

Thickness Dependence of the Optical Anisotropy for Porphyrin Octaester Langmuir–Schaefer Films[†]

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We have studied the optical anisotropy of porphyrin layers with different thicknesses deposited onto gold substrates by the Langmuir–Schaefer technique. In coincidence with the Soret band of the molecule, the optical spectral line shape as determined by reflectance anisotropy spectroscopy exhibits a characteristic, large structure, which changes from a "peaklike" to a "derivative-like" shape at a well-defined thickness (8–10 monolayers). We interpret this result in the framework of electronic effects due to structural changes in the layers, yielding solid-state effects originating from the coupling of the π orbitals of the porphyrin macrocycles.

Introduction

Molecular materials have aroused considerable interest in recent years due to their large potential impact on molecular nanotechnologies.^{1–4} However, their use in solar cells, optoelectronics, transistors, and so forth has not materialized because of intrinsic limits such as low carrier mobilities or instability and degradation of performance due to exposure to ambient conditions. Quite recently, some of these problems have been overcome and efficient p–n junctions have been built using an organic structure.⁵

Characterization of the electronic states in the fabricated molecular structures is essential; recently, reflectance anisotropy spectroscopy (RAS) has been applied to organic layers, showing that the spectra are reliably connected to the electronic properties of the molecule and to the morphological characteristics of the layer.^{6–10} We believe that RAS will have in organic films deposition an

impact similar to the one already encountered in inorganic growth.¹¹

In a previous work, by using RAS some of us have studied thick Langmuir–Blodgett (LB) layers of a free-base porphyrin (H₂THOPP).¹⁰ The optical spectra were dominated by a characteristic oscillation in the Soret band region, reminiscent of the derivative of the layer dielectric function. We proposed an explanation involving the existence of strain due to the deposition process, which would produce a slight variation with polarization in the transition energy and in the broadening factor of the Soret optical transition characteristic of the porphyrin layer.

In this paper, we present new results obtained with metalloporphyrin octaesters, having a true D_{4h} symmetry (H₂THOPP is D_{2h}), deposited onto a metal substrate using the Langmuir–Schaefer technique, which ensures a highly ordered deposition. The RAS line shape measurements were performed for every step of variable thickness. We also characterized the samples by atomic force microscopy (AFM); this gave us an independent determination of the sample thickness at each coverage stage. The main result we report is the abrupt change in the RAS line shape at 8–10 monolayer coverage: the line shape, which at lower coverage is essentially proportional to the Soret band absorption, becomes derivative-like.

Experimental Section

Film Deposition. The porphyrin complexes used in this work (NiC₁₀OAP and PdC₁₀OAP) have been synthesized according to

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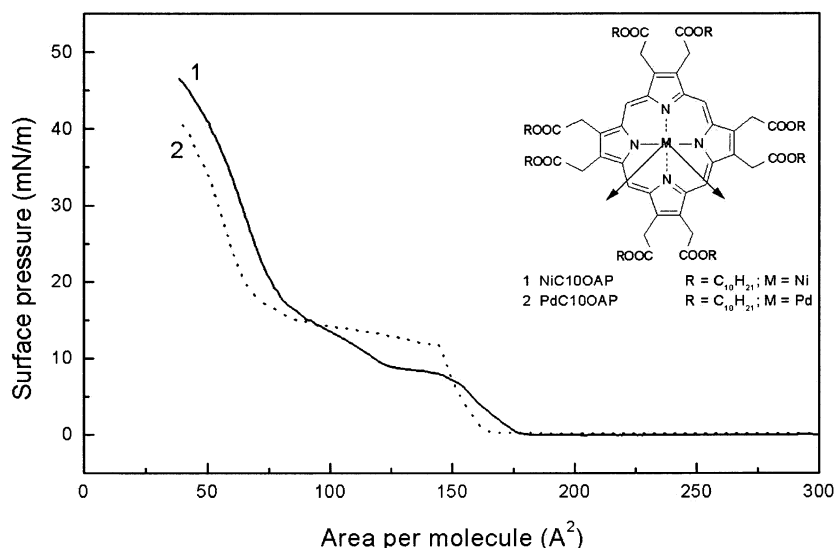


Figure 1. Surface pressure–area isotherms of PdC₁₀OAP (full line) and NiC₁₀OAP (dotted line) porphyrins spread at the surface of pure water. In the inset: structure of PdC₁₀OAP and NiC₁₀OAP porphyrins. The two perpendicular dipoles in the plane of the molecule are indicated.

the procedure described in ref 12. The compounds were dissolved in a mixture of chloroform and hexane (1:2, v/v) in the concentration of 0.33 mg/mL. The films were deposited with a KSV System 5000 from the surface of pure water prepared with a Milli Q system (resistivity of 18.2 MΩ cm). The monolayers of NiC₁₀OAP were compressed up to 30 mN/m at a rate of 10 mm/min. The deposition of the PdC₁₀OAP films was carried out after monolayer compression up to two different values of the surface pressure, that is, 10 and 30 mN/m, at the same rate because in these two cases different arrangements of molecules were expected (see discussion). The deposition quality was controlled with a Carl Zeiss optical microscope Axiotech in the reflection mode.

The deposition of stepped films of porphyrins was carried out onto gold-coated glass substrates 10 × 40 mm² in size. A thin sublayer of chromium (30–40 nm) was first thermally evaporated onto the glass surface, and then a gold film about 100 nm thick was evaporated over the chromium sublayer.

The boundaries of steps of the deposited film were parallel to the short side of the substrate, and the film thickness gradually varied from 2 to 22 monolayers with the increment of 2 monolayers along the long side. The width of each step was 3 mm.

We tried first to deposit the films with the Langmuir–Blodgett technique, but we did not achieve the high-quality deposition necessary for such studies. On the contrary, extremely uniform films were prepared with the Langmuir–Schaefer (LS) technique (or horizontal lifting technique).¹³ This was proven by the observation of films 80–100 nm thick deposited onto a hydrophobic silicon surface with an optical microscope at magnifications up to 1000.

The version of the LS technique with the separation of the monolayer surface into independent sections was applied, which was already successfully used for the deposition of various compounds.^{14,15} In this version of the LS technique, the monolayer is compressed up to the required surface pressure, the feedback is switched off, a Plexiglass grid with the dimensions of sections approximately equal to the dimensions of the substrate is placed onto the Langmuir trough surface, and the almost horizontally arranged substrate is successively transferred from one section to another touching the surface of water with the monolayer. However, in this case a problem arises with the fabrication of

steps because the monolayer is deposited over the entire surface of the substrate when the latter touches the surface of the water. For the preparation of the required step structure, we used masks of different dimensions (ranging from 37 × 10 mm² for the first 2 monolayer step to 7 × 10 mm² for the 10th and final step) made of stainless steel foil to protect the desired part of the substrate surface. This procedure yielded 10 steps 3 mm wide. The remaining area of gold surface (7 × 10 mm²) at the end of the substrate was not coated with the LS film to perform reference measurements and to provide an electrical contact.

In the inset of Figure 1, we have drawn the molecular structure of metalloporphyrin octaesters used in this work, exhibiting the typical 4-fold *D_{4h}* symmetry. The molecules possess two dipoles mutually perpendicular in the molecular plane. The related transitions are completely degenerate.

Multilayer Thickness Measurement. Precise and reliable film thickness measurements in this class of materials are not straightforward. Null-ellipsometry measurements can be very accurate, but the inversion of the ellipsometric angles Δ and Ψ into refractive index and sample thickness requires a priori knowledge of the optical absorption (or the imaginary part of the refractive index). In our case, this is not viable, as we anticipate variations of the optical properties as a function of sample thickness and of the nature of the substrate, due to the effect of molecular tilt angle on the orbital overlap. In particular, a small variation of optical properties as a function of the number of deposited layers might either mimic or hinder a structural change. X-ray reflectivity would be a very suitable tool, but no data are available at present for our particular system.

We resorted to a simple and direct approach: we removed part of the molecular multilayer deposited on a hard surface (silicon covered by its natural oxide) by means of a sharpened wooden toothpick soaked in ethanol and then rinsed. By this procedure, we could generate and measure clean edges between areas covered and completely uncovered by the organic multilayer. We then probed the surface by AFM imaging in noncontact mode. We used an Autoprobe CP Research instrument from Thermomicroscopes equipped with a large-area (100 μm²) scanner with optical feedback for the independent control of the lateral movements of the piezo scanner. We used Ultrasharp noncontact silicon cantilevers (from Silicon-MDT Ltd.) with a nominal curvature of about 10 nm and a typical resonance frequency of 150 kHz. In the typical case, the edges so produced are about 100–200 nm wide in space, thus being in a small enough region for the piezo to be considered linear. Finally, we also independently checked that the wooden tip does not modify the bare silicon substrate.

Optics. In reflectance anisotropy spectroscopy, one measures, in normal incidence, the difference of the sample reflectivity for

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light polarized alternatively, with frequency ω_0 , along two perpendicular directions (a and b).^{16,17} Usually, a and b coincide with well-defined symmetry directions of the system. Different from metals and semiconductors, for organic systems the identification of such directions is not straightforward, since in this case they cannot be gathered from the crystalline structure of the material but must be obtained from the superstructure yielded by growth.

In RAS, the ratio between the variation of the sample reflectance (Δr) and the average reflectance (r) is measured as a function of the photon wavelength:

$$\Delta r/r = 2(r^a - r^b)/(r^a + r^b) \quad (1)$$

where r is the complex reflectance coefficient.

$\Delta r/r$ is a complex quantity, whose real and imaginary parts exhibit different modulation frequencies, ω_0 and $\omega_0/2$, respectively.¹⁸ This allows measurement of the two components one at a time with a lock-in amplifier. However, in the present work only the real part of $\Delta r/r$ has been measured. It results that

$$2 \operatorname{Re}(\Delta r/r) = 2(R^a - R^b)/(R^a + R^b) \quad (2)$$

where R^a (R^b) is the reflectivity coefficient for light having polarization a (b). The right-hand term in eq 2 represents the anisotropy signal intensity, justifying the use of $2 \operatorname{Re}(\Delta r/r)$, that is, the *peak-to-peak* amplitude of the $\operatorname{Re}(\Delta r/r)$ signal detected by lock-in.

All of the spectra have been recorded in the wavelength range 250–800 nm. The samples have always been kept in air at room temperature. The linearly polarized electric field of the light has been modulated at a frequency of about 50 kHz between two directions a and b which, for all the spectra reported below, were aligned with the edges of the substrate (inset of Figure 3). This experimental configuration has been chosen by measuring the dependence of RAS spectra upon the azimuthal rotation by an angle ϕ around the axis perpendicular to the substrate (coincident with the incidence direction of light) and looking for the maximum signal amplitude.

Results and Discussion

The surface pressure–area isotherms of the NiC₁₀OAP and PdC₁₀OAP porphyrins are shown in Figure 1. The curves reveal a plateau in the region of area per molecule approximately between 70 and 150 Å² and accordingly two regions where the surface pressure increases rapidly under the monolayer compression. Thus, one may expect different arrangements of molecules in the monolayer at the surface pressure values below and above the plateau. In particular, for the case of ZnC_nOAP porphyrins,¹⁹ the porphyrin rings were thought to be arranged either side-on or edge-on with respect to the water surface. The existence of a metastable flat zone in the isotherm indicates that the LB or LS films of PdC₁₀OAP should be deposited below and above the plateau, for example, after the monolayer compression up to 10 and 30 mN/m, respectively. (The PdC₁₀OAP was chosen because the isotherm of this compound has a more well-defined plateau.) The areas per PdC₁₀OAP molecule extrapolated to zero surface pressure in these two regions are equal to about 155 and 75 Å², respectively, which is in agreement with the model of the monolayer structure proposed for the ZnC_nOAP porphyrins.

The typical absorption spectrum of our porphyrin layers is displayed in Figure 2. Here we show the spectra obtained for the PdC₁₀OAP porphyrin deposited onto a quartz

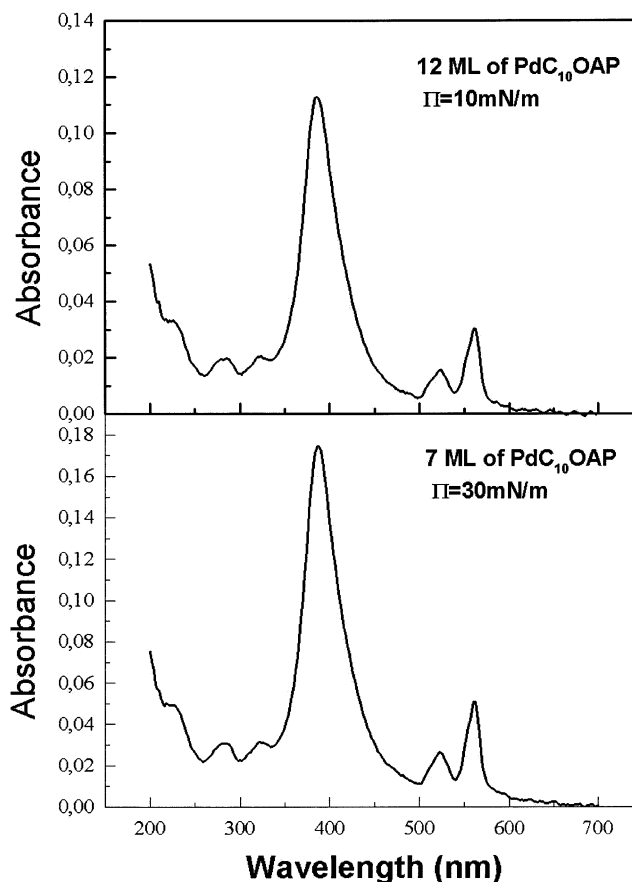


Figure 2. UV–vis absorption spectrum measured for different layers of PdC₁₀OAP deposited onto a quartz substrate by the Langmuir–Schaefer technique: (a) upper panel, 12 ML at $\Pi = 10$ mN/m; (b) lower panel, 7 ML at $\Pi = 30$ mN/m.

substrate at 10 mN/m (12 monolayers) and 30 mN/m (7 monolayers). The number of layers was changed to balance the different molecular densities in the two samples. The spectra feature the prominent Soret band at about 390 nm and the Q-bands at longer wavelengths. Within the experimental accuracy, the spectra seem to be identical. However, a closer examination of the Soret band indicates small changes both in peak position and half-width.

In Figure 3, we report $2 \operatorname{Re}(\Delta r/r)$ spectra of PdC₁₀OAP porphyrin layers deposited onto gold at the surface pressure $\Pi = 30$ mN/m, the thickness varying between 0 and 22 monolayers. For a comparison, the RAS spectrum measured at the uncovered, isotropic Au substrate has been reported as zero-line. It is evident that all the visible spectral features are characteristic of the organic overlayer. The main structure always falls in the energy region of the Soret band (at about 390 nm), while the peaks at lower photon energies (522 and 561 nm) agree with the Q-bands of the molecule.

Just after 2 monolayers, the anisotropy spectrum exhibits a well-defined peak at 395 nm, which is in fair agreement with the position of the absorption maximum (as reported in Figure 2), but not totally. At 4 and 6 monolayers, apart from a negative broad minimum appearing above 420 nm, the spectra have a similar aspect. But at 8 monolayers, the change is evident: the positive maximum shifts to a lower wavelength (about 374 nm), and an almost symmetric minimum appears at 394 nm. On the whole, the spectrum assumes a “derivative” line shape. Up to 12 monolayers, no appreciable spectral changes occur. Above 14 monolayers, the amplitude diminishes at all photon energies, rapidly converging to

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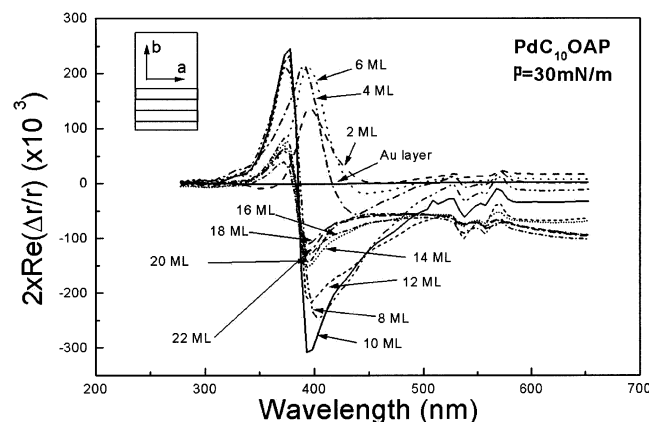


Figure 3. $2 \operatorname{Re}(\Delta r/r)$ spectra measured at Langmuir–Schaefer layers of $\text{PdC}_{10}\text{OAP}$ porphyrin deposited onto gold ($\Pi = 30 \text{ mN/m}$). Total coverage ranges from 0 to 22 monolayers. The absolute sign of the quantity $2 \operatorname{Re}(\Delta r/r) = 2(R^a - R^b)/(R^a + R^b)$ is arbitrary. In the inset: a and b directions (defined in the text) with respect to the substrate. The layers (3 mm large) of different thicknesses deposited by the LS technique have also been reported.

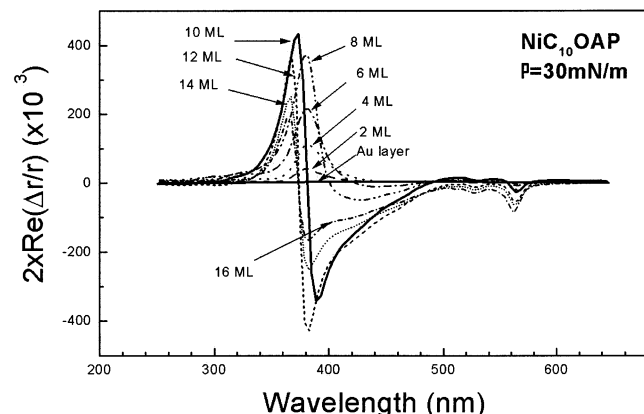


Figure 4. $2 \operatorname{Re}(\Delta r/r)$ spectra measured at Langmuir–Schaefer layers of $\text{NiC}_{10}\text{OAP}$ porphyrin deposited onto gold ($\Pi = 30 \text{ mN/m}$). Total coverage ranges from 0 to 16 monolayers. The absolute sign of the quantity $2 \operatorname{Re}(\Delta r/r) = 2(R^a - R^b)/(R^a + R^b)$ is arbitrary.

a limit value which remains steady up to the maximum thickness of 22 monolayers.

When $\text{PdC}_{10}\text{OAP}$ layers are deposited on gold at the lower value of surface pressure ($\Pi = 10 \text{ mN/m}$), RAS spectra exhibit a completely different behavior: in the whole range of thickness (2–22 monolayers), the appearance is *always* peaklike, with a maximum at about 390 nm and amplitude increasing with coverage. No transition to the derivative-like line shape is observed.

In Figure 4, $2 \operatorname{Re}(\Delta r/r)$ spectra of $\text{NiC}_{10}\text{OAP}$ layers deposited onto gold are reported. The dependence of the RAS signal upon thickness (here ranging from 0 to 16 monolayers (ML)) and the spectral characteristics are completely analogous to the case of $\text{PdC}_{10}\text{OAP}$. The main difference is the thickness value (10 ML) at which the spectral line shape varies, passing from the “peaklike” to the “derivative-like” regime, probably depending upon the different molecules.

It could be surprising that a molecule expected to be isotropic produces anisotropy spectra such as the ones reported in Figures 3 and 4. However, it is known from spectroscopic results that porphyrin molecules in LB layers are likely adsorbed forming an angle θ with the normal to the substrate.^{20–24} As a consequence, an anisotropy factor $[1 - \sin^2(\theta)]$ is naturally introduced between the two directions sampled by the light electric field. In this

case, the resulting $\operatorname{Re}(\Delta r/r)$ is proportional to the imaginary part of the dielectric function ϵ , explaining the behavior of the RAS spectra up to 6 (8) monolayers of $\text{PdC}_{10}\text{OAP}$ ($\text{NiC}_{10}\text{OAP}$) (see for example eq 2 in ref 7).

The interpretation of the derivative line shape appearing at 8–10 monolayers requires a different argument. We schematize our samples within the *three-layer model*, a macroscopic theory, originally developed for surfaces, in which the organic film is treated as an absorbing film of thickness d , much smaller than the light wavelength λ (an approximation that in our case may be criticized at higher coverage), on top of a semi-infinite solid.²⁵ It is possible to show that $\operatorname{Re}(\Delta r/r)$ is expressed in terms of the optical functions of the deposited organic layer and of the underlying substrate. The latter is assumed isotropic; actually, no appreciable anisotropy is detected by experiment (see the curves for the gold substrate in Figures 3 and 4). At normal incidence and with a vacuum (or air) as the external medium, the formula for $\operatorname{Re}(\Delta r/r)$ reads

$$\operatorname{Re} \frac{\Delta r}{r} = \operatorname{Re} \left[-i \frac{2\omega d}{c} (A + iB)(\epsilon_{\text{layer}}^a - \epsilon_{\text{layer}}^b) \right] \quad (3)$$

The A and B coefficients are real quantities depending upon the dispersive (ϵ'_{sub}) and the dissipative (ϵ''_{sub}) parts, respectively, of the complex dielectric function of the substrate:

$$A = \frac{\epsilon'_{\text{sub}} - 1}{(1 - \epsilon'_{\text{sub}})^2 + \epsilon''_{\text{sub}}^2} \quad B = \frac{\epsilon''_{\text{sub}}}{(1 - \epsilon'_{\text{sub}})^2 + \epsilon''_{\text{sub}}^2} \quad (4)$$

Their dependence upon photon energy is well-known from published data.

$(\epsilon_{\text{layer}}^a - \epsilon_{\text{layer}}^b)$ represents the complex anisotropy of the organic layer dielectric function for light polarized along the a and b directions. Finally, c is the speed of light, and ω is the photon frequency.

It is plain from eq 2 that in general RAS signals contain both the real and the imaginary anisotropies of the organic layer dielectric function. When B is negligible, the above expression can be simplified. For gold, A and B coefficients have been computed in the energy range 250–800 nm²⁶ and reported in Figure 5. As one can see, in the region of the porphyrin Soret band both A and B have non-negligible values, and eq 2 must be considered in its complete form.

Following ref 10, we have fitted the experimental spectra in terms of the energy derivative of the layer dielectric function. Although the porphyrin molecule is symmetric, let us assume heuristically that the critical point energies E_i and broadening parameters Γ_i of the film optical transitions slightly depend on light polarization. Near a critical point, to first order the layer dielectric function for polarization a (b) differs from ϵ^{bulk} by small increments ΔE^a (ΔE^b) and $\Delta \Gamma^a$ ($\Delta \Gamma^b$):^{27–29}

$$\epsilon_{\text{layer}}^a(E) = \epsilon^{\text{bulk}}(E) + (-\Delta E^a + i\Delta \Gamma^a) \left(\frac{d\epsilon^{\text{bulk}}}{dE} \right) \quad (5)$$

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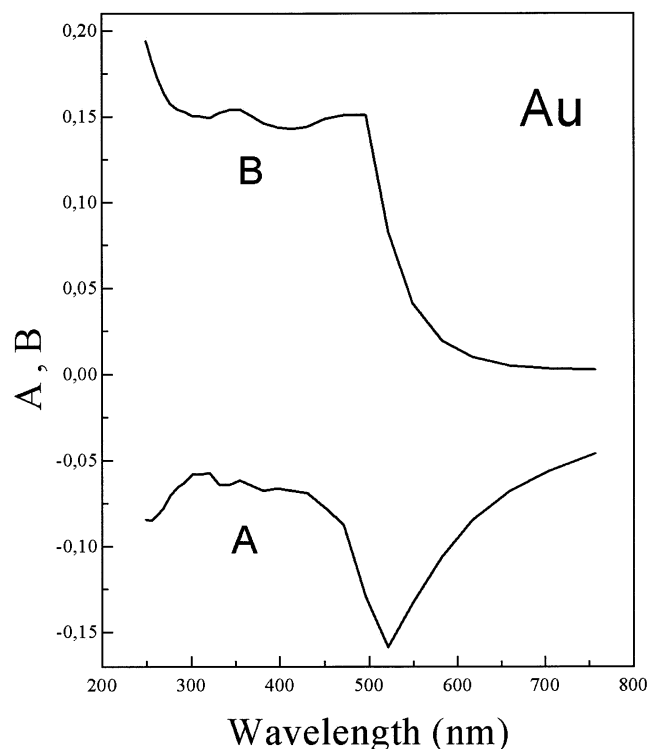


Figure 5. *A* and *B* coefficients computed for gold after ref 26.

Introducing eq 5 for both polarizations into eq 4, we obtain

$$\text{Re} \frac{\Delta r}{r} = \text{Re} \left[-i \frac{2\omega_{\text{light}} d}{c} (A + iB)(-\Delta E + i\Delta\Gamma) \left(\frac{d\epsilon^{\text{bulk}}}{dE} \right) \right] \quad (6)$$

where $\Delta E = \Delta E^a - \Delta E^b$ and $\Delta\Gamma = \Delta\Gamma^a - \Delta\Gamma^b$.

The complex dielectric function ϵ^{bulk} of the PdC₁₀OAP porphyrin layer has been computed using Lorentz oscillators whose transition photon energies and broadening factors have been taken from the spectra of Figure 2. The agreement between eq 6 and the experimental results is good as displayed in Figure 6, where the curve computed with $\Delta E = 3.4$ meV and $\Delta\Gamma = 6.9$ meV has been reported to fit the 8 ML experimental spectrum of Figure 3, the first to exhibit clearly a derivative appearance for PdC₁₀-OAP. The dominant oscillatory line shape is well reproduced, while features corresponding with the Q-bands have been not considered in the calculations.

In ref 10, we concluded that the origin of the anisotropy in porphyrin films was not clear. We just proposed, in a speculative way, a possible explanation involving strain due to the deposition method. Such a possibility was suggested by the experimental observation that the anisotropy maximum was measured when the *a* and *b* directions were parallel and perpendicular, respectively, to the dipping direction. But the present result rules out strain as responsible for the derivative line shape. In fact, while in ref 10 we studied LB layers, in this case we have examined LS layers. In LS growth, the samples are not dipped into the liquid but lowered horizontally onto the liquid surface, and the whole layer deposits just about simultaneously onto the substrate.

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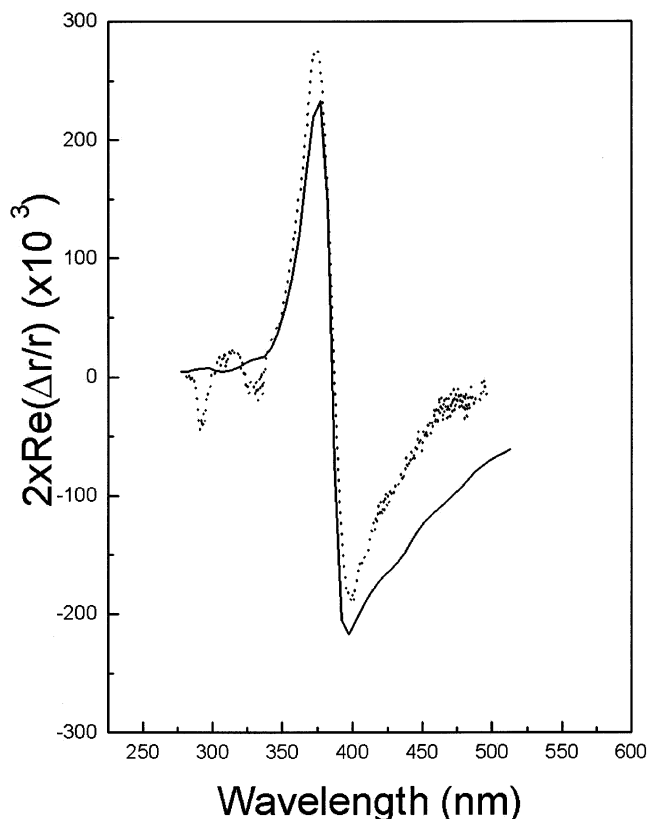


Figure 6. The $2 \text{Re}(\Delta r/r)$ spectrum measured at an 8 ML thick Langmuir-Schaefer layer of PdC₁₀OAP porphyrin deposited onto gold. Only the spectral range 270–500 nm (related to the Soret band transition) has been reported. The dotted line represents the fit obtained by using eq 6, with $\Delta E = 3.4$ meV and $\Delta\Gamma = 6.9$ meV.

Therefore, the sudden line shape change observed is more likely due to some effect connected to the number of deposited layers producing a transition from an *interface*-dominated situation (substrate–monolayer and monolayer–air interfaces) to a *bulk*-dominated situation. Such a transition has already been observed at a similar thickness value in dynamical and structural properties of LB multilayers.^{20,21,30} We believe this is the first time it is observed for its effects on the electronic states of the film.

A possible explanation of the transition could be a collective change in the average molecular tilt angle θ (defined as the angle between the molecular plane and the normal to the substrate) as the thickness is increased above 8–10 monolayers. More specifically, at low coverage the molecules tend to be more inclined relative to the substrate, due to stronger interactions with it. As the thickness increases, the substrate influence decreases, and the molecules tend to straighten up. This however is a cooperative process so that there is a specific threshold thickness which separates one regime from the other.

Electronic states are coupled to this morphology change since the average molecular separation changes (decreasing) as the average tilt angle decreases. This implies a stronger overlap of the electronic π orbitals. As a consequence, the weight of solid-state effects on the optical absorption line shape augments: in particular, the absorption maximum shifts to shorter wavelengths, and some broadening is induced. This is consistent with the

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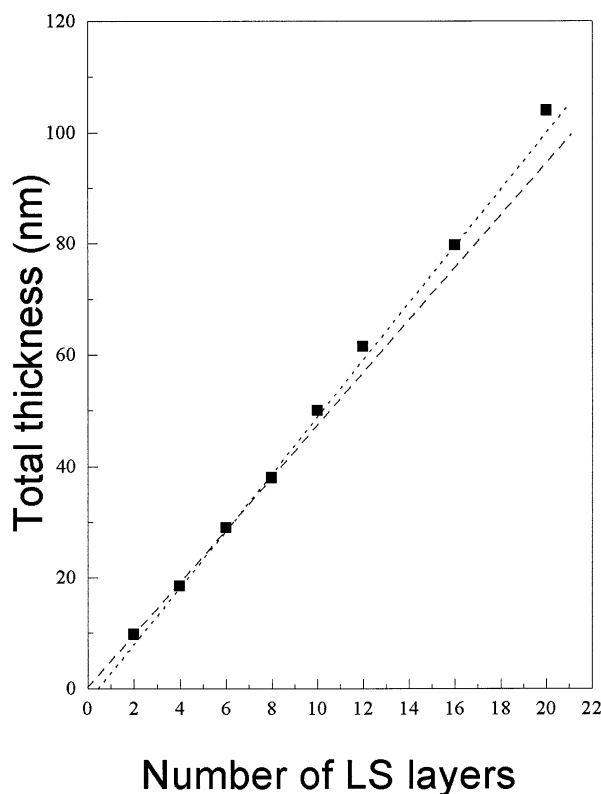


Figure 7. Dependence of the film thickness on the number of deposited layers for PdC₁₀OAP ($\Pi = 30$ mN/m). The dashed and dotted lines are obtained by fitting the data *below* and *above* 8 ML. The change of slope is compatible with a slight variation in the tilt angle of the molecule.

observed change in the RAS line shape across the transition.

Actually, results of calculations for the structural and electronic properties of porphyrin molecular stacks show that band dispersion of the molecular superstructure depends strongly upon the tilt angle.³¹ As an example, a transition from indirect gap to direct gap happens when, from face-to-face stacking, the final tilted equilibrium structure is reached.

For coverage higher than 8 ML for PdC₁₀OAP (10 ML for NiC₁₀OAP), optical spectra maintain a derivative appearance up to the thicker layer studied. We can infer that the structure of the layer changes slightly with thickness, probably with the exception of some disorder resulting from growth, which reduces the total amplitude of the structure at 400 nm.

We have tried to verify the above model by careful study of the eventual changes in the optical absorption spectra as a function of the number of deposited layers and by precise determination of the thickness per monolayer using AFM. Within the accuracy of the AFM technique, we could determine that in the multilayers of PdC₁₀OAP deposited at 30 mN/m each deposited monolayer is 45–50 Å thick. In Figure 7, we show our result, which basically indicates that either there is no change in the thickness per monolayer or, if there is one, it is barely above the error bars of our measurement. If we choose the more conservative approach, the conclusion would be that such a quantity should be a constant, that is, that no tilt angle

change takes place in the neighborhood of the 8 layer coverage. However, to explain the observed band effects in the RAS spectra, only a minute change in the tilt angle (hence the average macrocycle distance) would be sufficient. Actually, from Figure 7 we can estimate that, just at 8 monolayers, there is a slight variation in the slope of the thickness dependence upon deposited layers, bringing a change in the coverage per monolayer of about 0.3–0.4 nm. This should mean about a 15% decrease in the average molecular distance in the tilted configuration. This change is certainly sufficient to considerably increase the molecular orbital overlap and hence explain the observed band effects. On the contrary, in films of the same porphyrin deposited at lower pressure ($\Pi = 10$ mN/m), each monolayer is just 14–15 Å thick. All these findings are confirmed by high precision null-ellipsometry on the same deposited structures, assuming refractive index $n = 1.58$. The lower thickness measured for deposition with $\Pi = 10$ mN/m is consistent with RAS data: as reported above, the spectra measured at such layers exhibit a *peaklike* line shape for all coverages.

The above-mentioned results suggest that the porphyrins adopt different conformations as the surface pressure is increased. To understand if this is a consequence of structural changes already present in the Langmuir monolayer, we performed null-ellipsometry measurements at the air–water interface. A more detailed report will follow; however, here we anticipate that we obtain a value for the monolayer thickness of about 13 Å up to a surface pressure of 10 mN/m, while above this pressure the monolayer thickness increases progressively up to a value of 43–45 Å, which would nicely fit the size predicted for the macrocycle in an upright vertical position with the alkyl chains fully extended. A similar conformational change has already been observed in closely related porphyrin systems.²²

In conclusion, we have studied the optical anisotropies of thin layers of porphyrin octaesters deposited via the Langmuir–Schaefer technique onto gold substrates. The RAS spectra are dominated by characteristic, large oscillations in correspondence with the Soret band of the molecules, which we assign to the derivative of the layer dielectric function. The sudden occurrence with coverage of the derivative spectrum and the characteristics of the Langmuir–Schaefer deposition method are strongly in favor of some mechanism connected to a *critical* thickness value separating interface-dominated from bulk-dominated behavior. The physical origin of this mechanism can be related to a collective change in the average tilt angle.

Finally, it is remarkable that such a change in the molecular packing would happen at a rather large distance from the substrate–film interface. Such a structural change is not uncommon in molecular layers but usually is placed at a smaller distance from the substrate, typically 4–5 molecular layers.^{30,32} To understand this unusual behavior, we must recall the mesogenic properties of our molecules:¹² it is reasonable that molecular order propagates over larger distances due to the strong tendency of liquid crystal materials to maintain their surface alignment in the bulk.

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