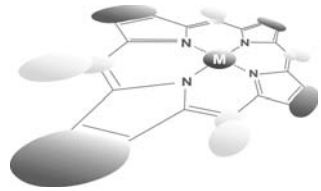
Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2009; **13**: 1159–1167

Published at http://www.worldscinet.com/jpp/



New insights into sensors based on radical bisphthalocyanines

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Received 29 September 2008
Accepted 30 October 2008

ABSTRACT: The unique semiconducting, optical and electrochemical properties of radical lanthanide bisphthalocyanines make them ideal materials for sensing applications. A variety of chemical sensors have been developed using rare-earth bisphthalocyanine thin films. In this paper, the characteristics of sensors based on bisphthalocyanines are reviewed. The advantages of these sensors with respect to sensors developed using other metallophthalocyanines are discussed. Resistive sensors based on bisphthalocyanines change their conductivity when exposed to a variety of pollutant gases and volatile organic compounds. Because bisphthalocyanines are intrinsic semiconductors, the conductivity of their thin films is higher than the conductivity of metallophthalocyanine thin films. This facilitates the electrical measurements and enhances the sensitivity of the sensors. Optical sensors have also been developed based on the rich optical properties shown by bisphthalocyanines. Films characterized by a bright green color change to red or to blue upon oxidation or reduction. The changes also affect the charge-transfer band associated to the free radical that bisphthalocyanines show in the near infrared region. This band coincides with telecommunication wavelengths, making possible the fabrication of fiber optic sensors where a phthalocyanine film is deposited at one of the ends of the fiber. Electrochemical sensors have been developed taking advantage of the unique electrochemical behavior associated to the one-electron oxidation and one-electron reduction of the phthalocyanine ring. These reversible processes are extremely sensitive to the nature of the electrolytic solution. This has made possible the development of voltammetric sensors able to produce particular signals when immersed in different liquids. In the last part of the paper, the fundamentals and performance characteristics of electronic noses and electronic tongues based on bisphthalocyanines are described. Such devices have been successfully exploited in quality control, classification, freshness evaluation and authenticity assessment of a variety of food, mainly wines and olive oils.

KEYWORDS: bisphthalocyanine, sensor, electronic nose, electronic tongue.

INTRODUCTION

The observation that physicochemical properties of metallophthalocyanines (MPc) are modulated by the adsorption and desorption of gases has led to significant efforts to use them as sensing material in chemical sensors. A variety of transduction methods have been used that include resistive, optical, electrochemical, impedance or mass sensors [1–7].

Sandwich-type rare-earth bisphthalocyanines ($LnPc_2$) are among the most interesting materials for sensing applications (Fig. 1). In the double-decker complexes a lanthanide ion is coordinated with two phthalocyanine rings [8]. The $LnPc_2$ molecules bear one unpaired electron that is delocalized over the two macrocycles. The free radical character and the strong π-π interactions between

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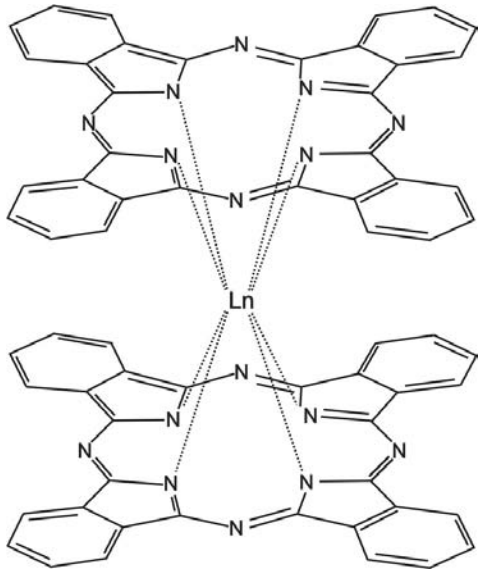

Fig. 1. Scheme of a rare-earth bisphthalocyanine

the two Pc units result in intriguing physicochemical properties. One of the most important properties of $LnPc_2$ is the high intrinsic conductivity ($\sigma = 10^{-6}$–10^{-3} S.cm^{-1} at T = 300 K) while MPcs are insulators with conductivities ranging from 10^{-10} to 10^{-12} S.cm^{-1} at 300 K [9–12]. This high intrinsic semiconductivity is an advantage for electric measurements. Rare-earth bisphthalocyanines have a particularly rich electrochemistry due to the accessibility of several oxidation states. Electrochemistry of $LnPc_2$ solutions in organic media revealed that the molecules can be reduced, or oxidized through many reversible one-electron steps [13–16]. These redox processes are usually accompanied by color changes, being green in the neutral state, reddish in the oxidized form and blue in the reduced form. The first oxidation and reduction potentials of monophthalocyanines are ≥1.5 V apart [17]. The accessibility of the oxidation states of $LnPc_2$ has made possible to study the electrochemistry of chemically modified electrodes (as thin films or carbon paste electrodes) immersed in aqueous solution. Changes in the oxidation state are usually accompanied by changes in the electronic absorption spectra and $LnPc_2$ are well-known as electrochromic materials [18–22].

The UV-vis spectra of MPcs and $LnPc_2$ 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 [17–22]. $LnPc_2$ also show a band at 1400–1600 nm, related to the unpaired electron. The band corresponds to an intramolecular charge transfer: the radical monoion Pc ring acts as electron donor and the second Pc ring as an electron acceptor [23–26].

The electrical, optical and electrochemical properties of $LnPc_2$ are extremely sensitive to environmental conditions. The changes produced by the presence of other molecules can be monitored by different transduction methods [3, 4, 27, 28]. In addition, $LnPc_2$ can be deposited as thin films compatible with microelectronics. The methods used to prepare thin films include casting, dip coating, screen printing, spin coating, ultrahigh vacuum evaporation, the Langmuir-Blodgett (LB), the Langmuir-Shaeffer (LS) or the layer-by-layer technique (LbL), *etc*. [29–33]. Each method allows obtaining thin films with particular structures and properties. Special attention has been paid to the Langmuir-Blodgett technique that offers the possibility of controlling, in a very precise fashion, the organization in organic thin films [4].

In spite of their remarkable sensing behavior, bisphthalocyanines have not been so extensively studied as sensitive materials as the parent monophthalocyanine compounds. This is due to the difficulty of the synthesis and purification processes [17, 29]. Fortunately, an increasing number of groups are dedicating efforts to the synthesis of new bisphthalocyanine complexes [30–36]. In this paper, the sensing devices constructed using rare-earth bisphthalocyanines are reviewed (including sensors for electronic noses and electronic tongues) and their advantages discussed.

RESISTIVE GAS SENSORS

The first researches in gas sensors based on phthalocyanines were carried out using MPcs. It has been established that the electronic conductivity of MPc thin films can be modulated by the absorption and desorption of gases [1–4]. Resistive sensors based on MPcs have two advantages over conventional Metal Oxide Sensors (MOX). First, MPcs sensors can work at room temperature while MOX sensors need to be heated at *ca*. 300–350°C. The second advantage is the versatility of MPcs that allows tuning the selectivity of sensing materials so that the molecular chemical properties fit the gas-sensing application needs. The number of MPcs derivatives tested as gas sensors is increasing rapidly. MPcs have some disadvantages which are related to the low conductivity of MPc molecules and the long desorption times (typically several hours are needed to recover the original resistance). These have generated certain prevention towards phthalocyanines as sensitive materials for resistive sensors.

Sandwich-type bisphthalocyanines can overcome these important problems due to their high intrinsic conductivities that facilitate the experimental setup and increase the sensitivity. The exposure of $LnPc_2$ to oxidant gases such as NO_X causes drastic changes in the conductivity at room temperature [37–40]. The changes in the conductivity are intense and proportional to the concentration of gas in contact with the sensor. $LnPc_2$ based sensors can easily detect other gases such as halogens, HCl, H_2S, SO_2, NH_3 and a variety of Volatile Organic Compounds (VOCs) [41–45].

The nature of the central metal ion coordinated to the Pc rings and the presence of chemical groups linked to the

peripheral benzene rings can modify the sensing properties of the phthalocyanines [37–47, 63]. The presence of electron-donating substituents such as *tert*butyl, phenyl, propyloxy, octyloxy, or crown ether groups decreases the conductivity of the films and modifies the sensitivity towards oxidant gases [32, 48–50]. Other interesting bisphthalocyanine derivatives have also been synthesized and tested as sensors. For instance, double-decker bisphthalocyanines bridged by a calixarene have shown interesting sensing properties [32].

Resistive sensors based on $LnPc_2$ have been prepared using different techniques. Each method allows obtaining thin films with a particular structure. It has been demonstrated that the structure influences the sensibility and the kinetics and the responses. Special attention has been paid to the Langmuir-Blodgett technique that offers the possibility of controlling, in a very precise fashion, the thickness and the organization in organic thin films [28, 41–47].

It is well-known that the recovery ratio of resistance is related to the penetration of gas molecules into the bulk phase of the sensitive layer [51]. Decreasing the film thickness makes the recovery process faster. The control on the thickness provided by the LB technique improves the recovery times. This approach can be used with $LnPc_2$ due to the high conductivities of these phthalocyanine derivatives. In contrast, it is highly difficult to measure accurately the conductivity of MPcs LB films. As the changes in conductivity observed in $LnPc_2$ sensors are quite intense, the desorption process can be shortened by exposing the sensors to the gas for only a few seconds instead of working under saturation conditions (Fig. 2).

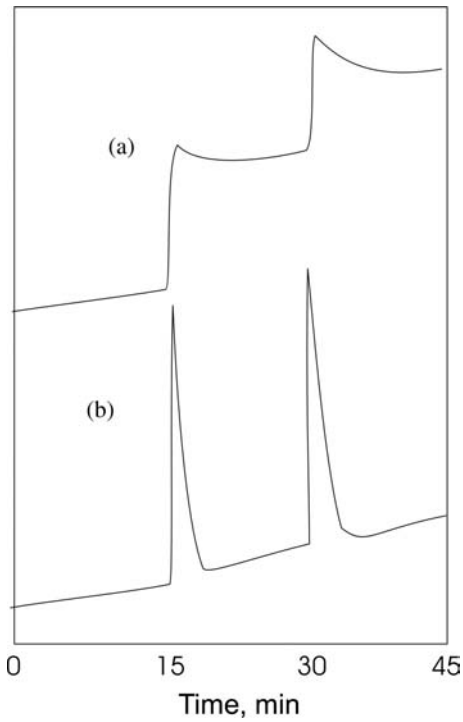

Fig. 2. Changes in conductivity of a $GdPc_2$ evaporated film (upper trace) and LB film (lower trace) exposed to NO_2

The above results have evidenced the potential application of $LnPc_2$ films in the detection of aromas of food and beverages [44, 52] or in environmental applications such as the detection of herbicides [53].

The fabrication of the first field-effect transistor based on phthalocyanines ($LuPc_2$ and ZnPc) was described 20 years ago [3, 55]. More recently, chemical field-effect transistor (ChemFET) was introduced as a new transducer for gas sensing, at first with a monophthalocyanine (NiPc) as active semiconductor [55, 76, 66–74], then by depositing an LB film of a $PrPc_2$ complex and octyloxy derivatives on the gate area of MOSFETs replacing the gate metal [52, 53]. Such LB film ChemFET gas sensors can detect NO_2 gas down to 5 ppm, whereas NiPc-based FETs have been used as ozone sensors in the ppb range [56].

OPTICAL SENSORS

The UV-vis spectra of thin films of MPcs can be modified by exposing the films to electron-donor or -acceptor gases. The sensors show a good sensitivity and selectivity depending on both the metal and the peripheral substituents [2–5]. The changes of electronic absorption spectra caused by gases are of special interest in $LnPc_2$ because the spectral modifications caused by gases are extraordinarily intense. For instance, exposure to NO_X causes a shift in the Q band to higher wavelengths that produces 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 (Fig. 3). Other gases such as SO_2, CO, Br_2 or Cl_2 have also been tested. The spectral changes are affected by the nature of the metallic ion and the peripheral substitutions. LB films of alkyl, phenyl, alcoxy and alkylthio-substituted bis(naphthalocyaninato) rare-earth complexes also show reversible changes in the UV-vis spectra when exposed to gases [19, 20, 32, 59–64]. Optical sensors based on bisphthalocyanines have found practical applications. For instance, LB films have been

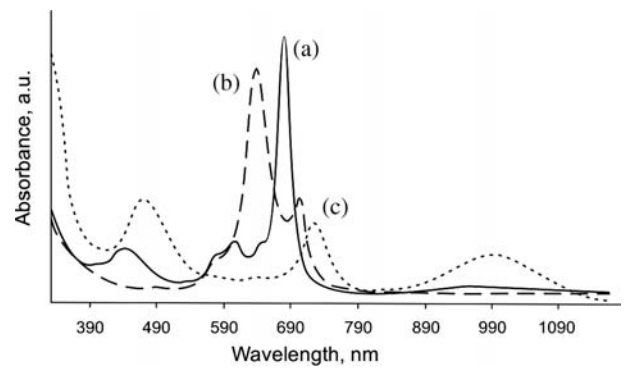

Fig. 3. UV-vis of a $LnPc_2$ (a) LB film (b) LB films exposed to NO_X (c) LB film exposed to NH_3

used to detect tobacco smoke, which is rich in ammonia (among other gases and particles) [66, 67].

$LnPc_2$ have an additional interest as optical gas sensors because the intramolecular charge transfer band in the near infrared region disappears upon the addition of hydrazine, HCl, or VOCs [26–28]. The reversible changes observed in the near-IR region occur at telecommunication wavelengths. This has made the fabrication of fiber-optic sensors possible where $LuPc_2$ Langmuir-Shaeffer films are deposited at one of the ends of the fibers; the other end is connected to an optical detector for measuring the reflected optical power that comes from the vapochromic material [68].

Spectroscopic studies have been carried out to elucidate the nature of the interaction gas-sensor. For instance, the interaction of NO_X causes changes in the vibrational modes related to the isoindole moiety [69].

MASS SENSORS

Phthalocyanines and porphyrins can be used to design sensors that analyze the increase in mass of a thin film using a Quartz Crystal Microbalance (QMC) or a Surface Acoustic Wave (SAW) device [2, 69]. However, few works have been carried out using bisphthalocyanine compounds. A composite of a $LnPc_2$ mixed with carbon nanotubes has been used as the sensing materials in quartz crystal microbalances and microcantilevers for the detection of amines [71]. Spin-coated films of a *tert*-butylcalix[4]arene bridged bis double-decker lutetium(III) phthalocyanine (Lu_2Pc_4) deposited onto a quartz crystal resonator has demonstrated to be sensitive to a variety of vapors [32].

ELECTROCHEMICAL SENSORS

Electrochemical sensors based on MPcs have been exploited as sensors for the assessment of many important inorganic, organic or biological compounds. A good review can be found in reference 13. Such devices have been developed using a range of electrochemical techniques. Amperometric sensors are based on the oxidation or reduction of electroactive compounds at the working electrode, when a constant potential is applied. The modification of the electrode surface with phthalocyanines can provide a range of electrodes with different selectivity. In electrocatalytic amperometric sensors, electrodes modified with certain phthalocyanines (mainly CoPc and its derivatives) have the ability to catalyze the oxidation or reduction of solved compounds by lowering the potential required for the catalyzed redox systems [13]. Amperometric enzyme sensors combining the specificity of enzymatic reaction using a phthalocyanine as a mediator have been developed [72, 73]. In ion-selective electrodes, potentiometric response of a metallophthalocyanine-doped membrane electrode is based on the coordination of the anion analyzed as an axial ligand to the central metal of the phthalocyanine molecule [13, 74]. Electrochemical impedance has been used to test the response of MPc films towards certain gases and liquids [75–77].

$LnPc_2$ have been used to develop only amperommetric and voltammetric sensors. Voltammograms of lanthanide (III) phthalocyanine thin films show two monoelectronic, fully reversible, oxidation and reduction processes. The redox transformations are accompanied by ion movements between the solution and the bulk material necessary for preserving the macroscopic electroneutrality of the electrode. For this reason, the peak positions and their sharpness depend on the nature and the concentration of the ions solved in the test solution and the electrochemical responses can be used to detect ions present in the solution [78]. This is illustrated in Fig. 4 where the electrochemical response of a $LuPc_2$ electrode immersed in KCl, $MgCl_2$, HCl and NH_3 is shown. The spectroelectrochemical response of Langmuir-Blodgett films of bisphthalocyanines bridged with calixarenes in the presence of different counterions has also been studied [22].

The technique used to prepare the electrodes influences the kinetics of the diffusion of ions. Electrodes prepared

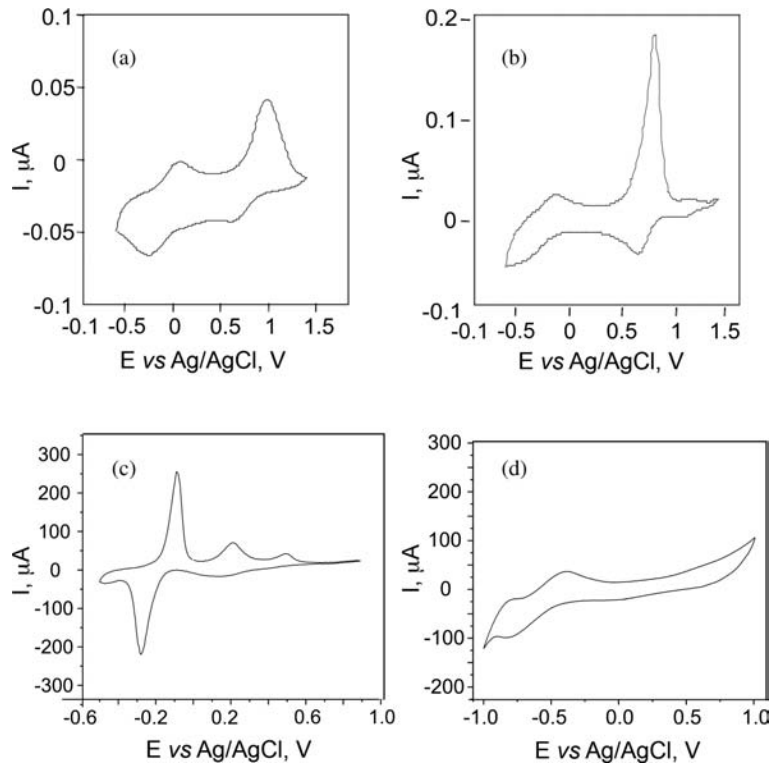

Fig. 4. Cyclic voltammograms of a $LuPc_2$ sensor exposed to 0.1 M (a) KCl (b) $MgCl_2$ (c) HCl and (d) NH_3

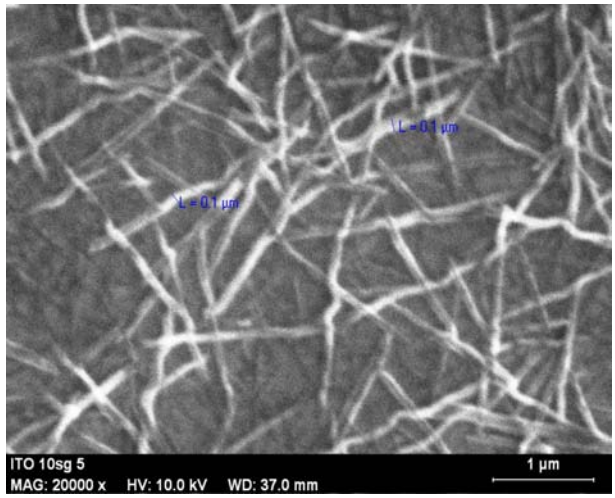

Fig. 5. Nanostructured films of $GdPc_2$ deposited under electrophoretic conditions onto ITO glass

using the Langmuir-Blodgett technique or by the carbon paste technique (mixing the bisphthalocyanine with carbon and a conglomerate) have been successfully used for the detection of ions and of a variety of electroactive substances. The kinetics is faster and the reversibility is improved when using Langmuir-Blodgett or Langmuir-Shaeffer films. However, carbon paste electrodes are easy to fabricate and their lifetime is longer [78].

Recently, nanostructured films have been prepared by means of electrophoretic techniques (Fig. 5). The electrochemical properties of the films have been evaluated towards solutions containing ammonia and a range of biogenic amines such as trimethyl amine and dopamine. It has been demonstrated that nanostructured films with a high surface/volume ratio can give rise to sensors with improved properties [79].

Electrodes modified with $LuPc_2$ dissolved in a thin film of nitrobenzene covering a graphite electrode have also been tested as voltammetric sensors for the detection of ions. In such electrodes, the $LnPc_2$ acts as a mediator for the electron transfer between the solid electrode and a substrate in the aqueous phase. The monoelectronic, fully reversible, oxidation and reduction processes, can be utilized for examination of anion and cation transfers between different phases [79, 80]. Similar studies have been carried out using bis(tetra-*t*-butylphthalocyaninato) (tetra-*t*-butylphthalocyaninato and hexadecachlorophthalocyaninato) derivatives [78]. The transfer of ions in microparticles of lutetium (bis-*tert*-butylphthalocyaninato) complex immobilized on the surface of paraffin-impregnated graphite electrode has also been studied [82].

Voltammetric sensors chemically modified with lanthanide bisphthalocyanines have also been used to analyze solutions containing electroactive substances. In this case, voltammograms show peaks of two different origins: peaks associated to the oxidation-reduction of the analytes present in the solution, and the transient responses associated to the electrode material. But the important issue is that the interactions that occur between the electrode and the solution can improve extraordinarily the selectivity of the electrodes. These interactions include: (i) the oxidant or reducing character of the solution can modify the oxidation potential of the electrode material, (ii) the electrocatalytic activity of the electrode material can facilitate the oxidation of the compounds dissolved in the test solution, and (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 [78, 83]. All these redox processes and interactions give rise to rich voltammograms with a high degree of selectivity.

Finally, an innovative sensor based on the electrochromic properties of spin-coated films of a bisphthalocyanine derivative has been used for the assessment of nicotinamide adenine dinucleotide hydride (NADH) in water solutions [84].

ELECTRONIC NOSES AND ELECTRONIC TONGUES

The most promising approach to finding applications for non-specific chemical sensors is the use of arrays of sensors. In such systems several sensitive materials which exhibit cross selectivity to various gases or liquids are coupled with signal processing methods. These methods include non-supervised techniques such as Principal Component Analysis (PCA). Using PCA it is possible to discriminate between samples with different characteristics. Classification techniques can also be used that address the problem of identifying an unknown sample and assigning it to a certain set of previously learned categorized samples. Typical classification models used in electronic tongues are Linear Discrimination Analysis (LDA) and Artificial Neural Networks (ANN).

These instruments are known as electronic noses (when they are applied to the analysis of gases) [85] and electronic tongues (when they are applied to the analysis of complex liquids) [74, 86–88].

Thin films of different metalloporphyrins have been used as sensing materials in arrays of QMC sensors to discriminate a variety of gases [89] and wines [90, 91]. Porphyrins and metallophthalocyanines have also been investigated as the sensing layer in electronic optical noses to detect VOCs of interest in food analysis [92, 93]. In spite of the potential advantages of $LnPc_2$, up to now arrays of mass sensors have not been designed. Phthalocyanines and porphyrins have not been extensively used as sensitive materials in resistive sensors for electronic noses due to their low conductivity. In contrast, the high conductivity of lanthanide bisphthalocyanines facilitates the electrical measurements in array of sensors. An array of rare-earth bisphthalocyanine sensors coupled with a data treatment software 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 [44]. This system has been able to discriminate among olive oils of different qualities [52].

Electrochemical sensors (potentiometric, impedimetric or voltammetric) are the most widely used sensing units in electronic tongues [94–97].

Arrays of potentiometric sensors based on metallophthalocyanines and porphyrins solved in polymeric membranes and glassy carbon electrodes modified with porphyrins have demonstrated to be efficient ionophores to detect a variety of ions [98, 99]. A porphyrin-based electronic tongue has been applied to the detection of alcohol in beverages and to the analysis of wines [100]. Arrays of impedimetric electrodes covered with various organic materials (including conducting polymers, perylenes, phthalocyanines, carbon nanotubes or lignine) have been used to detect simple substances such as phenothiazine [101] and to analyze complex solutions such as coffee [102].

Bisphthalocyanines have also been used to construct arrays of electrochemical sensors. In such arrays square wave voltammetry and cyclic voltammetry have been used as measurement method. The principle behind voltammetric electrodes chemically modified with electroactive materials was presented in previous paragraphs. When a voltage is applied, peaks associated to the oxidation-reduction of the analytes present in the test solution can be observed. In addition, transient responses caused by redox processes associated to the phthalocyanine deposited onto the electrode material are also observed. Interactions between the solution and the bisphthalocyanine give rise to rich voltammograms with a high degree of selectivity.

An array formed by voltammetric electrodes modified with bisphthalocyanines has been used to discriminate between model solutions of basic tastes (citric acid to produce sourness, saltiness produced by NaCl or KCl, $MgCl_2$ or quinine to produce bitterness, sweetness produced by sucrose or glucose, and umami produced by monosodium glutamate [78]). The system has also been able to detect model solutions of bitterness [103]. Substances under study included $MgCl_2$, quinine, and four phenolic compounds extracted from olive oils which are mainly responsible for their bitterness. Antioxidants usually present in foods (citric acid, vanillin or pyrogallol) have been discriminated using an array formed by bisphthalocyanines and heteroleptic derivatives [104]. The content of antioxidants has also permitted the use of the electronic tongue to distinguish between seed oils and olive oils [105].

In spite of the difficulty of using arrays of sensors for the analysis of extremely complex liquids such as red wines, electronic tongues based on voltammetry has been able to discriminate red wines with different organoleptic characteristics [83,106]. The capabilities of the array of voltammetric sensors has been improved by extending the array to other families of sensitive materials (bisphthalocyanines, perylenes and conducting polymers). Using this hybrid system, it has been possible to discriminate between wines elaborated with different varieties of grapes [107] to detect adulterations [108] or to follow the aging of red wines using different methods [109]. These electronic tongues are not only able to discriminate but also the results have been correlated with the chemical parameters measured in wines and in olive oils. Good correlations have been found with the polyphenol contents and with the parameters related with the acidity [110, 111].

It has been demonstrated that the simultaneous utilization of electronic noses and electronic tongues can increase the amount of information extracted from a certain sample. The combination of sensors operating in liquid (electronic tongue) and in the head space (electronic nose) based on metalloporphyrins has been successfully used in clinical applications and in food analysis [88,112]. A combination of an electronic nose (based on MOX sensors) and an electronic tongue (based on bisphthalocyanines) has been used to discriminate wines with different organoleptic characteristics [113].

CONCLUSIONS AND FUTURE WORK

The particular properties of $LnPc_2$ make them one of the most interesting organic molecules in the fabrication of chemical sensors. The high conductivity of $LnPc_2$ and their derivatives facilitates the electrical measurements in resistive sensors. The color changes that occur after exposure to oxidant and reducing gases are the basis of optical sensors. The unique spectral variations in the NIR region at telecommunication wavelengths have permitted the development of fiber optic sensors. Finally, the rich electrochemistry of $LnPc_2$ is the basis of voltammetric sensors with a high degree of cross-selectivity.

Such sensors have been used to detect a variety of gases, VOCs and a variety of compounds of interest in the food industry and in environmental applications, among others.

Finally, arrays of sensors based on bisphthalocyanines have been developed because there is a wide variety of different bisphthalocyanine molecules with large ranges of sensitivity available. Such systems have demonstrated enormous potential due to their advantageous performance characteristics.

The number of bisphthalocyanine derivatives tested as gas or liquid sensors is increasing rapidly. The possibility of having new molecules with purposely designed properties will provide a way of improving the selectivity of the sensors.

Acknowledgements

Financial support from CICYT (Grant no. AGL2006-05501/ALI) and Junta de Castilla y León (VA-052A06) is gratefully acknowledged.

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