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Amphiphilic porphyrin-cardanol derivatives in Langmuir and Langmuir–Blodgett films applied for sensing

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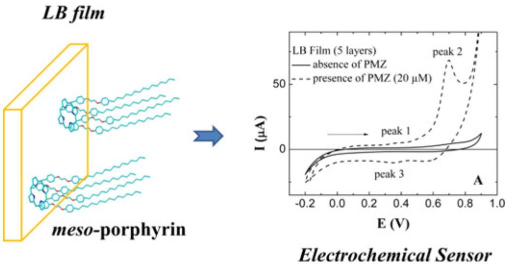
HIGHLIGHTS

- Nanostructured films were formed using amphiphilic meso-porphyrin derived from cardanol.
- Acidified water reduce the self-aggregation of the meso-porphyrin in Langmuir films.
- Preferential orientation perpendicular to the water and parallel to the substrate surface.
- Langmuir–Blodgett films were tested as a promethazine sensor.

GRAPHICAL ABSTRACT



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ABSTRACT

This study presents the preparation of a nanostructured films with an amphiphilic *meso*-porphyrin whose side chains are derived from cardanol, a byproduct of the cashew industry. The Langmuir films were prepared on acidified water to reducing the self-aggregation of the complex and the mean molecular area for the *meso*-porphyrin measured by surface pressure isotherms was 177 $Å^2$ and confirmed by compressibility modulus. The 700 nm band observed in the Langmuir films supports the coexistence of monomers and dimers similar to the spectra of the solution ($CHCl_3/CH_3COOH$). The formation of bright block domains with different sizes and shapes for the monolayer disappears after surface pressure starts to increase ($\pi \geq 2\,mN\,m^{-1}$), as observed by Brewster angle microscopy measurements. Results of UV–vis spectra of the Langmuir films and FTIR reflection of the Langmuir–Blodgett (LB) films of *meso*-porphyrin indicated that the molecules exhibit preferential orientation with the planes perpendicular to the water (Langmuir) and parallel to the substrate (LB) surface. The LB films were tested as a promethazine sensor, which detected a concentration of 2 μM, a value greater than those obtained by other nanostructured systems.

1. Introduction

Porphyrins are a class of macrocyclic compounds with interesting optical properties, *e.g.* a high optical absorption coefficient for UV–visible light and extended conjugation length that spreads all over the central core of the structure [1]. Such characteristics

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allow porphyrins to be used in applications such as photodynamic therapy [2] and as dyes in dye-sensitized solar cells [3]. Usually in these applications, porphyrins are employed in water or organic solutions, or in thin films on solid substrates. For the latter, in spite of the use of bulky cast and spin-coated films [4,5], ultrathin films produced by the Langmuir–Blodgett (LB), self-assembly and thermal evaporation techniques are receiving much attention [6–8] as alternative bottom-up techniques. Such techniques are helpful for the fabrication of solid nanostructured films with advantageous properties for electronic and optical devices [9,10].

Since the 1980s many studies in the literature have described the use of porphyrins in Langmuir films [11–22], some of them characterizing film properties, while yet others have focussed on applications. Crucial characteristics of these monolayers include the aggregation state and pseudo-crystalline organization of the molecules on the surface. Normally the macrocycles are not completely in contact with water, lying flat on the surface, but exists a preferential orientation angle. In studies with the heterocomplex(phthalocyanato)(tetra-4-pyridylporphyrinato)cerium [Ce(TPyP)(Pc)] [16] the authors showed the orientation angles of porphyrin and phthalocyanine macrocycles with respect to the substrate to be 33–28°. They also describe the connected use of the other molecules in the surface or the subphase to disperse the aggregates.

One common application for LB films is as the focus for sensors [13,18,19,23–27], in particular optical sensors as the UV–visible absorption spectra for porphyrins present distinctive bands due to their highly conjugated π-electron systems. 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. Recently, Giancane and Valli reported that the integration of typical electrical and optical characteristics of porphyrins with the potentialities of the Langmuir–Blodgett multilayer have produced not only encouraging devices but have also afforded certainties on the accomplishment of operative chemical sensors [6].

In this context, electrochemical sensors are very promising due to their high degree of selectivity and sensitivity for determining lower concentrations of various analytes [28]. In particular, in LB systems the better sensitivity of the films can be explained by its nanostructured nature, since film thickness, organization and homogeneous distribution of electroactive species are known to affect the electrochemistry of the system [13,23–25].

In addition to naturally occurring porphyrins such as heme, synthetic porphyrins also currently play an important role in academic and industrial laboratories, since advantageous properties can be obtained through on-demand synthetic approaches. The synthesis of porphyrins is usually conducted using commercial products derived from petroleum, which are a non-renewable source and lie outside of the scope of modern "green" chemistry. In this way, the search for new porphyrins derivatives produced using environmentally friendly strategies to turn porphyrins into a "green" compound is continually being explored [29].

In this study, an alternative synthetic route is described to obtain 5,10,15,20-tetrakis-[4-(2-(3-pentadecyl)phenoxy)-ethoxy]phenylporphyrin, a *meso*-porphyrin cardanol derivative [6]. Cardanol is a natural phenol contained in cashew nutshell liquid (CNSL) – a by-product of the cashew nut (*Anacardiumoccidentale L.*) industry [30]. It is presented in the literature as an antioxidant molecule [31], as a structural molecule in biomembrane models [32], and as a building-block for nanostructured polymeric matrix for nanoparticle immobilization [33]. Cardanol is an amphiphilic molecule having one long alkyl chain attached to the phenol unit and porphyrins synthesized from it are suitable to fabricate Langmuir and LB films. It will be seen that naturally derived *meso*-porphyrin forms stable Langmuir films and can be transferred as LB multilayers, which have applicability in chemical sensing for promethazine. The architecture of these films has been studied thoroughly using many techniques and the results are discussed in the following sections. The electrochemistry of *meso*-porphyrin was used to probe the catalytic activity of the fabricated electrode.

2. Material and methods

2.1. Materials

All reagents were commercial products of analytical grade used without further purification. Dibromoethane, 4-hydroxybenzaldehyde, boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), pyrrole and promethazine hydrochloride (PMZ) were supplied by Sigma–Aldrich and *N,N*-dimethylformamide (DMF), ethanol, dichloromethane, toluene, hexane, ethyl acetate and chloroform ($CHCl_3$) from Vetec Química.

2.2. Porphyrin synthesis

2.2.1. Precursors

The hydrogenated cardanol (3-n-pentadecylphenol) was obtained from Laboratory of Products and Technology in Process (LPT-UFC) by chromatography using silica gel 60, eluted with a mixture of hexane/ethyl acetate (9:1) v/v. The hydrogenated cardanol was collected in the first fraction eluted from the column with a yield of 87%. The fractions collected were characterized and shown to be consistent with literature data [34]. 1-(2-bromoethoxy)-3-pentadecylbenzene and 4-[2-(3-pentadecylphenoxy)ethoxy]benzaldehyde compounds were synthesized and characterized according to literature procedures [6].

2.2.2. Porphyrin

The 5,10,15,20-tetrakis-[4-(2-(3-pentadecyl)phenoxy)-ethoxy] phenylporphyrin (*meso*-porphyrin) was obtained by a variation of the procedure described in [37]. It was synthesized by adding 4-[2-(3-pentadecylphenoxy)ethoxy]benzaldehyde (0.577 mmol), pirrol (0.577 mmol) and NaCl (14.5 mmol) in $CHCl_3$ (58 mL with 0.8% ethanol). The reacting mixture was maintained under stirring and in N_2 atmosphere for about 10 min. The previous mixture was added to $BF_3 \cdot OEt_2$ (0.190 mmol), maintaining the reaction under stirring and inert atmosphere for additional 10 min. DDQ (0.434 mmol) dissolved in toluene was then added and the reaction took place for 1 h. The reaction product was then concentrated and added to 100 mL of a mixture of DMF/ethanol (7:3 v/v), and subjected to vigorous agitation. The resulting suspension was filtered through a sintered plate funnel and the solid obtained was washed with methanol. The product was purified by chromatography in a 60-column silica gel with a methylene chloride/hexane (6:4 v/v) eluent. The product was collected in the first fraction, then eluted, evaporated and obtained as a purple solid. Yield: 30%. Mp 98–101 °C. FT-IR: ν, cm^{-1}, 3326, 2916, 2850, 1608, 1579, 1508, 1471, 1448, 1350, 1288, 1245, 1224, 1172, 1066, 966, 804. UV–vis ($CHCl_3$): λ_{max}, nm, ($\log \varepsilon$) 421 (5.7), 518 (4.3), 555 (4.2), 593 (3.9), 649 (4.0). ^1H NMR ($CDCl_3$, 300 MHz): δ, ppm 8.90 (s, 8H, β position of the pyrrole moiety), 8.15 (d, 8H, Ar), 7.33 (d, 8H, Ar), 7.28 (t, 4H, Ar), 6.95–6.89 (m, 12H, Ar), 4.58–4.51 (m, 16H, OCH_2), 2.68 (t, 8H, Ar–CH_2), 1.39–1.30 (m, 96H, CH_2), 8.89 (t, 12H, CH_3), −2.66 (s, 2H, NH). MALDI-TOF-MS *m/z* $[M+H]^+$ 2000, 6 [6].