



State of art in porphyrin Langmuir–Blodgett films as chemical sensors

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ABSTRACT

Porphyrins are tetrapyrrolic macrocycles with a fascinating and multifarious variegation of properties of essential significance in up-to-date and leading technologies. From a different point of view, the Langmuir–Blodgett technique allows the immobilisation of films with an accurate regulation of molecular organisation and thickness. As a logical upshot, this manuscript concerns a substantial object of consideration in contemporary research, the utilisation of Langmuir–Blodgett multilayers of porphyrins in sensing elements for the detection of analytes in different matrices. Investigations on the morphological, optical, structural and surface characteristics of these films are remarkably related to the significant properties of sensors with the ultimate goal of rationalising the innermost intercourses between the sensing behaviour and the peculiarities and molecular organisation brought about by the deposition method. The integration of the typical electrical and optical characteristics of porphyrins with the potentialities of the Langmuir–Blodgett multilayer has originated not only encouraging projects but has afforded also certainties on the accomplishment of operative chemical sensors.

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1. Introduction

The developing attention paid to the improvement of chemical sensors for multifarious purposes, such as clinical, environmental, and military applications, has prompted the consequent exploration for sensors with adequate sensitivity, stability and ample selectivity spectrum.

Materials holding a broad π -electron cloud generally evidence semiconducting characteristics and exhibit intense absorptions in the UV–visible region of the spectrum. Upon exposure to several analytes, these materials experience significant variations of their electrical and optical properties, thus suggesting their use as active and sensitive moieties within chemical sensors.

Among such materials, porphyrins play a fundamental role due to their rich UV–visible absorption spectra and semiconducting characteristics, both tunable through the introduction of metal atoms inside

the heme core (almost all metals in the Periodic Table of Elements are capable of co-ordination to the porphyrins) or by functionalisation on the peripheral positions. The parent macrocycle consists of twenty carbon atoms and four nitrogen atoms, arranged in the famous heterocycle structure composed of four pyrrole subunits linked by methyne bridges. The two-dimensional geometry of porphyrins and their electronic structure both promote very rapid and vectorial electron transfer and the thorough interaction of these macrorings with analytes. In fact porphyrins exhibit environment sensitive physical properties. Porphyrins of paramount importance in many biological and biochemical processes contain sometimes small modifications of the elementary tetrapyrrolic macrocycle. For example, chlorophylls are the famous and fundamental green tetrapyrrole plant pigments that operate as photoreceptors of radiation in the photosynthetic event and haemoglobin is the iron-bearing moiety of the red blood cells of vertebrates responsible for the transport of oxygen. It is therefore obvious that porphyrins, owing to their multifaceted characteristics, have gained an important role in diverse areas ranging from materials science to photonic and opto-electronic materials, from data storage to medicine (for example, the photodynamic therapy),

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from photovoltaic cells to biotechnology and biology. Moreover this class of compounds exhibits very attractive properties as for well-established synthetic paths, thermal and photo-stability, moderate working temperature, chemical sensitivity, selectivity, response and recovery times, and reproducibility in chemical sensors are concerned. Moreover, pertaining to sensors, other researchers have already pointed out that two fundamental cooperative effects take place in the sensing phenomenon and mainly determine the performances of chemical sensors based on porphyrins: weak interactions (such as Van der Waals or London forces and hydrogen bonding) and the coordination of analytes [1].

The interaction of analytes with porphyrin active layers originates changes of various physical parameters, such as conductivity, mass, optical absorption, and work function. The chance to convert them into an electrical signal combining the macrocycle film with appropriate transducers has allowed the development of several kinds of chemical sensors; transduction methods concern dielectric changes, electrical changes, such as dc current, dc impedance, dc resistance, dc voltage, weight change and optical property variations. Many researchers have devoted their efforts to clarify the relationships among film structure and molecular arrangement with the performances of porphyrin active layers.

Among the methods utilised in order to immobilise the active layers based on porphyrins some of the most used are the simple and immediate solvent casting or spin-coating, and the more elaborated self-assembly, electropolymerisation, and Langmuir–Blodgett or Langmuir–Schäfer techniques. The Langmuir–Blodgett (LB) technique is a particular method for the fabrication monolayer after monolayer of considerably organised structures with thickness, composition and molecular architecture that can be manipulated a priori at the nanometric level; therefore, it permits better than other methods to accomplish size miniaturisation. Moreover, the LB technique imparts to the multilayers improved crystallinity and conjugation in the case of “electroactive” moieties. The propinquity with the active sites and the diffusion of analytes within the multilayer can be modulated by the film thickness and structure, both engineered by the LB technique. Finally the surface damages, which are the principal disadvantage connected with high energy growth method, are circumvented by the room temperature and humid LB method. Other authors already described the employment of chemical sensors based on LB active layers [2]. In Fig. 1 a pictorial view of the main steps during a LB experiment is reported.

2. Text

Porphyrins possess a wide conjugated electron system that results in a strong coloration; upon exposure to various analytes the absorption of these macrocycles can vary because of a modification of the electronic energy levels after absorption of analyte molecules (above all inorganic and organic vapours) either on the peripheral functionalisation or in the core of the cycle.

Spectral variations in the optical properties of organic substances have evidenced clear-cut advantages in comparison with other transduction principles as for response and recovery times, selectivity, sensitivity, absence of electrical connections and sophisticated electrodes, and consequently simplicity of the realisation of the sensing device, are concerned; in particular, as for the comparison with the homologue conductometric sensors, where an uninterrupted current flow through the sample is necessary, the involved electrical power is remarkably smaller. In fact in 1988 Beswick and Pitt published a thorough and elegant investigation about the optical detection of several toxic gases using fluorescent tetraphenylporphine (TPP) LB films [3]. Two different approaches were exploited: the deposition of mixtures of arachidic acid (AA) and TPP and then, in order to increase mechanical strength and response reversibility, the transfer of mixtures of TPP and the polymerizable compound

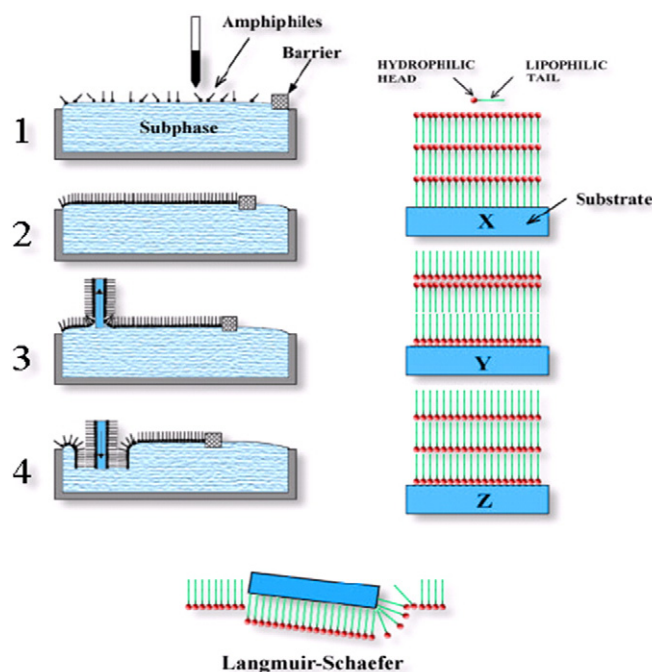


Fig. 1. Different stages of a Langmuir–Blodgett deposition: **1.** Solution spreading at the air–water interface; **2.** Compression of the floating film; **3.** First transfer onto a hydrophilic substrate during the up-stroke; **4.** Successive adhesion of the second layer during the down-stroke (for a Y-type films). On the right, the structure of X-, Y-, and Z-type films. At the bottom, a side view of the horizontal dipping method, also known as Langmuir–Schäfer technique.

pentacosanoic acid, that was later irradiated by UV light. In this way polymerisation of diacetylene-TPP multilayers was induced.

Since the whole sensing apparatus incorporated LB films deposited on a waveguide arrangement, the clear-cut convenience of using LB films resides in the accurate control of film thickness and in the knowledge of the refractive index. The Langmuir curve obtained for monolayers of arachidic acid mixed with TPP consists of two linear portions separated by a kink at 23 mN/m. The limiting area per molecule of AA obtained by extrapolation to zero surface pressure of the second high-pressure steep region of the curve is 22 Å²/molecule; the closeness of this value to the one reported for pure AA floating monolayers (19–20 Å²) [4] suggests that upon compression and at high surface pressures the macrocycle molecules are progressively squeezed out from the fatty acid monolayer and eventually lie above the alkyl terminations of AA. A similar and related behaviour has been also suggested in other instances for floating films consisting of AA and different hydrophobic molecules [5]. In the transferred multilayers it is plausible to suggest that TPP molecules are located in the hydrophobic regions within the LB multilayers. In the case of mixed films with pentacosanoic acid, the diacetylene cadmium salt was in reality transferred because of improved stability of the floating monolayers induced by the presence of Cd²⁺ ions in the subphase.

Both kinds (TPP-AA and TPP-diacetylene) of films were Y-type multilayers deposited onto hydrophobic glass substrates at the surface pressure of 20 mN/m and a transfer rate of 0.047 mm/s. The Soret band in the absorption spectra of LB films evidenced a remarkable band broadening and a bathochromic shift when compared with the solution spectra for both kinds of films (containing AA or pentacosanoic acid); this is typical for solid plane-to-plane interactions among macrocycles in the LB films. The presence of AA does not influence the fluorescence emission spectra of pure TPP. Moreover the independence of UV–vis absorption spectra from AA:TPP molar ratio in the spreading solution further confirms the inter-molecular ring interaction.

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