FABRICATION AND CHARACTERIZATION OF WELL-ORDERED MONO AND MULTILAYER LANGMUIR-BLODGETT FILMS INCORPORATING ZINC PHTHALOCYANINES

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Phthalocyanines (Pc) and metallo-phthalocyanines (MPc) have been used for many years as blue and green dyes, but recently they have also been investigated due to their applications as catalysts, chemical sensors, photosensitizers, and in electronic and photonic technologies. In particular, zinc phthalocyanines (ZnPc) had initially received less attention but recent investigations target on their use in photodynamic therapy. These applications usually require a thin film deposited on a solid substrate. Studies in Langmuir-Blodgett (LB) films of MPc are important in understanding of interfacial spectroscopic processes occurring in organic solid materials deposited on inorganic solid substrates for further developing of photovoltaics and optoelectronic devices.

In this work we report the fabrication of Langmuir and LB films of a substituted ZnPc (octakis(oxyoctyl)phthalocyanine of zinc, Figure 1B), and their characterization by means of several techniques including surface pressure (π-*A*) and surface potential (ΔV-*A*) isotherms as well as UV-Vis Reflection spectroscopy and Brewster Angle Microscopy (BAM) for the films at the air-water interface together with UV-Vis absorption and FTIR spectroscopies, Atomic Force Microscopy (AFM) and cyclic voltammetry for the LB films.

The π-*A* and ΔV-*A* isotherms and BAM images indicate a phase transition at a surface pressure of ca. 9 mN/m, a multilayer formation at surface pressures around 19-20 mN/m, and at a surface pressure around 27 mN/m a disordered collapse of the film occurs. In addition, AFM images of LB films at π=10 and π =20 show a monomolecular and multilayer film, respectively. The comparison of the UV-Vis spectra of ZnPc in solution, the reflection spectra of the Langmuir films and UV-Vis spectra of LB films reveals a significant reduction in the Q band intensity for the films (Figure 1A), indicative of a preferential orientation of ZnPc in the Langmuir and LB films versus the random distribution in solution. The LB films of this substituted ZnPc show different reduction and oxidation waves as is shown in Figure 2. The oxidation and reduction peaks I_o and I_r, respectively, are correlated with the redox process Pc^{-2}/Pc^{-1}. The reduction peaks II_r and III_r and the oxidation peak II_o, are correlated with the processes Pc^{-2}/Pc^{-3} and Pc^{-3}/Pc^{-4}. The different processes show an irreversible behaviour.

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Figures:

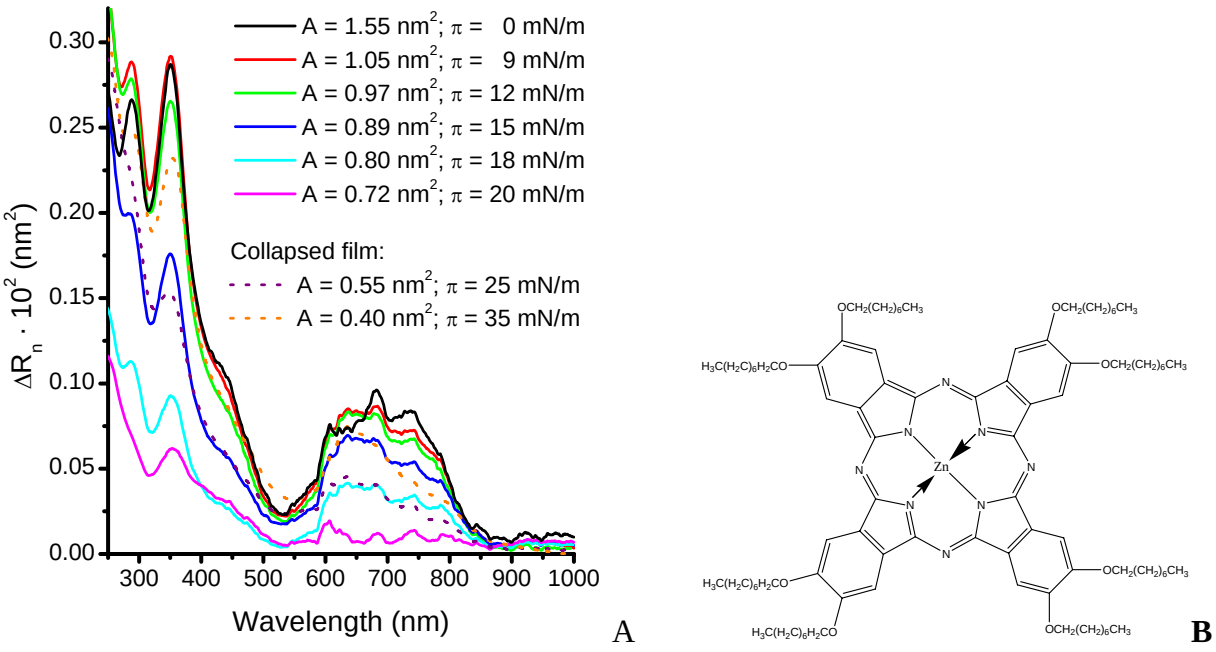

Figure 1. A) Normalized UV-vis Reflection spectra of ZnPc Langmuir films recorded upon the compression process at the indicated areas per molecule and surface pressures. B) Chemical structure of octakis(oxyoctyl)phthalocyanine of zinc, abbreviated as ZnPc in this contribution.

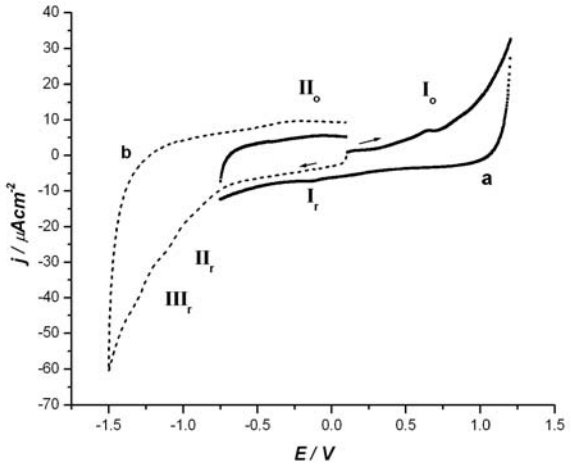

Figure 2. Cyclic voltammograms of a GCE modified with a LB film of ZnPc in a 0.1 M $NaClO_4$ solution, scanning toward: a) anodic potentials; b) cathodic potentials.