



## Langmuir and Langmuir–Blodgett (LB) films of tetrapyrrolyl metalloporphyrins

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### ABSTRACT

We report on the formation of Langmuir films of 5,10,15,20-tetra(4-pyridyl) 21*H*,23*H*-porphine, hereafter named tetrapyrrolyl porphyrins with distinct central ions ( $2\text{H}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ). The films were characterized with surface pressure and surface potential isotherms and in situ UV–vis absorbance. The measurements indicated strong aggregation of porphyrin monomers at the air–water interface, with a red shift of the Soret band in comparison with the spectrum obtained from  $\text{CHCl}_3$  solutions. The shift was larger for the non-substituted  $\text{H}_2\text{TPyP}$ , and depended on the metal ion. Significantly, aggregation occurred right after spreading of the Langmuir film, with no further shifts in the UV–vis spectra upon compression of the film, or even after transferring them onto solid substrates in the form of Langmuir–Blodgett (LB) films. The buildup of LB films from  $\text{H}_2\text{TPyP}$  and  $\text{ZnTPyP}$  was monitored with UV–vis spectroscopy, indicating an equal amount of material deposited in each deposition step. Using FTIR in the transmission and reflection modes, we inferred that the  $\text{H}_2\text{TPyP}$  molecules exhibit no preferential orientation in the LB films, while for  $\text{ZnTPyP}$  there is preferential orientation, with the porphyrin molecules anchored to the substrate by the lateral pyridyl groups.

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## 1. Introduction

Porphyrins have been widely applied in nonlinear optical applications [1–4], photo-sensitizing drugs in medicine [5], and chemical sensors (pH sensors) [6], in addition to being involved in natural processes such as photosynthesis and electron or oxygen transport [7]. Of particular interest of late has been the development of light-harvesting systems based on porphyrin complexes [8]. The diversity of properties exhibited by porphyrins arise mainly from the possible changes in molecular structure and insertion of a metal ion in the center of the square formed by the 4 pyrrole rings, as shown in Scheme 1 for tetrapyrrolyl porphyrins (TPyP) [9]. For the so-called metalloporphyrins, the formation of aggregates and the optical properties depend strongly on the central ion and on the lateral substituents, as the central ion M determines the symmetry of the molecule. Aggregates act as quenching centers [9,10] for energy transfer.

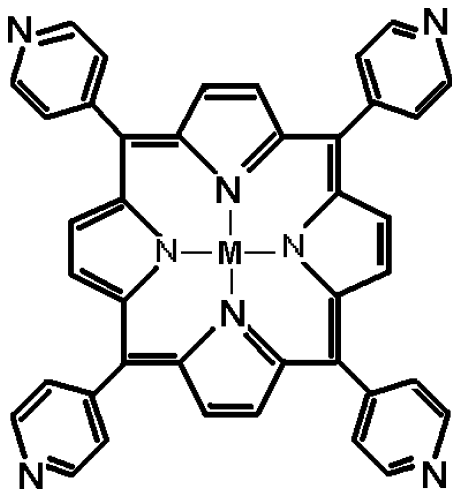
The absorption spectra of porphyrins generally consist of a strong band between 390 and 450 nm known as B-band or Soret

band, attributed to the second excited singlet state. Two other bands between 500 and 650 nm are observed. The first one is  $Q(0,0)$  (sometimes denoted by  $\alpha$ ) related to the lowest excited singlet state, while the other,  $Q(1,0)$ , is the next vibrational excitation of the lowest excited singlet state. The number of Q-bands depends on the symmetry of the molecule; the free base porphyrins with two H (referred to as  $\text{H}_2\text{TPyP}$ ) have reduced symmetry: from  $D_{4h}$  for the metalloporphyrins to  $D_{2h}$ . As a consequence, there is an increase from 2 to 4 Q-bands. The degeneracy of the vibrational modes is broken, thus splitting  $Q(0,0)$  into  $Q_x(0,0)$  and  $Q_y(0,0)$  and  $Q(1,0)$  into  $Q_x(1,0)$  and  $Q_y(1,0)$ . Hence, free base porphyrins have a unique sensitivity to protonation of the N atom at the center of the macrocycle.

Studying a given material in the form of a Langmuir film offers the unique opportunity of controlling the aggregation process by changing the area per molecule at the air–water interface. To our knowledge, Bull and Bulowski [11] were the first to investigate the free base *meso*-tetraphenylporphyrin (TPP) and metallo substituted derivatives using the Langmuir and Langmuir–Blodgett techniques, in which mixed films of porphyrin/surfactant were used to decrease aggregation as wrinkles were observed in pure TPP films during the compression isotherm. A red shift was observed in the Soret band of the UV–vis spectrum of monolayers

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**Scheme 1.** Tetrapyrrolyl porphyrin molecule.  $M = 2H^+, Zn^{2+}, Cu^{2+}$  and  $Ni^{2+}$ .

transferred onto glass substrates, in comparison with the  $CHCl_3$  solutions. This shift was attributed to distortion and possible self-aggregation of TPP. At least two mechanisms of aggregation are of major importance, namely the H-type aggregation consisting of a stack of molecules with aligned macrocycle rings and the J-type aggregates comprising a side-by-side arrangement of molecules. The type of aggregation may be obtained from the absorption spectra. In general, when no deformation of the macrocycle is expected, a blue or a red shift in the Soret band indicates H-type or J-type aggregation, respectively. This is consistent with the extended dipole model based on dipole–dipole interaction between neighbors.

The use of nanostructured films produced with the Langmuir–Blodgett (LB) method [12,13] has several advantages, including control over the molecular architecture, making it possible to combine materials in a synergistic way. Furthermore, film thickness may be controlled, which is important for achieving high sensitivity that is possible with ultrathin films [14]. With regard to LB films from porphyrins, they have been developed mainly for gas sensors. For porphyrins possess highly conjugated, delocalized  $\pi$  electrons resulting in electrical and optical properties that vary significantly when exposed to vapors [14,15]. The main gases detected with sensors based on LB films from porphyrins are  $NO_2$ ,  $NO$ ,  $Cl_2$ ,  $NH_3$ ,  $CO$ ,  $CO_2$ ,  $HCl$ ,  $SO_2$ ,  $H_2S$ , and  $NH_3$  and volatile organic solvents (methanol, ethanol, toluene, benzene, hexane, acetone) [14] and amines [16].

In order to further probe the TPYP films properties, here we investigated the surface pressure and surface potential isotherms together with in situ UV–vis absorbance measurements in a set of central substituted porphyrins:  $2H^+(H_2TPYP)$ ,  $Zn^{2+}(ZnTPYP)$ ,  $Cu^{2+}(CuTPYP)$  and  $Ni^{2+}(NiTPYP)$ . In addition, LB films were deposited from two of such porphyrins, namely  $H_2TPYP$  and  $ZnTPYP$ , which were characterized with UV–vis and FTIR spectroscopies, and used to detect HCl vapor.

## 2. Experimental methods

### 2.1. Synthesis

The free base tetrapyrrolyl porphyrin ( $H_2TPYP$ ) was synthesized by adding freshly distilled pyrrole (9.9 g, 0.15 mol) and 4-pyridinecarboxaldehyde (16.1 g, 0.15 mol) to 800 mL of the refluxing reagent grade, propionic acid. After refluxing for 1.5 h, the solution was cooled down to room temperature and filtered, and the filter cake was washed thoroughly with methanol. After

washing with hot water, the resulting purple crystals were dried in vacuum to remove absorbed acid. The 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine was purified on an alumina column using chloroform as solvent and 5% methanol–chloroform as eluent to yield 2.68 g (14% yield). The spectrophotometric analysis of the product was consistent with the literature [17]. Metalloporphyrins were synthesized according to the following procedure: 0.250 g ( $4.04 \times 10^{-4}$  mol) of  $H_2TPYP$  was dissolved in a mixture of 20 mL of acetic acid and 20 mL of dimethylformamide (DMF) under reflux. The corresponding metal salt was slowly added during 1 h, until reaching 2.5 times in mol of the amount of  $H_2TPYP$ . The mixture was left under reflux for another hour and then cooled in an ice bath with cold water to obtain a solid. The solid was filtered and washed with water to remove the excess of metal salt and dried in vacuum. When necessary, the product was purified on an alumina column using a mixture of 95% of chloroform and 5% of methanol as eluent [17].

### 2.2. Langmuir films

Langmuir films were spread from chloroform solutions of the porphyrin with concentrations around  $10^{-4}$  M, onto an ultrapure water subphase provided by a Milli-RO coupled to a Milli-Q purification system from Millipore (resistivity 18.2 M $\Omega$  cm, pH  $\sim$  6).  $CuTPYP$  and  $NiTPYP$  solutions were prepared by dissolving the solute in a (95:5) chloroform/methanol mixture to obtain complete solubilization. Surface pressure and surface potential experiments were performed on a KSV 5000 Langmuir trough in a class 10,000 clean room, with the Langmuir film compressed at a barrier speed of 20 mm/min. The mean molecular areas were calculated based on the molecular weight of the porphyrin monomer. The surface pressure was monitored with an electronic balance, using a Wilhelmy plate made of filter paper–chromatography paper Whatman Chr1. The system was computer controlled, allowing the surface–pressure and surface potential isotherms to be obtained automatically.

The apparatus for measuring in situ UV–vis absorbance on Langmuir films was described in ref. [18]. Briefly, a light-emitting diode (LED) with appreciable intensity in the range from 400 to 700 nm was used to illuminate the water/film interface. The absorption spectra were obtained by reflection and to increase the signal, an aluminum-coated mirror was placed on the bottom of the trough. The reflected light was collected through an optical fiber and guided into an USB 2000 Ocean optics spectrophotometer, which was computer controlled separately from the Langmuir system. UV–vis spectra, in the range of 400–700 nm, were acquired as a function of the surface pressure or area per molecule. The UV–vis isotherms were obtained by plotting the maximum absorbance value vs. the area per molecule. The absorbance spectra of solutions were measured with a Cary-17 spectrophotometer, in  $CHCl_3$  solutions prepared with a standard concentration of  $7 \times 10^{16}$  cm $^{-3}$  ( $1.2 \times 10^{-4}$  mol/L) and placed in a 2-mm optical path cell.

### 2.3. Langmuir–Blodgett films

$H_2TPYP$  and  $ZnTPYP$  LB films were prepared by spreading 150  $\mu$ L of porphyrin chloroform solution at a concentration of 0.22 mg/mL on the aqueous surface. The deposition pressure employed was 30 mN/m for  $H_2TPYP$  and 25 mN/m for  $ZnTPYP$ , while the dipping speed was 0.8 mm/min and 1.0 mm/min for  $H_2TPYP$ , for the upstrokes and downstrokes, respectively. For  $ZnTPYP$  the dipping speed was 0.3 mm/min for both upstrokes and downstrokes. LB films were produced by transferring porphyrin Langmuir films onto one of the following substrates: glass or glass

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