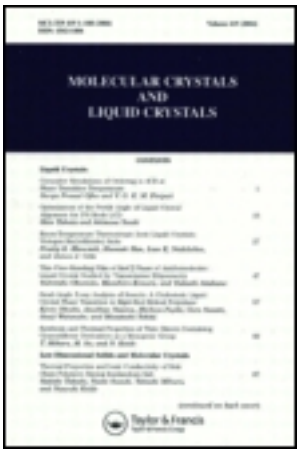

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Structure of Porphyrin Multilayers Obtained by the Langmuir Blodgett Technique

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STRUCTURE OF PORPHYRIN MULTILAYERS OBTAINED BY THE LANGMUIR BLODGETT TECHNIQUE

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ABSTRACT

Composite layers of behenic acid in 4 to 1 ratio to different tetraphenyl porphyrins (T.P.P) made amphiphilic by aliphatic chain grafting were transferred onto plane solid substrates (quartz and CaF_2) by the Langmuir-Blodgett method.

The present paper is devoted to the determination of the structure of these layers. We have studied both i) the monolayer films on water surface (before transfering onto the solid). ii) the built up layers after transfering onto the solid, by three methods : a-b) linear dichroïsm in the visible and infrared range c) Electron Paramagnetic Resonance. These three resonance methods give information on the orientation of the macrocycle axis with respect to the substrate.

We have synthesized the following functional macrocycles : i) T.P.P. $(C_{20})^4$: four chains, each $C_{20}H_{41}$, grafted at the ortho position of the phenyl rings ii) T.P.P. $(C_{12})^4$: four chains, each $C_{12}H_{25}$,

iii) T.P.P. $(C_{22})1$: one chain, $C_{22}H_{45}$, per macrocycle at the para-position of the phenyl ring.

For each type of molecule, we have studied the free base (denoted by H2), and the copper and cobalt bases.

We first obtained some structural information of the film on the water surface by the determination of the surface area occupied by a pigment at the transfer pressure (35 dynes/cm). The film rigidity was also evaluated. It showed that for the films containing (H_2,Cu,Co) T.P.P. $(C_{12})^4$, the pigments are totally expelled from the behenic acid film (phase segregation). For (H_2,Cu or Co) T.P.P. $(C_{22})^1$, the single C_{22} chains forms a solid solution with the acid layer but the macrocycle is once again expelled. For H_2 T.P.P. $(C_{20})^4$ about three of the four C_{20} chains form a solid solution with the acid, the macrocycle being outside the film.

The data are complemented by infrared spectra of built up layers which show whether or not the film is crystallised (splitting of the 1461-1471 cm^{-1} band) or dimerised via the COOH groups of behenic acid (1700 cm^{-1} band.

We obtained some further information by linear dichroïsm experiments studying the optical transmission of the built up layers (solid state) with polarised light (T.E. and T.M. waves) at different incident angle. If $\bar{M}$ is the dipole moment of a given optical transition, the mean value of

$\cos^2\theta$ ($< \cos^2\theta >$) where θ is the angle between $\bar{M}$ and the normal $\bar{N}$ to the substrate, may be obtained. If we know the position of $\bar{M}$ with respect to the axes of the macrocycle, we can then obtain $<\cos^2\zeta>$ where ζ is the angle between $\bar{N}$ and the main macrocycle axe. In the visible region we used the Soret band (located at 435 nm) and in the infrared, we used two bands of the pyrrole : =C-N-stretching at 1350 cm^{-1} and C-H rocking at about 1000 cm^{-1}. All three transitions are polarised in the macrocyle plane. For all our samples, we found that the macrocycle are neither flat on the substrat nor perpendicular to it. The values of ζ ($40° < \zeta < 70°$) include the "magic angle" $\zeta = 54°44'$ at which the order parameter $(3\cos^2\zeta - 1)/2$ is zero. In order to clarify this situation we obtained the distribution of the ζ angles directly by E.P.R. on Cu T.P.P. $(C_{20})^4$ samples. Our results are consistent with a Lorentzian distribution centered at $\zeta o = 67°$ and a width of 10° (1).

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