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Sensors based on double-decker rare earth phthalocyanines

J.A. de Saja *, M.L. Rodríguez-Méndez

Department of Condensed Matter Physics, Faculty of Sciences, Prado de la Magdalena s/n, 47011 Valladolid, University of Valladolid, Spain

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Abstract

Phthalocyanines are interesting materials for sensing applications because their physicochemical properties are susceptible to be modified by the presence of certain molecules. Among the large family of the phthalocyanines, the sensing properties of double-decker phthalocyanines (which are sandwich-type complexes where a lanthanide metal is co-ordinated with two phthalocyanine rings) are of special interest due to their unique physicochemical properties. Their high intrinsic semiconductivity and their rich electrochemical and electrochromic behaviour, facilitate enormously the measurement of the changes in the physicochemical properties caused by the environment.

In spite of their remarkable sensing behaviour, 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, and to the fact that these compounds are not commercially available. In this paper, the sensing devices constructed using rare earth bisphthalocyanines are revised (including sensors foe electronic noses and electronic tongues) and their advantages discussed.

Keywords: Phthalocyanine; Bisphthalocyanine; Sensor; Electronic nose; Electronic tongue

Contents

* Corresponding author. Tel.: +34 983 423196; fax: +34 983 423192.
E-mail address: sajasaez@fmc.uva.es (J.A. de Saja).

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1. Introduction

Phthalocyanines (Pc) are a large family of coordination compounds [1–4] that have attracted considerable attention as sensitive materials because their electrical, optical and redox properties can be modified in certain ambients [5]. The changes produced by the presence of other molecules can be monitored by different transduction methods [6–13]. The most widely studied sensors have been the chemo-resistive sensors were the changes in the conducting properties of phthalocyanines are modified in the presence of oxidant and reducing gases. These changes occur at room temperature and this constitutes an advantage with respect to other sensitive materials. The notable properties of Pc molecules have allowed using these materials as electro-chemical and optical sensors [5].

Phthalocyanines possess other properties that make them suitable for sensing applications. These properties include a good thermal and chemical stability or the possibility of depositing Pc molecules as thin films compatible with microelectronic devices, in particular Langmuir–Blodgett films [14–16]. The precise control of the organization and thickness of the films may enhance the performance of these devices.

Monophthalocyanines or metallophthalocyanines (termed as MPc) consist in a phthalocyanine ring coordinated to a metal placed in the central cavity. MPc species can be synthesized from more than 70 metallic or metalloid atoms [1,2,13] (Fig. 1a).

More complex structures are possible, and phthalocyanines can fuse to form polymeric structures where the Pc rings are (a) linked by covalent bonding (network polymers), (b) co-facially bridged or (c) Pc are side substituents in chain polymers. Phthalocyanines can also form double-decker complexes (also named sandwich-type or bisphthalocyanines derivatives) and triple-decker rare earth complexes. In the double-decker complexes a lanthanide ion is coordinated with two phthalocyanine rings ($LnPc_2$) (Fig. 1b).

Besides this variety of phthalocyanine structures, Pcs permit chemical modification through change of the central metal ion and through axial ligation to the central metal. The phthalocyanine fragment is also capable of a vast versatility through symmetric and asymmetric substitution of the main phthalocyanine skeleton or by modification of the ring system. This wide range of possibilities explains the vast number of phthalocyanine molecules synthesized until now and the increasing number of Pc molecules tested as sensitive materials.

Among all this variety of phthalocyanine derivatives, the group formed by the double-decker derivatives has demonstrated to have an additional interest for sensing applications due to their remarkable properties that are superior to those shown by other phthalocyanines [17]. For instance, the high intrinsic conductivity of $LnPc_2$ (several orders of magnitude superior to those observed in MPcs) facilitates the conductivity measurements in chemoresistive gas sensors. $LnPc_2$ have also rich electrochemical and electrochromic properties that are much more marked than in the MPc analogues. This fact has allowed preparing highly sensitive electrochemical liquid sensors and optical sensors [5]. Unfortunately, due to the difficulty of the synthesis and the purification of $LnPc_2$, and to the fact that they are not commercially available, these compounds have been studied in lesser extent.

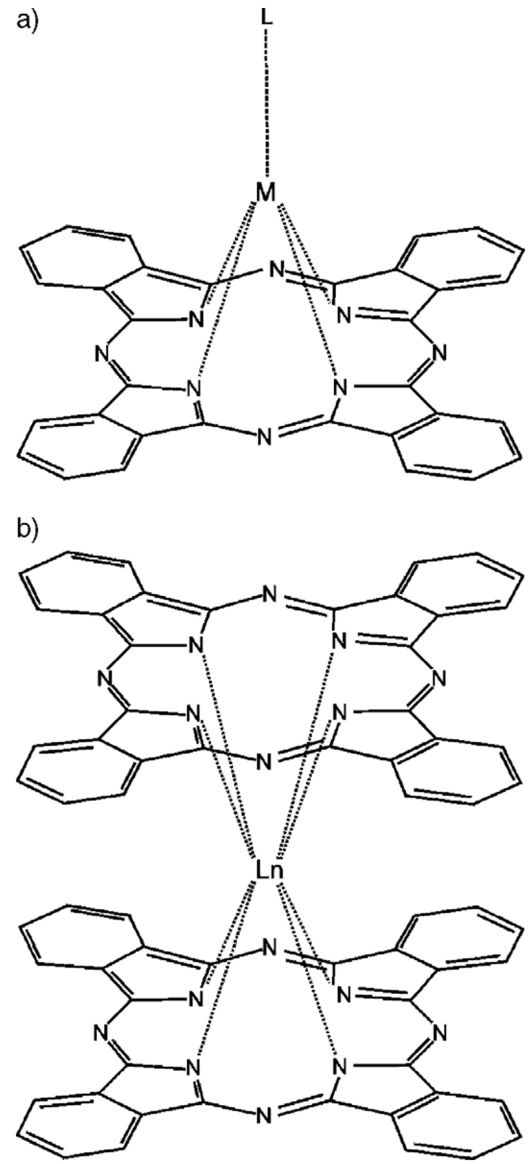

Fig. 1. Structure of (a) monophthalocyanine and (b) bisphthalocyanine.

In this paper, the sensing properties of the rare earth bisphthalocyanines will be described, and the works carried out using this family of compounds as sensitive materials will be revised. This will include not only the efforts carried out to design individual sensors but also the works carried out in which bisphthalocyanines have been used as the sensing units of arrays of sensors forming part of electronic noses and electronic tongues.