Floating Films of a Nonamphiphilic Porphyrazine at the Air–Water Interface and LS Multilayer Construction and Optical Characterization

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2,3,7,8,12,13,17,18-Octakis(methylthio)-5,10,15,20-21*H*,23*H*-porphyrazine, H₂OMTPz, was used for the preparation of thin films by the Langmuir–Shäfer technique. The related analysis of the floating layer on the water surface has revealed the existence of large and randomly oriented three-dimensional aggregates, investigated by Brewster angle microscopy and by UV–vis reflection spectroscopy. The transfer of the floating layer onto the solid hydrophobized substrates (quartz and glass) originated films that on the contrary have exhibited, by UV–vis spectroscopic analysis with polarized light, an average preferential edge-on arrangement of porphyrazine molecules with respect to the support surface. Finally, spectroscopic ellipsometry allowed us to measure the film thickness (consistent with previous data) and optical parameters.

Introduction

The preparation of new well-designed and -performing substances acting as building blocks for complex supramolecular structures and films, operating as active layers in functioning devices, is one of the most investigated subjects in the interdisciplinary field of materials science. In this light, the high self-organizing aptitude of porphyrazines (also denoted as tetraazaporphyrins) (Pzs) in the solid state, ascribable above all to the effective attracting interactions among their delocalized electron densities, the well-known $\pi - \pi$ stacking forces, offers the opportunity to construct organized supramolecular structures.

It is notorious the pronounced resemblance between the two macrocyclic systems of phthalocyanines (Pcs) and Pzs above all for the absorption spectra in the UV-vis region.¹ The nitrogen atoms in the meso positions induce supplementary electronic transitions with respect to other macrocycles such as porphyrins. Electronic absorption data accumulated so far indicate that the absorption coefficients of Pzs are generally smaller than those of Pcs having the same central metal and peripheral substituents.² Of course, also from a chemical point of view, Pcs and Pzs are analogous two-dimensional π -conjugated systems; for example, both macrocycles may coordinate many metal ions and have different pendant groups on the periphery. But, to the best of our knowledge, Pzs have rarely been studied in the field of materials science so far, especially in comparison with Pcs; therefore, this paper represents a contribution to weigh up the potential of Pzs as film-forming materials and, consequently, as possible active layers in functioning devices for future applications (for example, NLO and chemical sensors). The main rationale of this choice is that, since the central ring has the most important task in many phenomena, such as light absorption or charge transport, benzo

groups in Pcs could exert a sort of sterical hindrance in comparison with the case of $Pzs.^3$

The first tetraazaporphyrin, magnesium octaphenyltetraazaporphyrin, was prepared by Cook and Linstead during the 1930s.⁴ Moreover, it is long well-known that substituted Pzs are important catalysts⁵ or pigments,⁶ are suitable for the preparation of modified electrodes,⁷ and, in the form of thin films, are of growing interest as active layers for nonlinear optics^{8–10} or chemical sensors,¹¹ as organic semiconducting materials,¹² and as model compounds for the analysis of chemical reactivity in monolayers at the air—water interface.^{13–15}

To carry out the construction of ultrathin films containing Pz derivatives onto solid supports, several techniques such as self-assembly and Langmuir-Blodgett (LB) methods (in some films Pzs have been deposited in mixture with film promoting substances, such as fatty acids or long chain alcohols)^{3,16-18} and spin-coating⁹ have been utilized. Over the past decades, the Langmuir-Blodgett (LB) method has been widely used to construct ordered molecular assemblies of different macrocycles with well-controlled composition, thickness, and architecture.¹⁹ Thermal stability, rigidity, crystallinity, anisotropy, metal complex formation, gas adsorption, and possible polymerization are some desirable properties of such multilayers. The conjugated aromatic systems of the Pzs are good examples satisfying these requirements and, in addition, they evidence other interesting properties of semiconductors and photoconductors and demonstrate photovoltaic and nonlinear optical effects. Moreover, it has already been reported that usually such Pz assemblies contain three-dimensional structures rather than monodimensional molecular piles. Such aggregates are probably ascribable to electron hopping involving the delocalized electron density in the macrocycles rather than other weak physical forces.3

All these considerations prompted us to use a Pz derivative, 2,3,7,8,12,13,17,18-octakis(methylthio)porphyrazine,^{20,21} H₂OMTPz, in the construction of multilayered films and to check the structure of the floating film at the air—water interface not only by the registration of Langmuir isotherm, but above

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all through utilization of two innovative techniques, Brewster angle microscopy (BAM) and reflection spectroscopy in the UV-vis wavelength range. Also the film structure onto solid substrates was explored by transmission UV-vis spectroscopy and ellipsometry. Future developments will include also the utilization of this derivative in resistive chemical sensors for gases and vapors. Similar octaalkylthio-substituted Pzs have been reported to evidence semiconductor properties, the specific conductivities ranging from 10^{-11} to 10^{-9} S/cm.²¹

Experimental Details

Synthesis. All chemicals and solvents (Aldrich Chemicals Ltd.) were of reagent grade and used in the syntheses as supplied without further purification. Silica gel used for chromatography was Merck Kieselgel 60 (70–230 mesh). Solvents used in physical measurements were of spectroscopic or HPLC grade.

The proton ¹H NMR spectrum was recorded on a 500 MHz INOVA Varian spectrometer with SiMe₄ as internal standard.

H₂OMTPz: 2,3,7,8,12,13,17,18-Octakis(methylthio)-5,10,-15,20-porphyrazine. The free-base porphyrazine was prepared according to a modified literature method.^{20,22,23} This method involved the synthesis of *cis*-1,2-dicyano-1,2-bis(methylthio)ethylene by reaction of disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate with iodomethane in MeOH and its subsequent template condensation in a suspension of magnesium isopropoxide to form MgOMTPz. Dissolution of the Mg derivative in cold, concentrated CF₃COOH followed by careful neutralization produced H₂OMTPz in high yield.

cis-1,2-Dicyano-1,2-bis(methylthio)ethylene (1). Iodomethane (6.09 g, 43.0 mmol), dissolved in 5.0 mL of methanol, were added dropwise to a vigorously stirred suspension of disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate (4.0 g, 21.5 mmol) in methanol (15.0 mL) cooled by water-ice bath (0 °C). The temperature was increased to 25 °C and the solution was stirred continuously for 24 h in the dark. After removal of the solvent under vacuum, the compound was dissolved in CHCl₃, washed by water, dried over Na₂SO₄, and filtered. The compound, freed of the solvent using a rotary evaporator, appeared as a very malleable yellow-brown solid. The crude product was carefully purified by flash chromatography on silica gel using (1:1) (v/v) CH₂Cl₂/*n*-hexane as eluent. The yield of the reaction was >70%.

[2,3,7,8,12,13,17,18-Octakis(methylthio)-5,10,15,20-porphyrazinato]magnesium(II), MgOMTPz (2). Mg powder (0.3 g), previously washed with diethyl ether and dried, was refluxed for 8 h in *n*-propanol (50 mL). Compound 1 was added to the suspension under stirring and the solution was refluxed for 36 h. Subsequent addition of water to the cooled reaction mixture led to a dark green solid that was collected by filtration. The crude product was carefully purified by flash chromatography on silica gel using (1:1) (v/v) CH_2Cl_2/n -hexane as eluent (first band) (yield 70%).

[2,3,7,8,12,13,17,18-Octakis(methylthio)-5,10,15,20-21*H*,23*H*porphyrazine], H₂OMTPz. Pure solid 2 was dissolved in a small amount of concentrated CF₃COOH and carefully transferred on ice water. The solution was then washed with a NH₃ solution (30%) until the washing water was fully neutralized. The dark product was collected with CHCl₃ using a separating funnel, dried over sodium sulfate, and filtered. After removal of the solvent, the crude product was carefully purified by flash chromatography on silica gel (first band) using (7:3) (v/v) CH₂-Cl₂/*n*-hexane as eluent. The free-base porphyrazine was obtained in a yield of ca. 65% with respect to MgOMTPz. Anal. Found: C, 42.15; H, 3.70; N, 16.25; S, 37.80. Calcd for $C_{24}H_{26}N_8S_8$: C, 42.20; H, 3.84; N, 16.41; S, 37.55. ¹H NMR (499.6 MHz, CDCl₃, 297 K), δ /ppm: 3.42 (s, 24 H, S–CH₃), -3.26 (s, 2 H). UV–vis (CHCl₃), λ_{max} /nm (log ϵ): 356 (4.50) Soret; 504 (4.16), 621 (4.24), 700 (4.34) Q-bands.

Langmuir Experiments. Chloroform (Fluka, HPLC grade) was used in making up the spreading solution: 2.22 mg of H₂OMTPz was completely dissolved in 10 mL of chloroform (concentration of 3.3×10^{-4} M). Langmuir experiments were carried out using a KSV5000 System3 apparatus (subphase surface of 850 cm²). Ultrapure water (resistivity greater than 18 MΩ cm) from a Milli-Q/Elix3 Millipore system was used as the subphase (pH \approx 5.9). It was thermostated at 293 K by a Haake GH-D8 apparatus. A 200 μ L aliquot of the spreading solution was spread onto the subphase. After solvent evaporation, the floating film was compressed at a speed of 7 $Å^2$ molecule⁻¹ min⁻¹. During the depositions, the transfer surface pressure was fixed at 20 mN m⁻¹. Glass and quartz substrates were all rendered hydrophobic before deposition by storing overnight in a desiccator in contact with vapors of 1,1,1,6,6,6hexamethydisilazane. The transfer onto all substrates was performed by the horizontal lifting method (Langmuir-Schäfer technique).

Reflection Spectroscopy and Brewster Angle Microscopy. Reflection spectroscopy and Brewster Angle Microscopy analysis were carried out using a NIMA 601BAM apparatus. Also in this case, a compression speed of 7 Å² molecule⁻¹ min⁻¹ was utilized, after evaporation of chloroform spreading solvent. The reflection data (ΔR) here reported were obtained by an NFT RefSpec instrument. They were acquired under normal incidence of radiation according to the description given in ref 24 and correspond to the difference between the reflectivities of the floating film—liquid interface and the clean air—liquid interface. All reflection spectra were carried out at 293 K. Concerning BAM measurements, they were obtained by a NFT BAM2*plus* system with a lateral resolution of 2 μ m.

UV-vis Spectroscopy. Solution electronic spectra in 0.1 cm path length quartz cells in the region 250–800 nm were performed on a UV-vis-NIR 05E Cary spectrophotometer equipped with a polarized spectroscopy setup. A Glan-Taylor polarizer was set between the lamp and sample to obtain the desired polarized UV-vis irradiation.

Ellipsometry. The data were measured on a variable angle spectroscopic ellipsometer (VASE) manufactured by the J. A.Woollam Co. It was equipped with an AutoRetarder, which utilizes patented technology to achieve maximum measurement accuracy. VASE measurements for this report were taken from 280 to 2300 nm (0.54–4.43 eV) and at multiple angles of incidence ($60^{\circ}-75^{\circ}$ by 5°). The beam diameter was fixed at 1.5 mm. All data were acquired and analyzed (WVASE version 3.422). In addition, transmission intensity spectroscopic data had been acquired and fit together with the ellipsometric data.

Results and Discussion

Langmuir Experiments. The reproducible Langmuir isotherm of floating films of H₂OMTPz is illustrated in Figure 1. The Π vs *A* curve does not evidence a peculiar feature other than the smooth transition to the condensate state, as already observed in a previous study by the other researchers for a different tetraazaporphyrin.²⁵ The limiting area per molecule, $A_{\Pi\rightarrow0}$ (obtained by extrapolation of the steepest portion of the curve to 0 mN/m pressure), is 16 Å². Density functional calculations²⁶ have suggested that the area per molecule of H₂-OMTPz is at least 200 Å² when the molecule is prone on the water surface or about 70 Å² when it assumes an edge-on



Figure 1. Langmuir isotherm of H₂OMTPz at 293 K. Spreading solvent, CHCl₃; concentration, 3.3×10^{-4} M; spread volume, 200 μ L; barrier speed, 7 $Å^2$ molecule⁻¹ min⁻¹. In the inset, one of the possible conformations accessible to the H2OMTPz molecule is illustrated (see text).

configuration at the air-water interface. On the contrary, the analysis of the Langmuir isotherm evidences that the observed value of $A_{\Pi \to 0}$ (16 Å²) is too small in comparison with both values corresponding to the two previous limit orientations. A plausible rationale of such a small value of $A_{\Pi \to 0}$ is that, upon compression of the floating layer, a significant fraction of molecules are forced out of the interface in different arrangements. It is also probable that a small percentage of molecules are effectively at the air-water interface, while the rest essentially extends far from the contact with the water subphase because the hydrophobic nature of the whole macrocycle forces

the H₂OMTPz molecules out of the interface. We have also tried to improve the floating film homogeneity waiting for long periods after spreading (at least 2 h) in order to allow unspread fractions to diffuse to the water surface. But also in these cases, no variations in the behavior of the floating films (through Π vs A curves and BAM analysis) was monitored.

The collapse pressure of the monolayer is high (about 55 mN/ m), thus suggesting the high stability of H₂OMTPz floating film on the water surface. The film can sustain a surface pressure of 40 mN/m for at least 12 h with negligible area loss.

BAM investigations were carried out during the compression of the floating layer and gave a further confirmation about the presence of large aggregates on the water surface. The contemporaneous subsistence of three-dimensional aggregates and clean water surface was observed even just after solvent evaporation and at low surface pressures and low area densities. It is possible to distinguish bright regions of 3D aggregates and dark areas of pure water surface. Aggregates of H2OMTPz of different sizes are clearly evidenced at 0.5 mN/m (area per molecule of about 22 Å²) onto the water subphase and are illustrated in Figure 2a. During compression such domains coalesce and broaden; they begin to evidence more clearly facets and different shades of gray, suggesting the presence of aggregates with different thickness and arrangements. This is illustrated in Figure 2b, taken at a surface pressure of 2 mN/m (area per repeat unit of about 19 Å²). Further compression at higher surface pressures permits generation of progressively larger clusters on the average, even though for $\Pi > 15$ mN/m the morphology of the floating film appeared less sensitive to surface pressure variations than for smaller surface pressures. Such a trend is illustrated in Figure 2c-f, which cover the range from $\Pi = 5$ to 40 mN/m. This behavior is also consistent with the pattern shown in the Langmuir isotherm, whose slope is practically constant above 15 mN/m. In some cases, wide



a) 0.5 mN/m

b) 2 mN/m

c) 5 mN/m



d) 15 mN/m

e) 30 mN/m

f) 40 mN/m

Figure 2. BAM images of the floating layer of H₂OMTPz at different surface pressures and average areas per repeat unit: (a) $\Pi = 0.5$ mN/m and $A = 22 \text{ Å}^2$; (b) $\Pi = 2 \text{ mN/m}$ and $A = 19 \text{ Å}^2$; (c) $\Pi = 5 \text{ mN/m}$ and $A = 17 \text{ Å}^2$; (d) $\Pi = 15 \text{ mN/m}$ and $A = 14 \text{ Å}^2$; (e) $\Pi = 30 \text{ mN/m}$ and A = 11.5 mN/mÅ²; (f) $\Pi = 40$ mN/m and A = 10 Å². The field of view along the x axis is 430 μ m.

domains at least as large as the field of view of the BAM instrument (430 μ m) were evidenced (Figure 2d).

Such a rigid floating film is not transferable by the usual vertical dipping method, but multilayers have been fabricated by the horizontal lifting (Langmuir–Schäfer) technique onto different substrates. Films containing up to 160 layers were deposited, giving dark green multilayers.

The UV-vis absorption spectrum of H₂OMTPz reported in ref 20 for a solution in chlorobenzene contains four maxima at 709, 637, 515, and 367 nm, with molar extinction coefficients of 35.0×10^3 , 25.5×10^3 , 20.0×10^3 , and 42.3×10^3 L cm⁻¹ mol^{-1} , respectively (comparable values were obtained by us in different solvents, vide infra). The molecular organization of H₂OMTPz floating layers at the air-water interface was investigated by spectroscopic measurements through reflection of light. We have studied reflection of light under normal incidence at the water surface covered with the tetraazaporphyrin derivative layer. The reflection method constitutes a powerful investigation technique on the chromophore behavior on the water surface and was first introduced by Kuhn and Möbius.²⁷ It is particularly tailored for this purpose, since only chromophores at the interface contribute to the enhanced reflection. The difference ΔR in reflectivity from the chromophore floating layer on the subphase and reflectivity from the bare subphase surface was monitored as a function of wavelength. The corresponding reflection spectra from H₂OMTPz on the water surface at different fixed surface pressures after reaching equilibrium (i.e. no variation in surface pressure and enhanced reflectivity) are shown in Figure 3a. It is apparent that, upon compression, the reflection enhances because on the average the surface density grows, while its profile does not change. The reflection spectra were then normalized to the same surface density of H₂OMTPz by multiplying ΔR by the surface area, i.e., $\Delta R_{\text{norm}} = \Delta RA$, where A (nm² per repeat unit) is taken from the Langmuir isotherm at the relative value of surface pressure. The normalized spectra are illustrated in Figure 3b. The continuous increase in ΔR_{norm} , together with the constancy of the maximum wavelength, suggest that, after initial aggregation after solution spreading, the self-organized and associated clusters are dragged on the water surface and coalesce, while consequently the surface density of the floating layer enhances. As can be detected, the normalized reflection spectra of H₂OMTPz undergo continuous and monotonic enhancement during the compression process. This could be also rationalized considering that, after initial preaggregation, the 3D domains of aggregated molecules are constrained together but significant reorganization on the water surface does not take place. This spectral behavior is also consistent with the markedly hydrophobic character of the polymer (from the surface pressure vs area per repeat unit curve) and the BAM images.

In the ΔR spectra of H₂OMTPz molecules on the water surface, two peaks are apparent at 375 and 506 nm for all analyzed surface pressures. Their position is not sensitive to surface tension variations, thus suggesting that the average arrangement of molecules is not varying while increasing II pressure. A large plateau is evidenced in the range between 600 and 700 nm; a possible rationale could be the presence of another hidden minor peak in this region as suggested also by Blinov et al.,²⁸ who in the absorption spectra of 2,7,12,17tetrakis(*tert*-butyl)-5,10,15,20-porphyrazine in Langmuir– Blodgett films detected a Stark effect (relative change in transmittance). A new band appeared at 600–650 nm in the Langmuir–Blodgett film; the proposed rationale was that a



Figure 3. Absolute reflection spectra (a) and normalized reflection spectra (b) from the floating film on the water surface at different fixed surface pressures after equilibrium.

dense packing of 2,7,12,17-tetrakis(*tert*-butyl)-5,10,15,20-porphyrazine, determined by intermolecular charge transfer, was generated.

At last, two shoulders at about 345 and 470 nm are apparent in the case of the floating film at the air—water interface (irrespective of the surface pressure). These shoulders propose probably the existence of more than a single aggregation state and organization of H₂OMTPz molecules. Moreover, a dependence of the relative intensities of the main peak and the shoulders on the surface tension seems to be absent, thus suggesting that correspondingly the number of H₂OMTPz macromolecules in the two different associated states does not vary significantly with Π pressure.

UV-vis Spectroscopic Characterization of H_2OMTPz in Solution and in the Langmuir-Shäfer Film. Solution Spectra. Before discussing the polarized absorption UV-vis spectra of the LS films, we examine the salient features of the solution spectra of the constituent molecule.

Figure 4 shows the electronic absorption spectra of H₂OMTPz in *n*-hexane, chloroform, and toluene at the same concentration $(10^{-6}$ M, a value which is sufficiently low to prevent significant aggregation phenomena to occur) and experimental conditions. As inferred from Figure 4, the ground-state absorption spectrum of H₂OMTPz is quite solvent dependent, even in noncoordinating media. In general, the main features of the spectrum are shifted to the red in the aromatic solvent compared to chloroform



Figure 4. Ground-state absorption spectra of H_2OMTPz in *n*-hexane (continuum line), chloroform (dashed line), and toluene (dotted line).

and, particularly, to the purely aliphatic medium. Additionally, the peak extinction coefficient of the strong near-UV "Soret" band is, either in chloroform and in toluene, significantly smaller than in *n*-hexane. Similarly, the broad Q-bands and the prominent absorption with large sulfur lone pair to porphyrazine ring π^* charge-transfer character (SPCT) lying between the Q-region and the "Soret" band have, either in chloroform and in toluene, reduced peak intensity. Interestingly, in *n*-hexane the Q_y(0,0) absorption is partially resolved and shows up as a shoulder at about 629 nm.

The breadth of the absorption bands, which is large, regardless of the nature of the solvent, can be ascribed in large measure to inhomogeneous broadening due to the presence of multiple accessible conformations in solution and, in the second place, to the large number of excited states related to the presence of the heteroatoms at the periphery of the macrocycle. As for the broadening effects caused by the presence of multiple accessible conformations in solution, these most likely include rotating/ tilting of the multiple peripheral methylthio groups and their steric/electronic interactions with each other and with the prominent lone pair orbitals of the macrocycle bridging nitrogens. The differential stabilization of the accessible conformations on going from aliphatic to aromatic media is, most likely, at the origin of the observed sensitivity of the energy and intensity of the B, SPCT, and Q-bands to the nature of the solvent.

UV-vis Spectroscopy of the Langmuir-Shäfer Film. The LS films were characterized by UV-vis spectroscopy with both isotropic and polarized light. The spectrum of a LS film (62 runs/layers) of H₂OMTPz is characterized by the Soret band at 355 nm and a SPCT band at 492 nm, at the same wavelengths as in chloroform, toluene, and n-hexane, respectively. These bands are slightly broader then in solution, which is typical of quasisolid spectra. A more significant difference between solution and solid spectra is observed in the 600-750 nm range, where the typical Q-bands of alkyl(sulfanyl)porphyrazine systems are located. The $Q_x(0,0)$ absorption that occurs at 693, 700, and 703 nm in n-hexane, chloroform, and toluene, respectively, shifts to 728 nm, as is usually observed for tetrapyrrolic systems having a transition from fluid to solid phase. So for the $Q_{v}(0,0)$ absorption that is observed at 647 nm in the solid state, a value ~ 20 nm lower than in *n*-hexane is clearly discernible. Moreover, both the x- and y-polarized Q-bands are rather broadened (although to an extent not significantly larger than in solution). Both these spectral features, i.e., the red shift and broadening of the bands, are indicative of the fact that non-negligible interactions are operative between the molecules in their "frozen" conformations in the solid state.



Figure 5. Limiting orientations of the porphyrazine molecules on the quartz plane: (a) flat orientation; dichroic ratio = 1; (b) edge-on orientation to the substrate plane with the normal n of the macrocycle plane parallel to the dipping direction, R < 1; (c) edge-on orientation to the substrate plane with the normal n of the macrocycle plane perpendicular to the dipping direction, R > 1.

(We notice, in passing, that in view of the modest peripheral crowding, the planarity of the porphyrazine core should be largely preserved in the methylthioporphyrazine in the condensed phase, whatever the relative orientation of the peripheral methyl groups is. Accordingly, a substantially D_{2h} symmetry can be assumed for the porphyrazine ring.) When the film is investigated with polarized light by using the light polarization plane, **E**, parallel (E_p) or perpendicular (E_s) to the incidence plane of radiation at an incidence angle $I = 0^\circ$ of the light beam with respect to the plane normal, the main absorption features show a marked dependence on the direction of the electric field vector with respect to the dipping direction (see Figure 5).

The dichroic ratios $R = A(E_p)/A(E_s)$ (A = absorbance) calculated for the 359, 647, and 728 nm absorptions are 0.85, 0.58, and 0.74, respectively. These values indicate that a significant molecular order is present within the film. To get an idea of the type of molecular ordering, it is instructive to consider the polarization dependence expected for three limiting orientations of the free base porphyrazine with respect to the lifting direction, as shown in Figure 6.

With molecules flat (face-on) on the quartz substrate (case a), no polarization dependence of the light absorption would be expected, because the main absorption bands are polarized in the *xy* plane ($A(E_p) = A(E_s)$). Dichroic ratios smaller than 1 are expected when edge-on-oriented molecules have the normal to the macrocycle plane parallel to the lifting direction ($A(E_p) < A(E_s)$, case b). Finally, dichroic ratios larger than 1 are expected when edge-on-oriented molecules have the normal to the macrocycle plane perpendicular to the lifting direction ($(A(E_p) > A(E_s), \text{ case c})$. Our results point to case b. The dichroic ratio calculated for the $Q_y(0,0)$ absorption is, furthermore, significantly smaller than that calculated for the $Q_x(0,0)$ absorption.



Figure 6. Electronic spectrum in polarized light of the Langmuir– Shäfer film (62 layers) fabricated with H_2OMTPz : (dashed line) electric field vector parallel to the incidence plane; (solid line) electric field vector perpendicular to the incidence plane.

tion, suggesting that the porphyrazine molecules should face the substrate preferentially with their the *y*-edge.

Such variation in the absorption behavior constitutes a further confirmation that spectral features are determined not only by the structure of the molecule, but also by the overall organization of the macrocycles in the film. In particular, as far as the LS films, and the solid phase in general, are concerned, the mutual organization and orientation of the macromolecules influence significantly the characteristics of the spectrum. The optical properties of such macrocycles could therefore be modulated not only by ad hoc synthetic procedures but even by the organization of molecules.

The spectra evidence some noteworthy peculiarities. First of all, the band is significantly broader and less resolved in the case of the ΔR spectrum on the water surface and of the LS film absorbance spectrum in comparison with the solution absorption. This is typically ascribed to the generation of aggregates in the floating films on the water surface and in the multilayers on solid substrates.

The information obtained by the spectroscopic investigations of the LS films suggests that the hydrophobic surface of the substrates have induced a profound molecular organization. In fact, the visible portion of the spectra of the LS films does not show the huge loss of resolution exhibited by the spectra of the floating film on the water surface. This completely different behavior could be ascribed to the pronounced difference experienced by H₂OMTPz molecules when transferring from the polar water surface to the hydrophobized substrate. This is not the first time we have experienced such a strong effect induced by the substrate; in fact, a strong influence of the substrate on molecular organization was already found for a symmetrically functionalized phthalocyanine transferred onto a Mylar substrate.²⁹

The analysis by polarized light suggests that on the average the preferential orientation of molecules of H₂OMTPz is the so-called edge-on or playing-card arrangement, typical of similar macrocycles such as phthalocyanines. Therefore, even though the LS film evidences a high roughness from ellipsometric data (reported in the following), an average privileged disposition of H₂OMTPz molecules is apparent, also in this case according to similar data already found for the strictly similar phthalocyanine macrocycles.^{30,31}

Ellipsometry. The estimation of film thickness and refractive index have been performed by ellipsometry, a common and

highly sensitive method for the investigation of the optical properties of Langmuir–Blodgett films.^{32,33} Therefore, a film consisting of 62 layers, all transferred by the horizontal lifting (LS) method, was deposited onto a hydrophobized flat quartz substrate. A polarized light beam is reflected at oblique incidence from a surface; the reflection at the surface changes the polarization state of the light, which is measured. The measured polarization parameters are the relative phase change, Δ , and the relative amplitude change, Ψ , introduced by reflection from the surface. By using Fresnel's relation and, by assuming a proper model, we can get information about the optical constants and the thickness of the material.³⁴

 Δ and Ψ were measured for each possible wavelength $(\lambda)/$ angle (ϕ) combination (the values for λ were taken in the range from 280 to 2300 nm and for ϕ from 60° to 75° by 5°). Measurements at multiple angles improve confidence, as light travels on different paths through the film. After an ellipsometric measurement, data were analyzed to determine the optical constants and layer thickness of the thin film, the analysis consisting of multiple steps, as illustrated in the flowchart herewith reported.



Finally, experimental data were compared with theoretical ones using the mean squared error (MSE).^{35–37} MSE was minimized by adjusting each fit parameter, using a Levenberg–Marquardt fit algorithm,^{35,37} the lowest MSE suggesting the best agreement between theory and experiment within the boundary of the current model.

A graded profile and a thin surface roughness layer were required in the best model. The gradient described a decrease in optical constants from bottom to the top. The surface roughness layer was modeled using a Bruggeman effective medium approximation,^{38,39} composed of 50% LS material and 50% void.

In the first step we reduced the spectral range to 900-2300 nm, where the layer is transparent, and applied a Cauchy dispersion function to fit for the layer thickness parameters and the Cauchy parameters. The Cauchy dispersion equation⁴⁰ for transparent layers is

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4}$$

where A_n , B_n , and C_n are Cauchy parameters and λ is the wavelength in microns. Additionally, an Urbach absorption tail was taken into account.



Figure 7. Graphs for Ψ , Δ , and transmission vs wavelength, measured by spectroscopic ellipsometry, and refractive index and extinction coefficient vs distance from the substrate surface, as well as optical constants, according to the best model.

In the second step, we extended the spectral range further into the visible and UV by fixing the layer thickness and fitting n and k for each wavelength point-by-point. The optical constants had been checked afterward to be Kramers-Kronig consistent. The graphs for Ψ , Δ , and transmission vs wavelength, and refractive index and extinction coefficient vs distance from the substrate surface, as well as the optical dispersion, are reported in Figure 7.

The main results are herewith reported: roughness thickness = 10.8 ± 0.33 nm; layer thickness = 438.9 ± 0.57 nm.

The average film thickness is 438 nm, which implies an average thickness per LS layer of 7.1 nm. This value is markedly larger than the hypothetical value of about 1.4 nm for a homogeneous arrangement of molecules with an edge-on orientation with respect to the substrate plane. On the other hand, such a value is in accordance with the morphology of the floating film at the air—water interface: large 3D-aggregates are preferentially transferred from the water surface to the solid support, thus accounting for also the high roughness obtained by both models. In conclusion, ellipsometric data are consistent

with the information at the air—water interface got by BAM, reflection microscopy, and Langmuir isotherm. The ratio between the experimental value for each layer in the LS film (71 Å) and the theoretical one for the thickness of a uniform monolayer of H₂OMTPz molecules (14 Å) is about 5; on the other hand, the ratio between the expected value of the limiting area per molecule for a homogeneous monolayer with an edge-on arrangement of molecules (70 Å²) and the experimental one (15 Å²) is 4.7, thus suggesting that the floating layer is almost five monolayer equivalents thick. It is singular to observe that the values of the two ratios are in good accordance. This is probably a further suggestion that the floating layer on the water surface consists of large 3D aggregates randomly and isotropically oriented.

Conclusions

The main feature emerging from this research is the profoundly different molecular organization at the air-water interface and onto hydrophobic quartz and glass substrate. The rational probably is based on the poor amphiphilic character of Floating Films of a Nonamphiphilic Porphyrazine

H₂OMTPz molecules that precludes the formation of a real homogeneous Langmuir film on the water surface. This also justifies the presence on the polar subphase of large threedimensional aggregates evidenced by BAM images and by the Langmuir isotherm; correspondingly, the ΔR spectra on the water surface evidence very broad bands above all in the visible region of the spectrum. On the contrary, probably the so-called hydrophobic-hydrophobic interaction promotes a remarkable change in the disposition of molecules onto solid substrates; in fact, the analysis using polarized light displays the existence of a preferred molecular orientation with macrocycles having an edge-on orientation with respect to the substrate surface. At the same time, the loss of resolution in the UV-vis absorption spectra suggests that in the LS films H₂OMTPz molecules thoroughly interact with each other. Finally, also the data from ellipsometry confirm, through a thickness much larger than the one expected for a sequential monolayer transfer onto the solid and a high roughness, the existence of large three-dimensional aggregates.

Future developments of this research will concern the utilization of such films as active layers in resistive chemical gas sensors, above all in the light of the high specific conductivities evidenced by other octaalkylthio-substituted porphyrazines. Probably the high roughness of the LS films offers the presence of a large number of active sites for the interaction with the dopant gases or vapors.

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