

Nanostructured thin films based on phthalocyanines: electrochromic displays and sensors

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ABSTRACT: The group of the University of Valladolid is a multidisciplinary team formed by chemists, physicists and engineers. The activities of the group are focused to the study of the physicochemical properties of nanostructured Langmuir-Blodgett thin films based on phthalocyanines and their applications. Films of a variety of phthalocyanine molecules including several metallophthalocyanines, lanthanide double decker phthalocyanines and heteroleptic derivatives have been prepared. Their spectroelectrochemical properties have been described in detail and compared with those observed in disordered casted films or microcrystalline evaporated films. The group has dedicated special attention to films based on rare earth double decker compounds due to their unique semiconducting, optical and electrochemical properties. A rich electrochromism has been demonstrated in thin films of this family of compounds. The reversibility is improved in nanostructured Langmuir-Blodgett films. This has permitted development of an electrochromic display that can change its color from blue to green and finally to red. At the present moment, our main objective is the design of sensors able to detect gases and liquids. It has been demonstrated that thin film assemblies based on rare earth bisphthalocyanines modify their conductivity and their optical properties in the presence of electron donor or electron acceptors gases. Changes are also observed when the devices are exposed to Volatile Organic Compounds such as esters, alcohols or aldehydes which are responsible of odors in foods and beverages. Liquid sensors have also been developed. Their working principle is based in the fact that the rich electrochemical properties of phthalocyanine thin films are extremely sensitive to the nature of the electrolytic solution. Arrays of phthalocyanines have been used to construct an electronic nose able to discriminate odors from a variety of foods and beverages. Similarly, phthalocyanines have also been used to construct an electronic tongue based on voltammetric sensors. This is one of the main contributions of the group to the field of sensors.

KEYWORDS: bisphthalocyanine, rare earth phthalocyanine, sensor, electrochromism, Langmuir-Blodgett.

INTRODUCTION

Phthalocyanines (Pc) have appealing electrical, optical or electrochemical properties that are the basis of a number of applications in emerging technologies [1–9]. Pc compounds can be deposited as thin films compatible with microelectronics [10–12]. This opens the possibility

to develop a number of devices. The methods used to prepare thin films based on phthalocyanines include casting, dip coating, screen printing, spin coating, ultrahigh vacuum evaporation, the Langmuir-Blodgett or the Layer by Layer technique, *etc.* Each method allows obtaining thin films with particular structures and properties. Our group has paid special attention to the Langmuir-Blodgett (LB) technique that offers the possibility of controlling, in a very precise fashion, the organization in organic thin films [13–16].

[◇]SPP full member in good standing

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Films of a number of different metallophthalocyanines (MPcs) have been studied by our group with a variety of central metal atoms, axial ligands, peripheral substituents, *etc* [17–19]. This versatility can be used to tune the properties of the Pc material in order to improve the performance of the devices.

Most of the works have been carried out using sandwich type rare-earth complexes (LnPc_2) where a lanthanide ion is coordinated with two phthalocyanine rings. 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 its usual oxidation state (Pc^{2-}). The radical is essentially localized as a $\text{Pc}^{\cdot-}$ species on one of the rings. Such complexes, usually exhibit strong π - π interactions resulting in intriguing electronic and optical properties [8, 9, 20, 21]. These double decker derivatives have an additional interest due to their remarkable semiconducting, redox and electrochromic properties. Double and triple decker heteroleptic analogues containing phthalocyaninato and porphyrinato ligands have also attracted our interest [22].

The earlier works of the group of Valladolid in the field of phthalocyanines date from the beginning of the nineties. They were focused to the preparation and structural characterization of thin films based on a variety of phthalocyanines, paying special attention to lanthanide(III) bisphthalocyanines. The organization of these ordered films could be established using spectroscopic techniques, including UV-vis, FTIR and Reflection Absorption Infrared Spectroscopy (RAIRS) [23]. In addition, in collaboration with the group of Prof. R. Aroca in Windsor (Canada) important contributions to the analysis of single monolayers were carried out using Raman techniques that included Surface Enhanced Raman Spectroscopy (SERS) and Surface Enhanced Resonant Raman Spectroscopy (SERRS) [24–26].

Many efforts were devoted to the study of the rich electrochemical and sensing properties of LnPc_2 films. It was demonstrated that the reversible oxidation and reduction shown by LnPc_2 thin films was accompanied by reversible color changes that could be followed visually [27]. The electrochromism presented by a variety of LnPc_2 derivatives was used to design an electrochromic display that changed the color from blue to green and then to red.

The absorption and desorption of gases modified reversibly the spectroscopic, optical, semiconducting and redox properties of phthalocyanine thin films. This opened the possibility of using these compounds as the sensing material in gas and liquid sensors [9, 28, 29].

The sensing properties of phthalocyanine thin films have permitted development of resistive, optical and electrochemical sensors that have been used to construct an electronic nose (resistive sensors) and an electronic tongue (electrochemical sensors). Such systems have been used to evaluate the quality of a range of foods and beverages [9].

FILM FORMING METHODS

Thin films based on phthalocyanines have been prepared using different techniques. Depending on the method used, different film morphologies can be obtained which have a pronounced effect on the properties of Pc films. The main interest of our group is to obtain nanostructured films and for this purpose techniques such as the Langmuir-Blodgett (LB) (or the Langmuir Shaeffer (LS)) and the Layer by Layer (LbL) techniques have been employed. The structure and properties are compared with those of films obtained by casting, by vacuum sublimation or by spin coating.

Langmuir-Blodgett technique

This is a method of obtaining highly ordered thin films and enables one to gain direct access to precise thickness and orientation control at the molecular level [16, 30]. LB films are formed by spreading a solution of the film forming molecule onto the clean water surface contained in a Langmuir trough. 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 sub-phase. Repeated dippings allow multilayers to be obtained where the thickness can be controlled by the number of dipping cycles. Our group has prepared and studied LB films of different phthalocyanines derivatives, including MPcs coordinated with different central metal ions [31–34] and LnPc_2 coordinated with a range of rare earth elements and substituted peripherally with tertbutyl, phenyl, bromide, terbutoxy, crown ether, groups, *etc.* [13, 14, 23, 29] containing different tetrapyrrole ligands (phthalocyaninate, porphyrinate or naphthalocyaninate) ligands have also attracted our interest due to their unique properties [35].

The rigidity of the floating monolayer can make difficult the transfer of the floating film to the solid substrate. In those cases, two possible strategies can be followed. One possibility, used in collaboration with the group of Prof. L. Valli from the University of Lecce (Italy) and Prof. Jiang from the University of Jinang (China) is to use the Langmuir-Shaeffer (LS) technique. In this method, the floating monolayer is transferred by a vertical lifting to the solid substrate [35]. A second strategy consists in mixing the phthalocyanine molecule with a fatty acid such as arachidic acid. The high amphiphilicity of the long chain fatty acid promotes the formation of ordered monolayers [15, 30, 36].

Mixed films of phthalocyanines with other compounds can also be prepared. These mixed films form composite materials whose properties are the combination of the two starting materials. In particular, our group has dedicated some efforts to obtain mixed films of MPcs with perylene derivatives. Such systems are of interest due to

the occurrence of energy transfer between a donor molecule (a perylene) and an acceptor molecule (a phthalocyanine) [34].

Layer by Layer method (LbL)

Ordered multilayers have also been prepared by depositing alternatively bipolar cationic and anionic compounds or polyelectrolytes [37]. In a collaboration with Prof. O. Oliveira from the Institute of Physics of the University of Sao Paulo (Brasil) we have prepared LbL films of a water soluble sulphonated phthalocyanine acting as a polyanion and a protein (acting as a polycation). The influence of many factors such as the type of solvent used, the ionic strength, the pH, the concentration, the temperature of the solution and so on, in the structure and the spectroelectrochemical properties of the films have been studied [38].

Other techniques

In most of our works the structure and properties of nanostructured films have been compared with those of disordered films prepared by casting or dip-coating from organic solutions, or by spin coating. Several works have been carried out using thin films prepared by vacuum sublimation [17, 32].

STRUCTURAL CHARACTERIZATION OF THE THIN FILMS. SPECTROSCOPIC PROPERTIES

The first step in the evaluation of Langmuir-Blodgett films is the characterization of the floating Langmuir monolayers. The organization of the molecules in the floating films can be evaluated by means of the surface-area isotherms.

The typical surface-area isotherms of the Pc compounds are illustrated in Fig. 1 for the lutetium bisphthalocyanine (LuPc_2) and the octaphenyl substituted derivative ($\text{LuPc}_2^{8\text{Ph}}$). The limiting areas calculated from the slope of the curve indicate that usually, Pc molecules are arranged with the main molecular symmetry axis parallel to the water subphase, but showing a certain tilting angle [29–31]. Few examples of Pc molecules organized with the Pc ring lying flat on the surface have been reported [39]. Brewster Angle Microscopy (BAM) can provide information about the homogeneity of the floating films. Figure 2 shows the BAM images of the floating film of a neat lutetium bisphthalocyanine octasubstituted with bromine groups ($\text{LuPc}_2^{8\text{Br}}$) and the image of the floating layer formed by $\text{LuPc}_2^{8\text{Ph}}$ mixed with arachidic acid.

Ordered Langmuir films can be transferred to solid substrates by the dipping method or the LS techniques.

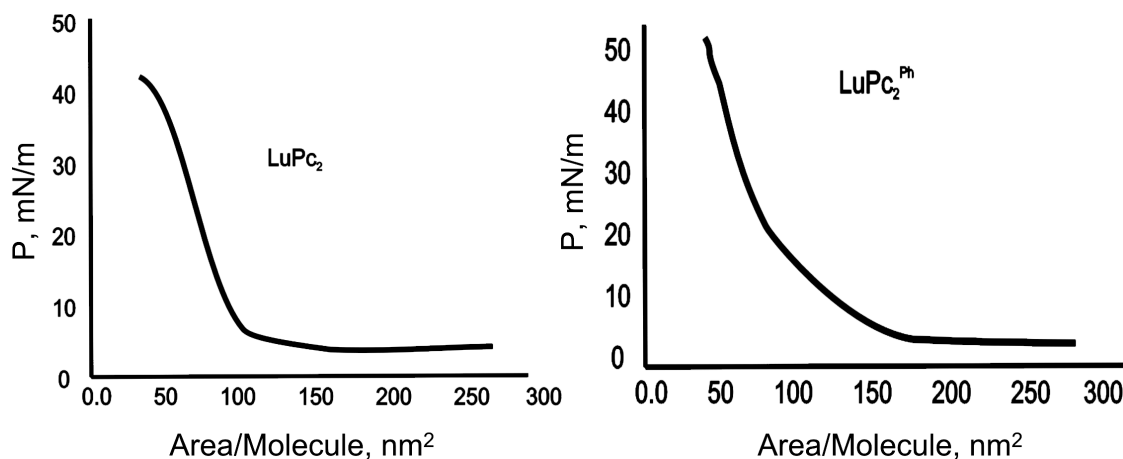


Fig. 1. Pressure-Area isotherms of (a) LuPc_2 and (b) $\text{LuPc}_2^{8\text{Ph}}$

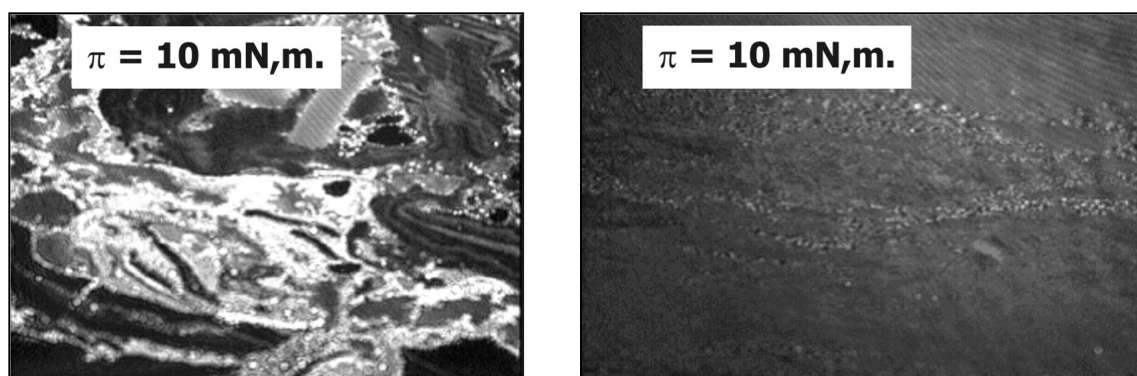


Fig. 2. Brewster Angle Microscopy images of a floating monolayer of a) $\text{LuPc}_2^{8\text{Br}}$ and b) $\text{LuPc}_2^{8\text{Ph}}$ mixed with arachidic acid (1:10)

Films are usually built by Z-type deposition with a transfer ratio close to 1 at surface pressures of *ca.* 20–25 mN.m⁻¹. The structure of the floating monolayers is maintained when transferring the films to the solid substrates. Thin films can be characterized by a variety of techniques including X-ray diffraction or AFM [40–42]. However, our main efforts have been dedicated to the spectroscopic analysis.

The UV-vis spectra of LnPc₂ are typically described by two main absorption bands that are assigned to $\pi \rightarrow \pi^*$ transitions: the Q band centered at about 640–690 nm, which is responsible for the blue or green color of the compound, and the B band centered at about 320–350 nm (Fig. 3). The position of the Q band is modified to some extent by the nature of the central ion and by the presence of substituents. Electron-donor groups cause a rise in the energy level of the HOMO that produces a red shift (bathochromic) of the Q band [43, 44].

LB films show spectra similar to solutions, but a broadening of the bands, and a noticeable red shift in the positions of the maxima are observed. According to the exciton theory [45], this red shift indicates the formation of *J*-aggregates in head-to-tail arrangement of transition dipoles. As illustrated in Fig. 3, the red shift is more pronounced in LB films than in evaporated or cast films indicating a spatially more extended coupling of chromophores in the same relative orientation [13, 15, 29, 31].

In some LB films the high degree of order produces a Davydov Splitting [23]. In such cases, the electronic absorption spectrum of the LB film shows a broad absorption band with both red and blue shifted components relative to the band observed in the spectrum of the material in solution.

Special attention has been paid to the near-infrared (NIR) region. LnPc₂ and their derivatives show an intense band at 1400–1600 nm, in the near-infrared region [46–49]. This band has been attributed to an intramolecular charge transfer, and disappears upon oxidation and reduction [50].

Our group has dedicated many efforts to the vibrational characterization of the phthalocyanine films.

Transmission and reflection-absorption infrared (RAIR) vibrational analysis is a powerful tool to determine the molecular alignment in Langmuir-Blodgett films. The molecular orientation of the films can be established by comparing the FTIR transmission spectra of the KBr pellet with the transmission FTIR and the RAIRS of the films. The bands in the FTIR spectrum associated to out-of-plane vibrations at 727 cm⁻¹ are particularly important for the discussion of the molecular orientation. In most of the LB films based on phthalocyanines studied, the out-of-plane γ -C-H bending at 727 cm⁻¹ is intense in the transmission spectrum and very weak in the RAIR spectrum [11–17]. This confirms that the edge-on organization proposed for the Langmuir layers is preserved during transfer.

Vibrational properties of the films have also been studied using Raman Spectroscopy. Conventional Raman spectroscopy suffers from low signal strength. As such it is not well suited to study Langmuir-Blodgett films of few nanometers thick. The Surface Enhanced Raman Scattering (SERS) technique is designed to overcome this problem. In SERS the Raman signal is enhanced when the film is deposited on the top of a film formed by small metal particles (Cu, Ag or Au). Due to this enhancement, monolayer analysis and single molecule detection is feasible [15, 51]. In Surface Enhanced Resonant Raman Scattering (SERRS), the laser line used is in resonance with the absorbance of the molecules, increasing the magnification of the signals. In the case of Pc molecules, the Laser Line of 570 nm is in resonance with the Q band. This allows clean and intense spectra can be obtained from single monolayers [14, 17, 24–26, 52, 53].

STUDIES ON THE PROPERTIES OF THE FILMS

Electrochemical properties and electrochromism

Phthalocyanines are able to add or subtract electrons while retaining molecular structure and stability, *i.e.* reversible redox behavior is common [1, 6, 9, 54–56].

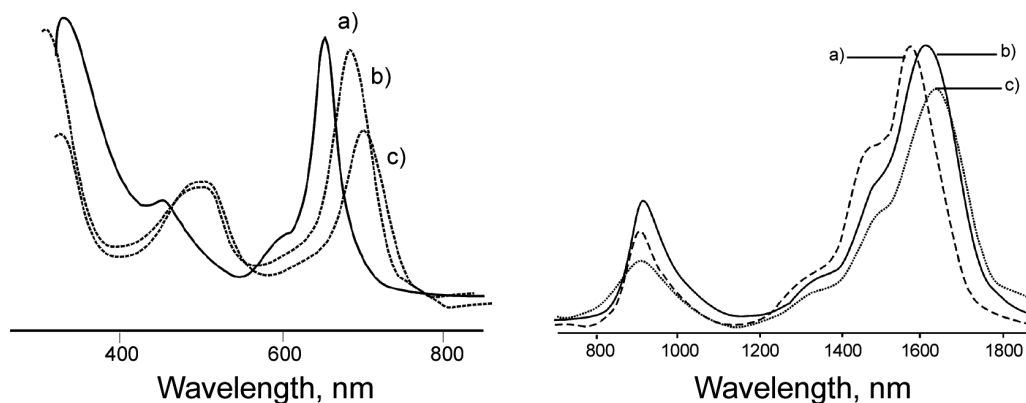


Fig. 3. UV-vis spectra (left) and NIR (right) of (a) solution (b) evaporated film and (c) LB film of a LuPc₂

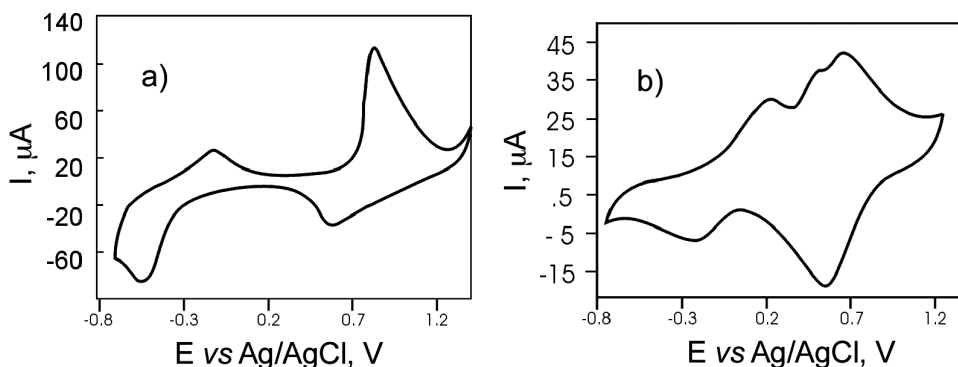


Fig. 4. Cyclic voltammogram of (a) LuPc₂ (b) LuPc₂^{8t}LB film immersed in KCl 0.1 M

The electrochemical behavior of phthalocyanine solutions has been studied by different authors in a variety of solvents and electrolytes. LnPc₂ have a particularly rich redox and electrochemical behavior due to the accessibility of a range of oxidation states centered on the ligand [19, 57–60]. Our group has dedicated many efforts to the study of the electrochemistry of their thin films when they are used as the working electrode in a conventional three electrode cell. In such studies, films are immersed in a water solution where an electrolyte (typically KCl or KIO₄) is added [8]. Figure 4 illustrates the electrochemical behavior of thin films based on rare-earth bisphthalocyanines. The cyclic voltammograms present two redox pairs corresponding to the one reversible electron ring oxidation Ln(III)Pc₂/Ln(III)Pc₂⁺ and one electron ring reduction Ln(III)Pc₂/Ln(III)Pc₂⁻ of the phthalocyanine molecule. Oxidation of LnPc₂ films occurs at lower potentials as the ionic radius increases; the oxidation is facilitated by the presence of electron donating groups [19, 20, 28, 44, 57–62]. Interesting results have been obtained using crown ether substituted bisphthalocyanines. In that case, the oxidation is facilitated and two consecutive oxidations could be observed [37].

Voltammograms are stable and LB films can be cycled up to thousand times without perceptible changes. In contrast, when using evaporated films or cast films, devices could be cycled only 5–10 times in a reproducible manner.

Changes in the oxidation state of LnPc₂ are accompanied by changes in the electronic absorption spectra. The Q band that appears at *ca.* 660 nm in the neutral free radical form, shifts to *ca.* 640 nm in the reduced form. Upon oxidation the Q band splits into two bands at 550 nm and 700 nm. The color changes from green to blue or to red are so drastic that they can be followed with the naked eye. This electrochromism has been found in all the bisphthalocyanines and substituted bisphthalocyanines studied (Ln = Pr, Sm, Eu, Gd, Tb, Dy, Ho, Lu), and in their heteroleptic derivatives [63–65].

Semiconducting properties

LnPc₂ were the first intrinsic organic semiconductors described in the literature. They have particularly high

intrinsic conductivities ($\sigma = 10^{-6} - 10^{-3} \text{ S.cm}^{-1}$ at $T = 300 \text{ K}$) which are several orders of magnitude higher than MPcs (10^{-10} to $10^{-12} \text{ S.cm}^{-1}$ at 300 K) [8, 66–69].

Their interesting electronic properties are due to their neutral radical state and to the strong electronic interaction between the two tightly bound Pc rings. Thus, measurements of the conductance can be achieved with higher precision than in MPcs.

The high density of intrinsically generated charge carriers is due to the fact that LnPc₂ can be easily oxidized and reduced [70]:



$$[\text{LnPc}_2^+] = [\text{LnPc}_2^-] \approx 9.1 \times 10^{16} \text{ carriers.cm}^{-3}$$

These intrinsically generated anions and cations act as charge carriers. The values of conductivity depend weakly on the central metal atom. They also depend on the nature of the substituents attached to the benzene ring. The presence of electron donor groups in the periphery of the aromatic ring decreases the conductivity while electron attractor groups increase the conductivity observed. The conductivity of phthalocyanines can be modified by exposing the films to oxidant and reducing gases. These changes are the basis of their use as resistive sensors [71, 72].

APPLICATIONS OF THIN FILMS BASED ON RARE EARTH BISPHTHALOCYANINES. DEVELOPMENT OF DEVICES

The interesting properties found in films of different phthalocyanine derivatives, particularly in rare earth double decker compounds has permitted development of devices such as electrochromic displays and sensors.

Electrochromic displays

The rich electrochromic properties of LnPc₂ derivatives were recognized in 1970 [73] Since then, several electrochromic devices were developed and reviewed in reference 74. The systems showed certain limitations mainly related to the lifetime of the device and the nature of the electrolyte. Our group designed an electrochromic display [27]. The device was developed in collaboration

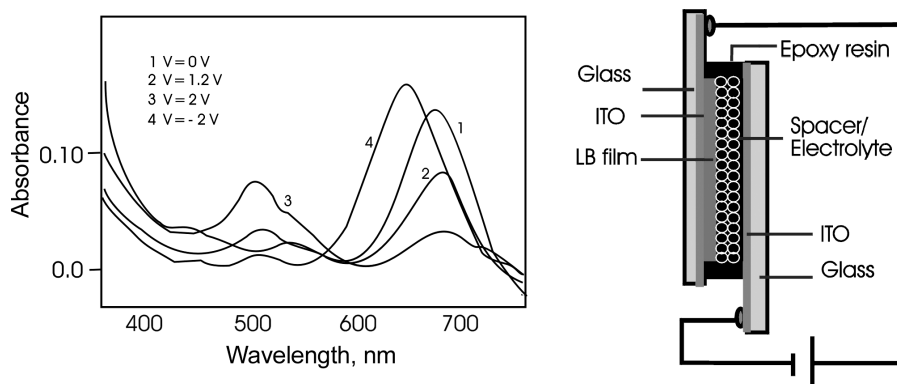


Fig. 5. (a) UV-vis spectra of the PrPc₂ device at different potentials. (b) Device cross-section

with DICRYL S.A., a Spanish company devoted to the development of displays based on liquid crystals. It was based on a Langmuir-Blodgett film of the praseodymium bisphthalocyanine complex. The design of the electrochromic display device is shown in Fig. 5. A very compressible adhesive was serigraphied onto the edge of an ITO covered glass, leaving a 1 cm orifice ready to be filled with the electrolytic solution. A dispersion of 14 μm spacers was used to cover the ITO glass. A second ITO glass coated with the LB film (20 monolayers) was placed against it. Using this method, a 14 μm separation between the two ITO glasses was obtained. The device was then filled with KClO₄ 0.1 M through the 1 cm orifice, and the gap was sealed with an epoxy resin.

The *in situ* UV-vis spectra of the display showed color changes of blue-green, yellowish, and red, when a potential ranging from -2 V to +2 V is applied. The device based on Langmuir-Blodgett films was extremely stable and retain its coloration under open-circuit conditions.

Sensors

Phthalocyanines are among the most interesting organic molecules in the fabrication of chemical sensors because their electrical, optical or redox properties are extremely sensitive to the environmental conditions and the changes produced by the presence of other molecules can be monitored by different transduction methods [71, 72, 75–77]. This behavior has motivated an intense interest to investigate the sensing properties of phthalocyanines and to produce processable forms of these materials.

Optical gas sensors. The UV-vis spectra of thin films of phthalocyanines can be modified by exposing the films to electron donor or acceptor gases such as NO_x, Cl₂ or NH₃ [31, 78–81]. The changes of electronic absorption spectra caused by oxidant and reducing gases are stronger in the case of the bisphthalocyanine rare earth compounds (LnPc₂) [13, 23, 38, 52, 64, 82–86]. For instance, the exposure to NO_x causes a shift in the Q band to higher wavelengths that produce a change in the color of the films from green to red; the adsorption of NO_x is reversible, and the original spectrum can be recovered

several hours later. The exposure to electron donor gases such as ammonia produces a shift of the Q band to lower wavelengths and films change their color to blue.

Thin films based on LnPc₂ have been used to detect other pollutant gases. A collaboration with Tabacalera (a Spanish company devoted to the fabrication of cigarettes) demonstrated that such optical devices could be used to detect tobacco smoke which is rich in ammonia (among other gases and particles) [87, 88].

LnPc₂ have an additional interest as optical gas sensors because the intense band at 1400–1600 nm disappears upon the addition of oxidant or reducing gases [50] or upon exposure to vapors of volatile organic compounds (VOCs) such as alcohols, aldehydes, and esters (which are mainly responsible for odors in foods and beverages). The reversible changes observed in the near-IR region occur at telecommunication wavelengths. This has made possible the development of fiber optic sensors (in collaboration with Prof. Matias from the Engineers School of the University of Navarra (Spain)) where LuPc₂ Langmuir-Shaeffer films have been deposited at one end of the fiber. The other end is connected to an optical detector for measuring the reflected optical power that comes from the vapochromic material [89].

Changes in vibrational spectra (FTIR and Raman) also occur upon exposure to NO_x. The interaction of NO_x causes changes in the vibrational modes related to the isoindole moiety [83, 84]. These changes could also be used with sensing purposes.

Resistive gas sensors. Probably the most widely studied sensors have been the chemoresistive sensors that consist of thin film assemblies that modify their conductivity in the presence of small gas molecules [8, 72]. The high intrinsic conductivity of LnPc₂ facilitates de measurements and increases the sensitivity. Usually, the experimental set up consists in the measurement of the dc conductivity across the surface of a Pc thin film deposited onto planar interdigitated electrodes.

LnPc₂ based sensors can easily detect electron donor or electron acceptor gases such as nitrogen oxides [90, 91]. The high conductivity allows also detecting Volatile Organic Compounds such as alcohols, carbonyls, amines and esters which are not strong electron donor or electron

acceptors [9, 84, 92–94]. The adsorption and desorption are readily achieved and these processes occur easily at room temperature. The changes in the conductivity are proportional to the concentration of gas in contact with the sensor. These results indicate the potential applications of LnPc₂ Langmuir-Blodgett and evaporated films in the detection of aromas of foods and beverages [95] or in environmental applications such as the detection of herbicides [96] or environmental tobacco smoke [88]. A hybrid system made from a polymer and a phthalocyanine can improve the performance of gas sensors, by combining the physical skills of the phthalocyanine and the mechanical properties of the polymer used as a support [32].

Electrochemical sensors. Probably the main contribution of our research group to the field of sensors has been the development a novel type of voltammetric electrodes based on phthalocyanines. Electrodes based on MPc, LnPc₂ and heteroleptic derivatives can be prepared using traditional methods, such as the carbon paste electrode technique (CPE). In addition, phthalocyanines can be conformed as thin films onto a conductive surface by using the Langmuir-Blodgett or the Layer by Layer techniques. When a voltage is applied, peaks associated to the oxidation-reduction electrode material can be observed. The shape and position of the peaks depend on the nature of the electrolytic solution (Fig. 6) [97, 98]. The selectivity is enhanced when the solution contains electroactive substances. In such case, voltammograms show peaks of two different origins: peaks associated to the oxidation-reduction of the analytes present in the

solution and transient responses associated to the electrode material. The important issue is that the interactions that occur between the electrode and the solution can improve tremendously the selectivity of the electrodes. Such interactions include the following aspects: i) the oxidant or reducing character of the solution can modify the oxidation potential of the electrodic material; ii) the electrocatalytic activity of the electrode material can facilitate the oxidation of the compounds solved in the test solution; iii) the response of the electrode material is related to the ability of the sensors to allow the diffusion of the counterions between the solution and the bulk material, an influx necessary to preserve the macroscopic electroneutrality of the electrode. Due to the interactions between the material electrode and the solution, the electrochemical responses obtained for each tested solutions are different and are the reason of the enhanced specificity of the sensors (Fig. 6).

Development of electronic noses and electronic tongues based on phthalocyanines

During the last twenty years, the concept of “electronic nose” has been developed [99]. An “electronic nose” is a new class of instrument inspired by biological sensory systems able to analyze complex mixtures of gases. The system is based on an array of chemical gas sensors with a broad and partially overlapping selectivity towards the volatile compounds present in the headspace of a sample. The array of sensors is combined with computerized multivariate statistical data processing tools. An array of

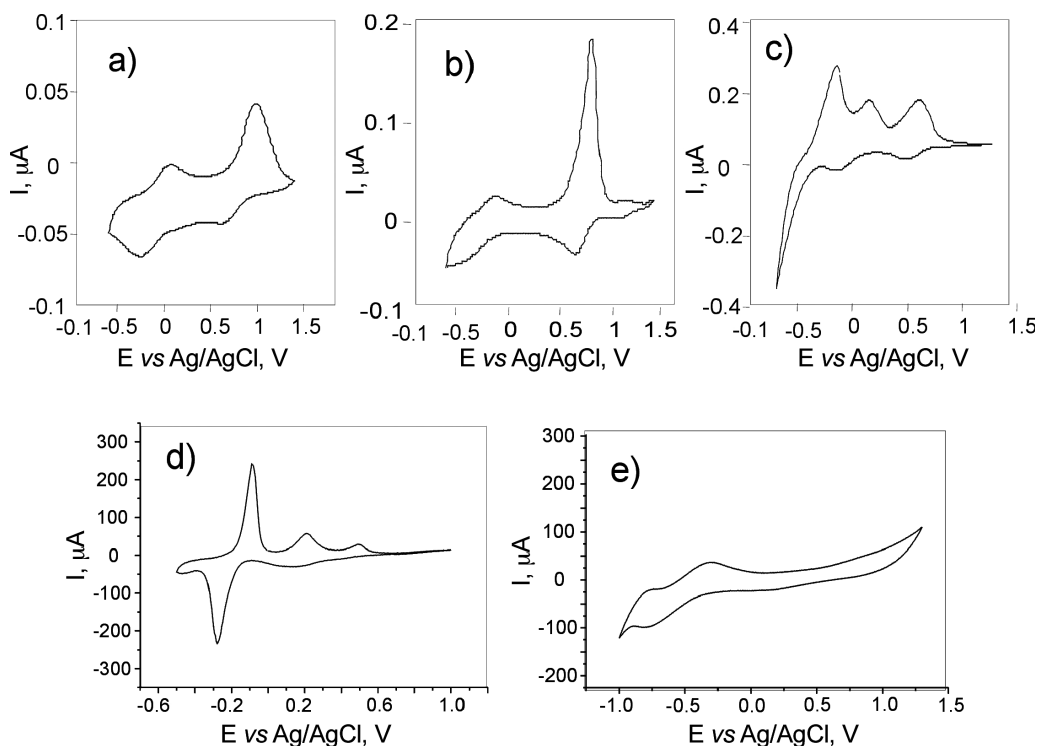


Fig. 6. Response of LuPc₂ LB film towards different solutions (a) KCl, (b) MgCl₂, (c) citric acid (d) HCl and (e) NH₃

rare earth bisphthalocyanine sensors coupled with a data treatment system has been used to discriminate among VOCs belonging to the main families of odorant molecules (alcohols, carbonyls and esters) usually present in foods and beverages. This system has been able to discriminate olive oils of different qualities [95].

A similar concept has been applied to the analysis of complex liquids. Such systems are known as “electronic tongues” and consist of an array of liquid sensors coupled with a pattern recognition software. The first work in this field involved signal generation from potentiometric sensors. An array of tetraphenylporphyrins and phthalocyanines have been used as ionophores and shown an enhanced cross-sensitivity towards a range of metallic ions [100]. An array of voltammetric electrodes based on phthalocyanine compounds as the sensing units of an electronic tongue has been developed by our group. Such arrays are able to discriminate among simple solutions of basic tastes [97, 98] or antioxidants [35]. Our electronic tongue has been able to discriminate wines of different qualities, grape variety or among wines aged in different types of oak barrels [101–107]. Arrays of sensors purposely dedicated to the analysis of oils have also been developed [108–110]

CONCLUSION

Phthalocyanines can be used to prepare thin films using a variety of techniques. Nanostructured films obtained using the Langmuir-Blodgett technique have a particular interest for a number of applications because of the control on the organization of the molecules. The unique physical and chemical properties of lanthanide bisphthalocyanines make this family of materials one of the most interesting candidates for the fabrication of electrochromic displays and sensors. The role of phthalocyanines in sensing technologies is of particular importance in the field of chemoresistive gas sensors working at room temperature, in fiber optic sensors and in electrochemical sensors. Using lanthanide phthalocyanines, it has been possible to develop arrays of resistive sensors. Sensor arrays coupled with pattern recognition software have been used as an electronic nose able to discriminate odors coming from a variety of foods and beverages. Similarly rare earth bisphthalocyanines have been the basis of an electronic tongue based on voltammetric sensors.

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