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Full Length Article

Supramolecular architectures of iron phthalocyanine Langmuir-Blodgett films: The role played by the solution solvents

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ABSTRACT

The developing of organic-based devices has been widely explored using ultrathin films as the transducer element, whose supramolecular architecture plays a central role in the device performance. Here, Langmuir and Langmuir-Blodgett (LB) ultrathin films were fabricated from iron phthalocyanine (FePc) solutions in chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), dimethylformamide (DMF), and tetrahydrofuran (THF) to determine the influence of different solvents on the supramolecular architecture of the ultrathin films. The UV–vis absorption spectroscopy shows a strong dependence of the FePc aggregation on these solvents. As a consequence, the surface pressure vs. mean molecular area (π-A) isotherms and Brewster angle microscopy (BAM) reveal a more homogeneous (surface morphology) Langmuir film at the air/water interface for FePc in DMF. The same morphological pattern observed for the Langmuir films is preserved upon LB deposition onto solid substrates. The Raman and FTIR analyses indicate the DMF-FePc interaction relies on coordination bonds between N atom (from DMF) and Fe atom (from FePc). Besides, the FePc molecular organization was also found to be affected by the DMF-FePc chemical interaction. It is interesting to note that, if the DMF-FePc leads to less aggregated FePc either in solution or ultrathin films (Langmuir and LB), with time (one week) the opposite trend is found. Taking into account the N-Fe interaction, the performance of the FePc ultrathin films with distinct supramolecular architectures composing sensing units was explored as proof-of-principle in the detection of trace amounts of atrazine herbicide in water using impedance spectroscopy. Further statistical and computational analysis reveal not only the role played by FePc supramolecular architecture but also the sensitivity of the system to detect atrazine solutions down to 10^{-10} mol/L, which is sufficient to monitor the quality of drinking water even according to the most stringent international regulations.

1. Introduction

The design of supramolecular structures has been at the forefront of technological applications [1–5] paving the way for developing nanoarchitectonics [6]. Different strategies can be employed to produce such structures, but the emphasis has been given to techniques that allow controlling molecular architectures, including Layer-by-Layer [7] physical evaporation, [8] Langmuir and Langmuir-Blodgett films [9–12]. In these cases, different supramolecular architectures can be achieved by tuning experimental conditions, such as i) deposition methods [1] ii) thermal annealing [13] iii) solvent interaction [14,15] among others. For instance, Xiao et al. [16] have shown the influence of different solvents on the morphology and crystallinity of poly(3-hexylthiophene) (P3HT) thin films. The importance of the o-xylenesolvent to improve the Langmuir–Schaeffer (LS) deposition of copper tetra-(tertbutyl)-phthalocyanine was presented by Kolker et al. [17–19]. Chiang et al. [14] have found the methyl sulfoxide solvent interferes with the PEDOT conformation, affecting the electrochemical properties of the films. PEDOT with linear conformation displays higher conductivity and reversibility for ion exchange, which increases the sensitivity of electrochromic devices [14].

Phthalocyanines (Pc) attract great attention due to their thermal and chemical stability, electrical and optical properties, and the possibility of thin film fabrication [20–24]. However, the strong π-π stacking interactions significantly reduce the solubility of metal Pc in organic solvents [25–28]. In this work, Langmuir and

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Langmuir-Blodgett (LB) films were fabricated from FePc solutions in chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), dimethylformamide (DMF), and tetrahydrofuran (THF) to investigate the influence of these different solvents on both optical absorption and morphological properties of the films. The solvents were chosen according to their polarity (Fig. S1) and presence (or not) of N e O atoms in their molecular structure. The FePc was chosen mainly due to the metal core (Fe), susceptible to coordination with nitrogenous and phenolic groups [29–31]. As proof-of-principle, FePc LB films with distinct supramolecular architectures were evaluated as sensing units in the detection of trace amounts of atrazine herbicide in water through impedance spectroscopy. The impedance data were further analyzed using multidimensional projection techniques and principal component analysis (PCA) to demonstrate the effect of the different LB supramolecular architectures on the sensing unit distinction ability. Atrazine belongs to the s-triazine family, being widely used in combating weeds in many different crops [32], which can potentially lead to contamination of the environment, especially the groundwater. Depending on the concentration, it can act as an inhibitor of photosynthesis [33,34] and may present endocrine disruptor or carcinogenic effects [35–37].

2. Materials and methods

2.1. Reagents and solutions

Iron phthalocyanine (FePc, MW = 568.38 g/mol) was purchased from Kodak and used as received. FePc solutions were prepared at 0.5 mg/mL (8.8×10^{-4} mol/L) using chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), and dimethylformamide (DMF), whose molecular structures are given in Fig. S1. The atrazine pesticide ($C_8H_{14}ClN_5$, MM = 215.68 g/mol, Fig. S1), purity = 98.8%, was purchased from Fluka Analytical-Brazil. The solutions were prepared by simply adding FePc powder to the reagents followed by 30 min of sonication. All solvents are HPLC grade acquired from Merck. The ultrapure water (18.2 MΩ cm) was acquired from a Milli-Q system, model Simplicity.

2.2. Langmuir and Langmuir-Blodgett (LB) films

The FePc Langmuir and Langmuir-Blodgett (LB) films were fabricated using a KSV Langmuir trough, model 2000. Langmuir films were prepared by spreading 350 μL of FePc solutions (8.8×10^{-4} mol/L) onto the water subphase (1.3 L). The solvent was allowed to evaporate for ca. 20 min before the first compression. The Langmuir monolayers were characterized by surface pressure vs. mean molecular area (π–A) isotherms at 23 °C using the Wilhelmy method. The monolayer was symmetrically compressed under a constant barrier speed of 10 mm/min. Brewster angle microscopy (KSV, model micro-BAM) images were also acquired for different areas during the Langmuir film compression.

The LB films were obtained by transferring the FePc Langmuir monolayers from the air/water interface to different solid substrates depending on the characterization technique to be applied. The surface pressure was kept constant at 25 mN/m during ca. 15 min prior the LB deposition, controlled by the displacement of the barriers (1 mm of displacement every 5 min). Y-type LB films were obtained by using an upstroke and downstroke speed of ca. 2.0 mm/min. FePc LB films containing up to 21 layers were deposited onto quartz substrate for ultraviolet-visible (UV–vis) absorption spectroscopy and onto ZnSe for FTIR measurements. FePc LB films containing five layers were deposited onto Pt interdigitated electrodes (IDE, 50 pairs of digits with 10 μm width, 0.5 mm length and 100 nm height, and 10 μm apart each other) for impedance spectroscopy.

2.3. Characterization techniques

The UV–vis absorption spectra were recorded for FePc solutions and LB films using a Varian spectrophotometer, model Cary 50, from 190 to 1100 nm. The micro-Raman scattering experiments were conducted with a micro-Raman Renishaw spectrograph, model in-Via, with laser excitation at 633 nm. The system is equipped with a Leica microscope, whose 50x (NA 0.75) objective lens allows collecting spectra with ca. 1 μm^2 spatial resolution. Single-point spectra were recorded with ca. 4 cm^{-1} resolution and 10 s accumulation time using a computer-controlled motorized stage (XY). The FTIR spectra were taken on a Bruker spectrometer, model Tensor 27, between 4000 and 500 cm^{-1}. FTIR measurements were performed using the transmission mode with 128 scans and spectral resolution of 4 cm^{-1}. The surface morphology was characterized through AFM using a Nanosurf Instrument, model easyScan 2, with a tip of silicon nitride and using the tapping mode. All topographic images were collected with a resolution of 512 lines per scan at a scan rate of 0.5 Hz. The images were processed with the software Gwyddion 2.19.

Impedance spectroscopy measurements were performed using a Solartron analyzer model 1260 A. Impedance spectra were acquired from 1 Hz to 1 MHz using 50 mV of amplitude. The sensing array is composed of four sensing units: a bare Pt interdigitated electrode (IDE) and three Pt IDEs coated with 5 LB layers built up from FePc solutions in CH_2Cl_2, DMF/freshly prepared and DMF/aged for one week, as illustrated in Fig. S2. The bare Pt electrode was used to monitor any change in the electrical response caused by the ultrathin films. The measurements were performed with sensing units immersed into ultrapure water (18.2 MΩ cm) used as a reference and into atrazine aqueous solutions at 0.1×10^{-9}, 1.0×10^{-9}, 15×10^{-9}, 50×10^{-9}, and 100×10^{-9} mol/L. The course of measurements started from the lowest (0.1×10^{-9} mol/L) to the highest (100×10^{-9} mol/L) atrazine concentrations. Between each set of measurements involving a specific concentration of atrazine, the sensing units were carefully washed with ultrapure water. The sensing units were left soaking 20 min inside the solutions before data acquisition to enable a stable reading. The impedance data were further analyzed using multidimensional projection techniques, whose details can be found in Oliveira et al. [38] and Paulovich et al. [39].

3. Results and discussion

3.1. FePc Langmuir films

3.1.1. π-A isotherms

Fig. 1 shows the π-A isotherms for FePc in $CHCl_3$, CH_2Cl_2, THF, and DMF. Similar profiles are found for both FePc/CH_2Cl_2 and FePc/$CHCl_3$ π-A isotherms, considering all the compression stages. The corresponding liquid-phase (up to 15 mN/m) of the FePc/THF is displaced towards larger molecular areas, which suggests an interaction between FePc and THF, unperceived for $CHCl_3$ and CH_2Cl_2 solvents. There is a possibility of a coordination of the DMF oxygen with the FePc iron, leading to the formation of dimeric species of FePc, as reported by Barbosa et al. [30] working with Mg–Al hydrotalcite-like materials used as support for the immobilization of Fe(III) tetrasulfonated phthalocyanine (FePcTs). However, at higher surface pressures (above 15 mN/m) the FePc/THF π-A isotherm tends to overlap the FePc/CH_2Cl_2 and FePc/$CHCl_3$ π-A isotherms. The later indicates the FePc-THF interaction is not strong enough, and the final packaging of FePc molecules is substantially the same as in $CHCl_3$ and CH_2Cl_2. Therefore, the formation of FePc dimeric species through coordination interaction can be minimized. Besides, the FePc solutions in $CHCl_3$, CH_2Cl_2, and THF have