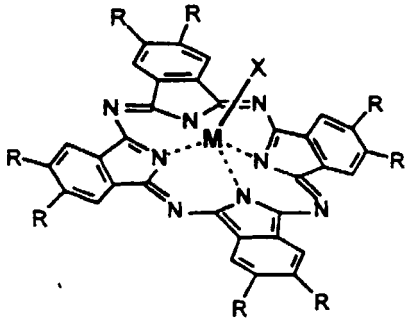
NOx sensors containing Pc derivatives exhibit reasonable performances at room temperature. The conductivity change of a LB film of a MPc is sufficient to detect NOx in a concentration range of 250–3000 ppb at 40°C[7]. However the response time is relatively slow (about 20 minutes at this temperature). The ability of working at room temperature is an advantage when compared with other gas sensors, for instance tin oxide sensors that work at temperatures of 350°-400°C.

Due to the small conductivity of the MPc materials, when using conventional electrodes, voltages of 10–700V are necessary to obtain measurable signals. For this reason films are usually prepared on microelectrodes prepared onto silicon, alumina or glass, with electrode spacing of 1–25 microns.

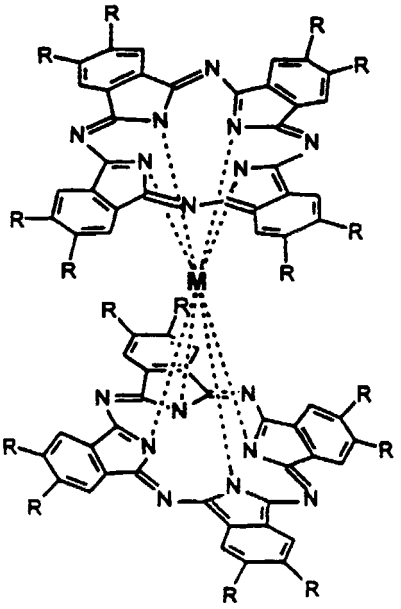
The reactivity towards electron donor or electron acceptor gases is of special interest in the case of the bisphthalocyanine compounds ($LnPc_2$), which are sandwich type complexes where a lanthanide metal is co-ordinated with two phthalocyanine rings (Fig. 2.b). The $LnPc_2$ complexes are neutral radical species in which the oxidation state of the metal ion (+3) and overall electronic neutrality imply that at least one of the Pc rings is not in is usual oxidation state ($Pc^{2-}$). The radical is essentially localised as a $Pc^{\cdot-}$ species on one of the rings. These molecules have particularly high intrinsic conductivities ($\sigma=10^{-6}$-$10^{-3}$ S/cm at T=300K)[16–20] that can be modified by exposure to electron donor or electron acceptor gases[17–24].

The interaction of the $LnPc_2$ LB film with a strong oxidising agent such as NOx causes a reversible increase of the conductivity of the film. The interaction of NOx with the LB film, partially oxidise the bisphthalocyanine molecules, modifying the number of charge carriers and hence the conductivity of the film.

These changes have been correlated to the redox and electrochemical behaviour of the $LnPc_2$ molecules due to the accessibility of a range of




(a)




(b)

FIGURE 2 (a) Monophthalocyanine molecule; (b) Bisphthalocyanine molecule

oxidation states centered on the ligand. The electrochemical potentials of the phthalocyanine molecules indicate that the oxidation of $LnPc_2$ is easier than that of MPc.

Moreover, due to the high conductivity of $LnPc_2$, using conventional electrodes voltages of only 1–5 V are sufficient to obtain measurable signals. If microelectrodes are used, small voltages produce quite intense signals.

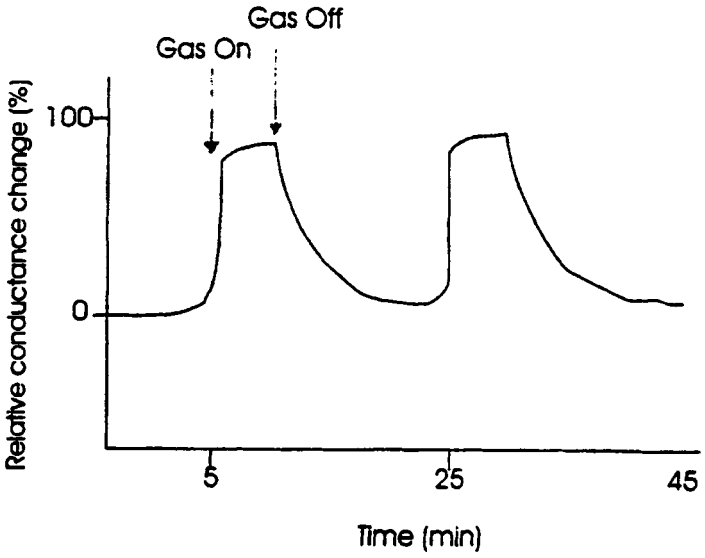



FIGURE 3 Response of a MPc LB film towards pulses of NOx

It is surprising that, in spite of the interesting sensing properties showed by $LnPc_2$, most of the attempts of using Pc as sensitive materials have been carried out using MPc instead of $LnPc_2$.

This is probably related with the high number of research groups dedicated to the synthesis of MPc and the study of their optical properties (dies or non-linear optics). In contrast the number of groups working with $LnPc_2$ is comparatively very small. In addition, it is difficult to obtain $LnPc_2$ materials with the high degree of purity required for sens-

ing applications[25]. The purification is even more complicated in the case of substituted molecules, where the synthetic route usually leads to isomers extremely difficult to separate.

It would be highly desirable the development of new synthetic methods and purification procedures of new bisphthalocyanine molecules. The possibility of having available new molecules with purposely-designed properties will provide a way of improving the selectivity of the sensors.

## 3. DETECTION OF VOCS

The LB films of $LnPc_2$ have been successively used for the detection of pollutant gases such as NOx that behave as strong electron donor or acceptor gases. In addition, the possibility of using these films for the detection of aromas has been explored.

The odours and aromas arisen from a complex mixture of Volatile Organic Compounds (VOCs) each of different concentration. The actual odour perception is dependent upon the mutual interactions (synergics, antagonists, additives, etc.) of all these compounds.

The problem has a degree of difficulty. On one hand, humans can perceive these odorant molecules even at very low concentrations (ppb). For this reason, sensors devoted to the detection of VOCs must have a high degree of sensitivity. On the other hand, VOCs are not strong electron donor or electron acceptors and the redox process between them and the phthalocyanine molecules would occur in lesser extent than using NOx.

In spite of these difficulties, LB films of lanthanide bisphthalocyanines have been successfully used for the detection of several VOCs belonging to the main families of odorant molecules (alcohols, carbonyls and esthers). It has been shown that the exposure of the $LnPc_2$ LB films to these molecules causes an increase of the resistance of the films[26].

Fig. 4 shows the typical response of the $LnPc_2$ sensors expressed as the fractional change in Voltage ($\Delta V/V$) towards hexanol, hexanal, n-buthyl acetate and hexane. The exposure to the VOCs results in a sharp increase of the resistance of the films. For the adsorption process, the time for current changes of the gas sensors is about 1 second. The desorption process is slightly longer and the base line is reached after

four minutes. The above observation suggests that the adsorption and desorption are readily achieved and these process occur at room temperature easily.

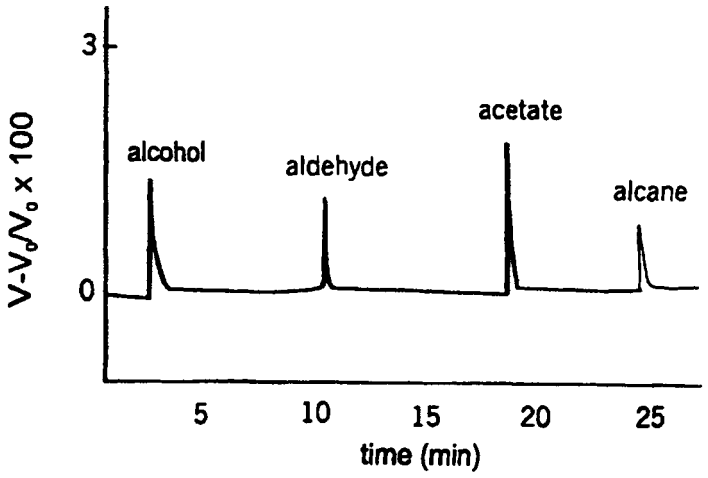



FIGURE 4 Response of a $LnPc_2$ LB film towards towards a series of VOCs (hexanol, hexanal, n-buthyl acetate and heptane)

The changes in the conductivity are proportional to the concentration of gas in contact with the sensor. The linearity of the response at low concentrations, would allow the quantification of trace amounts of organic vapours.

The thickness of the LB films influences strongly their electronic behaviour. Thicker films, for instance 40 monolayers thick, show more intense responses and larger desorption times than thinner films (for instance, 10 monolayers). This observations can be explained taking into account the occurrence of bulk processes, that difficult the desorption step. In turn, the large surface area per unit volume in thinner films, facilitates the desorption process.

The mechanism of the interaction between the VOCs and the sensors is uncertain. In a first approach, it could be thought that VOCs would act as weak electron donors or acceptors and its interaction with $LnPc_2$

would result in a partial reduction or oxidation of the phthalocyanines molecules and hence in a variation of the number of charge carriers in thin organic films. Nevertheless, spectroscopic studies in the UV-Vis-NIR region indicate that the redox processes cannot explain by themselves the changes of the conductivity. It has been proposed that the increase of the resistance can also be due to a swelling effect that leads to a decrease of the mobility of the carriers[27].

## 4. ARRAY OF SENSORS

The above results have opened the possibility of using thin films of $LnPc_2$ as sensing units in electronic noses for the detection of aromas.

In fact, the problem with all chemical sensors of this type lies not with their sensitivity but with their selectivity. The possibility of incorporating functional groups on the aromatic Pc rings or to change the central metal atom can improve the selectivity towards different gases[11,12]. The introduction of substituents can also improve the solubility of the Pc molecules necessary for LB film preparation.

The selectivity of the sensors may be further enhanced by using an array of sensing elements, each with slightly different response, coupled with signal processing methods based on pattern recognition or artificial neural networks.

Using Langmuir-Blodgett (LB) films of lanthanide bisphthalocyanines it has been possible to design and construct an array of sensors able to discriminate among different VOCs. The array is formed by eight different sensors based on unsubstituted and octatertbutyl substituted bisphthalocyanines. The sensors are mounted in a test box and polarised using a constant voltage of 1–5 V provided by a power supply. An air flow is passed trough the reaction camera until the stabilisation of the electric signal. The aromatic samples are placed in the vial and injected in the test box using a Dynamic Headspace sampler. The data collection is controlled through a data acquisition card interfaced by a personal computer. The array has been coupled with a Principal Component Analysis (PCA) software.

As shown in Fig. 5, such an array of sensors has been able to discriminate among different VOCs (hexanol, hexanal, n-buthyl acetate and heptane). The design of an array of sensors based on $LnPc_2$ able to discriminate among different types of olive oils is currently under progress.

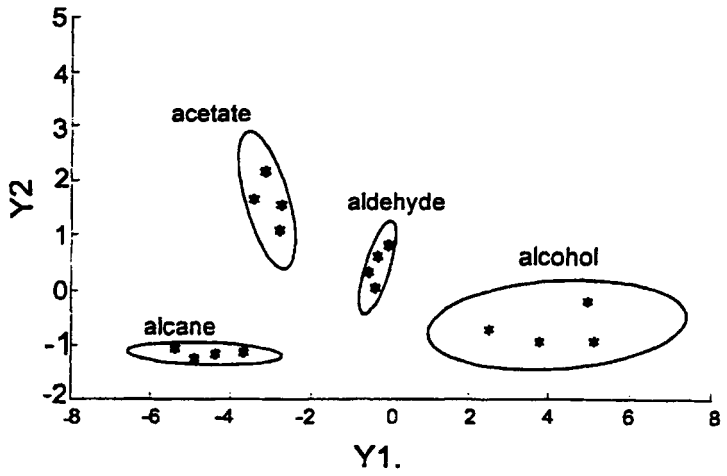



FIGURE 5 Principal Component Analysis of four different VOCs

## 5. LB FILMS AS GAS SENSORS

During the last years, it has been a certain controversy about the convenience of using LB films in gas sensor devices. The LB technique allows preparing films with a high degree of control of the structure, the thickness and the surface of the films. This control has several advantages for gas sensing applications when compared with other types of films. Nevertheless, the limitations of the LB technique as a method for thin film preparation should be noted. It is an intensively time consuming process, expensive, and for some applications, it does not provides advantages over other fabrication techniques[1].

The gas sensing process occurs in three steps. The initial step involves the interaction of the gaseous species with a solid surface. The gas molecules impinge on the surface, and are then adsorbed by the surface. Gas adsorption can be followed by a second step that consists in the diffusion of gas species in the bulk of the multilayer. For semiconducting gas sensors, the adsorption and diffusion process result in a change in the electronic state of the solid and hence in a change in the conductivity.

The third step consists in the desorption of the reactant gas. That is, the process must be reversible and the original conductivity has to be recovered.

The advantages of using LB films can be summarized as follows. By using LB films of few monolayers thick (even monomolecular layers) it is possible to avoid complex formation and bulk diffusion processes that would lengthen interaction times. LB films have a high ratio of surface area to bulk volume. This type of structure causes important differences between the electronic behavior LB films and that of other type of films. Finally, since the reversible adsorption of gases is primarily a surface phenomenon, the homogeneous nature of the surface of LB films increases the performance of the sensors.

In fact, it has been demonstrated that $LnPc_2$ LB films showed faster responses and recovery times than evaporated films of the same sensing substance[26]. This behaviour is related to their rough heterogeneous surfaces that lead to sites that adsorb gas molecules at various energies owing to their differences in geometry. The LB technique allows producing films that are smoother and more homogeneous than the microcrystalline sublimed films. In addition, very thin films can be obtained using these techniques. Consequently, the processes based on the slow diffusion of gas molecules into the bulk material are less important.

## CONCLUSIONS

The conductivity of LB films of lanthanide bisphthalocyanines is dramatically altered by the presence of strong electron donor or acceptors. The presence of VOCs, responsible of the aromas also modifies the conductivity of the films. The precise control of the structure, the surface and the thickness provided by the LB technique, enhances the performance of the gas sensor devices. The sensors are stable, reproducible and the sensitivity and selectivity can be modified by introducing substituents in the benzene rings or by changing the central metal atom.

The comparatively high conductivity showed by $LnPc_2$ (when contrasted with MPcs) and their ability of forming LB films offer the possibility of producing sensitive electronic sensors of gases. These chemiresistors have a promising future as sensing units in electronic noses for the detection of aromas.

### *Acknowledgements*

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