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Effects of Molecular Organization on Photophysical Behavior. 1. Steady-State Fluorescence and Fluorescence Quantum Yield Studies of Langmuir–Blodgett Monolayers of Some Surfactant Porphyrins

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The surface chemistry of two new groups of surfactant carboxyporphyrins is described. These materials exhibit well-behaved monomolecular films at an air–water interface. In compressed monolayers, the porphyrin ring appears to be oriented so that the plane of the ring is perpendicular to the surface. The surface-pressure–molecular area isotherms change with the length and nature of the side chains in a manner suggesting that a long side chain allows the porphyrin rings to acquire the most ordered packing. A rigid chain structure was found to restrict the orientational flexibility of the porphyrin rings and hence prevented them from acquiring a well-ordered monolayer structure. The solid-state photophysical properties of Langmuir–Blodgett monolayers of these materials are strongly dependent on their degree of order. The absorption, fluorescence, and fluorescence excitation spectra of single monolayer films transferred onto quartz and SnO₂ slides using the Langmuir–Blodgett technique indicate that increasing the order in porphyrin monolayers leads to an increased red-shift of the Soret band and to decreased fluorescence quantum yields. On a SnO₂ semiconductor surface, the monolayers exhibit enhanced fluorescence quenching. This is interpreted as evidence for isoenergetic electron transfer from the porphyrin to the semiconductor. An approximate interfacial electron-transfer rate (k_{et}) was estimated on the basis of the fluorescence yields on quartz and SnO₂ surfaces, respectively.

Introduction

Porphyrins and phthalocyanines have recently been the subject of considerable interest in connection with semiconductors,¹ molecular metals,² catalysis,³ and nonlinear optics.⁴ While the parent molecules have a number of useful properties, considerable effort has been expended to synthesize novel structures, both with a view to engineering new molecular materials that may show improved or novel characteristics and to mimicking naturally occurring systems. In addition, much attention has focused on the formation of ordered thin-film assemblies, such as *Langmuir–Blodgett* (LB) films,⁵ which may be useful in applications, such as molecular devices. The optoelectronic properties of thin films of organic semiconductors, such as porphyrins and phthalocyanines, have attracted attention for both practical⁶ and theoretical^{7,8} reasons. The mechanisms of electronic conduction, energy transfer, and radiationless deactivation of excited

states in single crystals of organic semiconductors are still not well understood.⁸ An understanding of these processes in the less well-ordered, but technologically more important, thin films is still in a primitive stage.

In the solid state, porphyrins and many other organic semiconductors, behave as quasi-one-dimensional conductors;^{8,9,10} their intermolecular overlap, and therefore their conductivity, is greatest in a direction perpendicular to the molecular planes. Because of the low dimensionality of the conducting pathway, crystal dislocations and bond resistances should have a greater effect on the optoelectronic properties of organic semiconductors than on three-dimensional semiconductors, such as silicon. Such considerations led us to synthesize a series of porphyrins¹¹ (Figure 1) possessing surface active properties, in an effort to investigate the effects of order on the photophysical and photoelectrochemical properties of *Langmuir–Blodgett* monolayer films made from these porphyrins and grow large area, well-ordered thin films for use in organic semiconductor devices.

A number of papers dealing with the photophysical properties of porphyrin thin films have appeared. Gouterman et al.^{12a,b} have studied sublimed films of octaethylporphyrin (H₂OEP) and report that films thicker than ~10 nm have some tendency to crystallize spontaneously.

(1) (a) Simon, J.; Andre, J.-J. *Molecular Semiconductors*; Springer: Berlin, 1985. (b) Nevin, W. A.; Chamberlain, G. A. *J. Appl. Phys.* **1991**, *69*, 4324.

(2) Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1983**, *16*, 15.

(3) (a) Kobayashi, N.; Janda, P.; Lever, A. B. P. *Inorg. Chem.* **1992**, *31*, 5172. (b) Collman, J. P.; Zhang, X.; Lee V. J.; Brauman, J. I. *J. Chem. Soc., Chem Commun.* **1992**, 1647.

(4) Norwood, R. A.; Sounik, J. R. *Appl. Phys. Lett.* **1992**, *60*, 295.

(5) Snow, A. W.; Barger, W. R. In *Phthalocyanines-Properties and Applications*; Leznoff, C. C.; Lever, A. B. P., Eds.; VCH Publishers: New York, 1989; Vol. 1, Chapter 5.

(6) (a) Lecompte, C.; Boudin, C.; Ruadel-Teixer, A.; Barraud, A.; Momenteau, M. *Thin Solid Films* **1985**, *133*, 103. (b) Loutfy, R. O.; Sharp, J. H.; Hsiao, C. K.; Ho, R. *J. Appl. Phys.* **1981**, *52*, 5218.

(7) Cave, R. J.; Siders, P.; Marcus, R. A. *J. Phys. Chem.* **1986**, *90*, 1436.

(8) (a) Gutmann, F.; Lyons, L. E. *Organic Semiconductors, Part A*; Robert E. Krieger: Malabar, FL, 1981. (b) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Solids*; Oxford University Press: New York, 1982. (c) Simon, J.; Andre, J.-J. *Molecular Semiconductors*; Springer-Verlag: Berlin, 1985.

(9) (a) Blanzat, B.; Barthou, C.; Tercier, N.; Andre, J.-J.; Simon, J. *J. Am. Chem. Soc.* **1987**, *109*, 6193. (b) Markovitsi, D.; Tran-Thi, T.-H.; Briois, V.; Simon, J.; Ohta, K. *J. Am. Chem. Soc.* **1988**, *110*, 2001.

(10) (a) Marks, T. J. *Science* **1985**, *227*, 881 and references therein. (b) Gaudiello, J. G.; Almeida, M.; Marks, T. J.; McCarthy, W. J.; Butler, J. C.; Kannewurf, C. R. *J. Phys. Chem.* **1986**, *90*, 4917.

(11) (a) Choudhury, B. Ph.D. Dissertation, University of Western Ontario, London, Ontario, 1995, p 106. (b) Choudhury, B.; Bolton, J. R.; Weedon, A. C. Manuscript in preparation.

(12) (a) Bonham, J. S.; Gouterman, M.; Howell, D. B. *J. Lumin.* **1975**, *10*, 295. (b) Kampas, F. J.; Gouterman, M. *J. Lumin.* **1976**, *14*, 121. (c) Kampas, F. J.; Gouterman, M. *J. Lumin.* **1978**, *17*, 439.

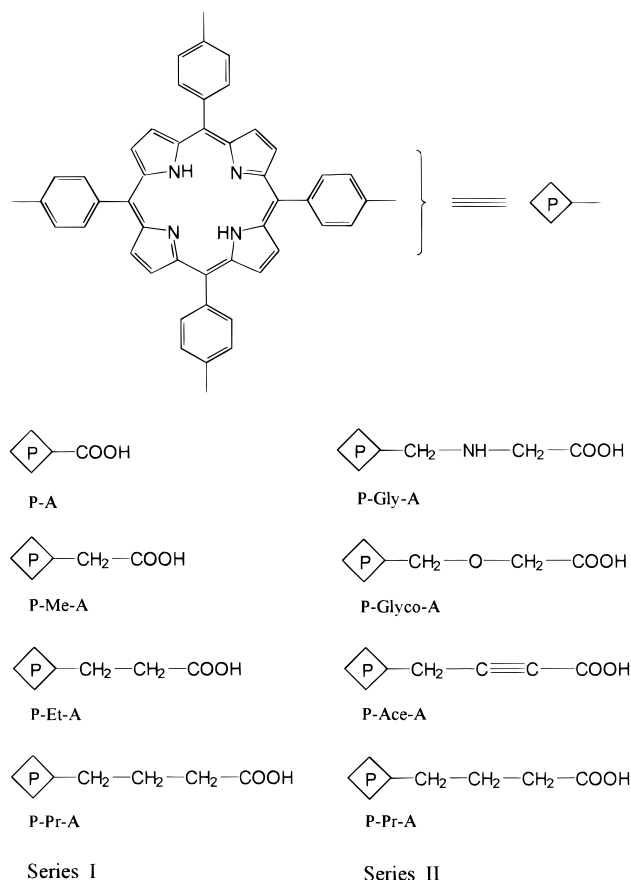


Figure 1. Designed surface active porphyrin molecules.

These films showed increased impurity fluorescence, which was attributed to a longer exciton diffusion length in the polycrystalline materials, as compared to the amorphous films. They also noticed a substantial quenching of the Soret band in the fluorescence excitation spectrum of the polycrystalline films,^{12a} although this was later thought to be a reflection effect.^{12b} These workers later showed^{12c} that the fluorescence intensity from both the host and the impurities was enhanced by sublimation onto a heated substrate, rather than at room temperature.

A substantial effort has been devoted to the characterization of monolayer films of porphyrins, both as the pure porphyrins^{13,14,15a,b,d} and as mixtures of surfactants.^{15c} The optical properties of porphyrins in monolayers resemble those of the dimerized or aggregated species in solution.^{13c,14,15a,c} A number of examples of conductivity measurements^{13b,15b,d} and photoelectron transfer^{13a,b} have also been reported. Kampas et al.¹⁶ prepared both sublimed and spin-coated thin films of a large number of porphyrins for testing in photoelectrochemical (PEC) cells. The amorphous films obtained by spin-coating showed higher quantum efficiencies for photocurrent generation than the polycrystalline films obtained by sublimation,

although this result might be explained by the possibility of a large number of pinholes in the polycrystalline layers. Armstrong et al.¹⁷ have carefully optimized the sublimation conditions for the deposition of a number of phthalocyanines and have correlated the changes in the absorption spectra with the type of crystals formed. They obtained the highest efficiencies in PEC cells for films consisting of large crystals that spanned the thickness of the layer.

With the availability of some *newly synthesized porphyrins* (Figure 1),¹¹ we are now able to exercise more control over the order of the porphyrin chromophore in the monolayer than was possible previously. This paper details how the photophysical properties of the new porphyrins change as a function of the degree of film order (i.e., aggregation) and the nature of the side chain attached to it. The present work contains the following points: (1) a demonstration that the degree of order of the porphyrins in monolayers depends on the nature of the side chain and the surface of the substrate; (2) a description of the photophysical changes in a system of a single chromophore (tritolyldiporphyrin) whose degree of order can be almost continually varied due to the different chain lengths attached to it; (3) an explanation of why the "B" or "Soret" porphyrin absorption band experiences a bathochromic shift in the monolayer; (4) a demonstration that the fluorescence quantum yield of the monolayers ϕ_f is dependent on the degree of aggregation (and hence the order) and on the nature of the side chain linkage, and (5) a comparison of the photophysical properties of porphyrin compounds with those of the monolayer films and the dissolved species (i.e., in solution).

To the best of our knowledge a number of these points are novel.

Experimental Section

The Langmuir balance and the monolayer deposition technique used in these studies are described in ref 11a. The LB trough (13 cm \times 60 cm \times 1 cm deep) was fabricated from Teflon. The surface area of the air-water interface was adjusted by a movable barrier riding along the top of the sides of the trough. Surface pressure was measured by a movable Teflon float attached to a torsion balance coupled to a linear transducer. The apparatus was cleaned periodically by soaking in a solution of detergent Decon (BDH Chemicals) followed by thorough rinsing with filtered water. It was also rinsed before every deposition with absolute ethanol followed by Fisher spectral grade methanol.

The subphase, unbuffered water, was purified as follows. House distilled water was passed through scale elimination, deionization, and organic removal columns (D8291, D8922 SYBRON/Barnstead), distilled in a quartz bidistillation apparatus (Bi4, Englehart, Amersil Quartz Division), and then stored in Pyrex volumetric flasks fitted with inverted ground glass stoppers. The conductivity of the water was measured to be $\sim 10^{-6} \Omega^{-1} \text{ m}^{-1}$.

Quartz slides (Corning) and n-type Sb-doped SnO_2 -coated glass slides (Cherry Display Products Corp.) were used as a substrate for LB films in the photophysical studies. The slides were cleaned by soaking in concentrated chromic acid for 3 days and then washed (10 rinses) with Barnstead filtered water, followed by sonication for 15 min in 0.01 M NaOH. This was followed by five rinses with filtered water, five rinses with triply distilled water, and sonication for 15 min in the final rinse. The slides were then dried with prepurified nitrogen.

The model porphyrin compounds (Figure 1) were prepared and purified as described previously.^{11a,b} Fisher spectral grade chloroform and methanol were used as solvents throughout. A

(13) (a) Janzen, F. A.; Bolton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 6342. (b) Bardwell, J. A.; Bolton, J. R. *Photochem. Photobiol.* **1984**, *40*, 319. (c) Bardwell, J. A.; Bolton, J. R. *Photochem. Photobiol.* **1984**, *39*, 735. (d) Janzen F. A. Ph.D. Dissertation, University of Western Ontario, London, 1978, p 200.

(14) Zachariasse, K. A.; Whitten, D. G. *Chem. Phys. Lett.* **1973**, *22*, 527.

(15) (a) Miller, M.; Knoll, W.; Moewald, H.; Ruau-del-Teixer, A. *Thin Solid Films* **1985**, *133*, 83. (b) McArdle, C. B.; Ruau-del-Teixer, A. *Thin Solid Films* **1985**, *133*, 93. (c) Bull, R. A.; Bulkoeski, J. E. *J. Colloid and Interface Sci.* **1983**, *92*, 1. (d) Jones, R.; Tredgold, R. H.; Hoorfar, A. *Thin Solid Films* **1985**, *123*, 307.

(16) Kampas, F. J.; Yamashita, K.; Fajer, J. *Nature* **1980**, *284*, 40.

(17) Kolfat, T. J.; Sims, T. D.; Pankow, J. W.; Danziger, J.; Nebesny, K. W.; Armstrong, N. R. *J. Phys. Chem.* **1987**, *91*, 5651.

Table 1. Surface Pressure–Area Isotherms, Absorption, and Fluorescence Emission Characteristics of Porphyrin Model Compounds^a

compound	area/molecule (Å ² molecule ⁻¹) ^b	λ_{\max} (nm) ^c quartz	red shift (nm)	λ_{\max} (nm) ^c SnO ₂	red shift (nm)	λ_f (nm) quartz	red shift (nm)	λ_f (nm) SnO ₂	red shift (nm)
P-A		418 (in CHCl ₃)				652 (in CHCl ₃)			
P-A	79.7 ± 0.5	434 ± 2	16	430 ± 2	12	654 ± 1	2	655 ± 1	3
P-Me-A	70.6 ± 0.4	436 ± 2	18	432 ± 2	14	657 ± 1	5	658 ± 1	6
P-Et-A	61.4 ± 0.4	438 ± 2	20	434 ± 2	16	661 ± 1	9	661 ± 1	9
P-Pr-A	39.3 ± 0.3	442 ± 2	24	436 ± 2	18	664 ± 1	12	664 ± 1	12
P-Gly-A	24.8 ± 0.3	446 ± 2	28	438 ± 2	20	667 ± 1	15	666 ± 1	14
P-Glyco-A	74.7 ± 0.3	434 ± 2	16	430 ± 2	12	655 ± 1	13	654 ± 1	12
P-Ace-A	87.0 ± 0.4	432 ± 2	14	426 ± 2	8	652 ± 1	0	651 ± 1	-1

^a Measurements carried out at 22 ± 2 °C. ^b Areas were measured at 20 mN m⁻¹ surface pressure. ^c λ_{\max} were measured using an integrating-sphere assembly. ^d Red shift is the band peak shift defined as λ_{\max} (monolayer) - λ_{\max} (CHCl₃ solution).

solution of a given model porphyrin ($\sim 2 \times 10^{-4}$ M) was deposited onto the subphase (20 ± 2) °C with a Pressure-Lok syringe (Precision Sampling Corp.), with a minimum of 3 s between each drop. Compression was begun 1 min after the end of deposition at a rate of 55 cm² min⁻¹. The film was compressed to a surface pressure of 20 mN m⁻¹ at which point the slide was dipped in and out of the water at a rate of 2.0 cm min⁻¹. During transfer of the monolayer, the surface pressure was maintained at 20 mN m⁻¹ by continual reduction of the surface area. Only slides exhibiting a deposition ratio of 1.0 ± 0.1 were accepted for the study.

Absorption spectra were measured on a Hewlett-Packard model 8450 diode array spectrophotometer. A slide holder was specifically designed to hold the monolayer-coated slides vertically against the detector. All the measurements were corrected for reflectance and scattering of the transmitted light by quartz and SnO₂ slides coated with LB film. This was accomplished by a Shimadzu UV-260 double beam spectrophotometer provided with an integrating sphere assembly. The references used were an uncoated quartz and/or SnO₂ slide depending on the substrate used.

Fluorescence spectra were measured using a PTI LS-100 luminescence spectrometer and a Perkin-Elmer 650 fluorescence spectrometer with data station. Both these instruments feature signal averaging for improved signal-to-noise ratio on weekly fluorescent samples. The slide was attached perpendicularly to a slide holder especially designed for this purpose. The excitation spectra were recorded from 410 to 470 nm and were corrected for instrument response. Corrected fluorescence spectra were measured over a range of 600–760 nm.

All spectral measurements were made on visibly dry samples within 24 h of fabrication, and samples were stored in the dark at room temperature.

Results and Discussion

Surface Pressure–Area Isotherms. The surface pressure–area isotherms of series I and series II of the model compounds (Figure 1) are shown in parts a and b of Figure 2, respectively. The observed molecular areas for monolayers of the model compounds under study, at 20 mN m⁻¹ surface pressure and 22 °C subphase temperature, are tabulated in Table 1.

The molecular areas for the compounds of series I (Figure 1), that is, P-A, P-Me-A, P-Et-A, and P-Pr-A, decreased as the chain length was increased. During the compression of the monolayer, a smooth transition from the gaseous state to the quasi-liquid state and then to a solid state was observed for all series I compounds. This suggests that these molecules undergo a slow rearrangement to adopt the most suitable orientation of the porphyrin ring, which results in the most ordered packing in the monolayer. Again from Figure 2a we can see that P-Pr-A, the compound with longest chain, has the slowest transition from the quasi-liquid state to the solid state. The fact that P-Pr-A in series I has smallest area per molecule suggests that P-Pr-A exhibits the most aggregated monolayer packing and, hence, remains in the

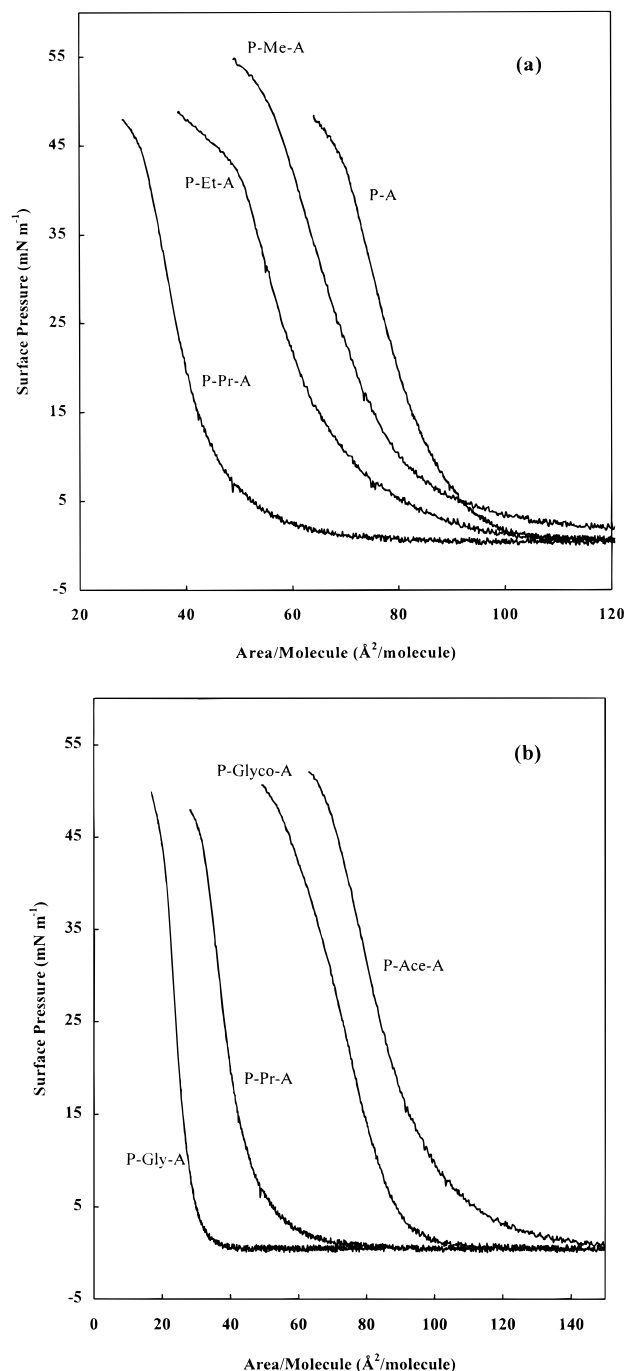


Figure 2. (a) Surface pressure–area isotherm of P-A, P-Me-A, P-Et-A, and P-Pr-A. (b) Surface pressure–area isotherm of P-Ace-A, P-Glyco-A, P-Pr-A, and P-Gly-A. Subphase was unbuffered water at 22 ± 2 °C for all the compounds.

intermediate liquid state for a longer period. In P-A, the porphyrin ring is directly attached to the carboxylic acid group, which is bound to the surface of the subphase. This gives the porphyrin ring of P-A very few degrees of freedom to arrange itself into an efficient packing arrangement in the monolayer, and so P-A occupies the largest area in the monolayer.¹⁸ Therefore in the series I compounds, an increase in chain length allows the porphyrin rings to approach closer to each other, resulting in a better packing of the molecules in the monolayer, and so a more ordered and aggregated monolayer is formed.

In the previous paragraph, we showed that the molecular area of the surfactant molecules in the monolayers is dependent on the chain length. If this holds true for all the molecules, then the molecular areas of the series II (Figure 1) compounds, that is, P-Gly-A, P-Glyco-A, P-Ace-A, and P-Pr-A would be expected to be comparable to each other, since the chain lengths are similar. From Figure 2b and Table 1, we see that the observed result is quite different from that predicted. P-Pr-A and P-Ace-A have molecular areas that differ by almost a factor of 2. This difference is probably due to the presence of the rigid $\text{-C}\equiv\text{C-}$ group in the chain of P-Ace-A. The porphyrin ring attached to the $\text{-CH}_2\text{-CH}_2\text{-}$ group in P-Pr-A is much more flexible than when it is attached to the $\text{-C}\equiv\text{C-}$ group, and thus in P-Pr-A it undergoes an ordered stacking with a considerably lower molecular area. The hypothesis that the side chain is relatively rigid in P-Ace-A is supported by the fact that its area per molecule is comparable to that of P-A.

P-Glyco-A also showed an unexpectedly high molecular area, compared to its analogue P-Gly-A. Both these molecules possess an sp^3 -hybridized central atom in the chain. The C-N-C bond angle in the $\text{sp}^3\text{-NH-}$ group is larger compared to the angle between C-O-C bonds in the $\text{sp}^3\text{-O-}$ group. This contributes to a larger bend in the side chain of P-Glyco-A, which may result in an inefficient aggregation of the porphyrin rings in the monolayer, and hence a larger molecular area was observed. Janzen^{13d} reported a similar behavior for stearic and eladic acids, which possess similar chain lengths. Eladic acid occupies a larger surface area in the monolayer than does stearic acid because of the presence of a *cis*-double bond in its long chain, which causes a bend in the chain. Due to the absence of a uniaxial chain structure, eladic acid cannot adopt a highly ordered conformation as can stearic acid and hence occupies a larger surface area in the monolayer. P-Gly-A exhibits the smallest area per molecule among all the compounds studied. This suggests the presence of the most efficient packing of molecules in this monolayer. The long glycinate chain attached to the porphyrin ring in P-Gly-A is apparently very flexible allowing the porphyrin rings to pack very closely. The zwitterionic air-water interface could also be responsible for close packing of P-Gly-A.

Absorption Spectra of Porphyrin Monolayers.

The absorption spectra of the porphyrin monolayers, which are influenced by the degree of order in the films, vary according to the nature of the side chains attached to them. Table 1 summarizes the spectral data of the monolayers of all the model compounds. Figure 3, curve 1, shows the Soret or B band region of the absorption spectrum of P-A in chloroform solution. The absorption spectra of all compounds in chloroform were almost identical. Curves 2, 3, and 4 in Figure 3 show the Soret band of the absorption spectra of the monolayer films of P-Ace-A, P-Et-A, and P-Gly-A, respectively.

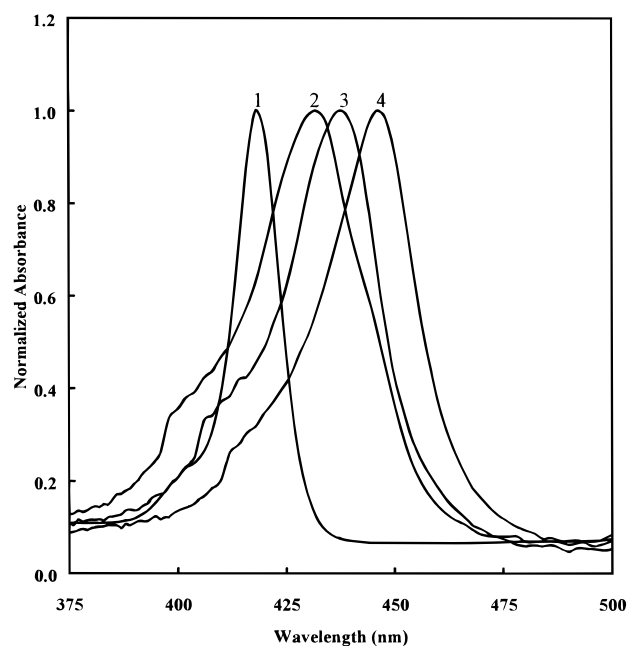


Figure 3. Absorption spectra: (1) P-A in CHCl_3 solution, 1 cm cell; (2) P-Ace-A monolayer; (3) P-Et-A monolayer; (4) P-Gly-A monolayer. Spectra are normalized to their λ_{max} . See Table 1 for spectral data.

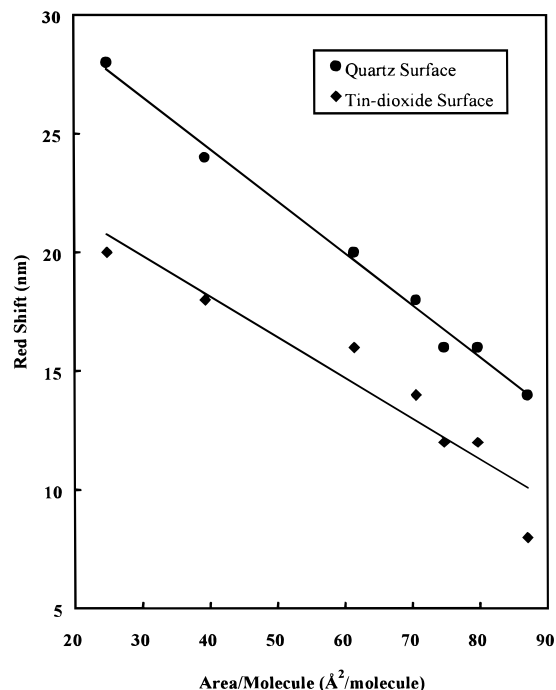


Figure 4. Plots of the red shift of the Soret bands versus the area per molecule.

and P-Gly-A, respectively. All the absorption bands are broadened in the monolayer state relative to the solution and the Soret bands are red shifted. There is an excellent linear correlation (see Table 1 and the upper data set in Figure 4) between the red shift of the Soret band on quartz compared to that of P-A in chloroform solution. Thus we can conclude confidently that an increased red-shift arises from a closer packing of the porphyrins in the monolayer. Bardwell et al.^{13b,c} and Dick et al.¹⁸ have reported a similar red-shift of the Soret band associated with aggregate formation in monolayers.

The trend of the spectral properties of the model porphyrin compounds was not changed substantially by

(18) Dick, H. A.; Bolton, J. R.; Picard, G.; Munger, G.; Leblanc, R. M. *Langmuir* **1988**, *4*, 133.

changing the substrate from quartz to a SnO_2 -coated glass plate (see Table 1 and the lower data set in Figure 4), except that the red shifts are 4–8 nm less than those on quartz. This smaller red shift can be explained by different surface textures of the two substrates. When the smooth surface of the quartz is substituted with the rough SnO_2 surface, the order of the monolayers gets disturbed and the aggregation of the molecules is diminished. Hence, it was concluded that except for monolayer disorder, no additional effect is experienced by the porphyrin compounds with different linkages when deposited onto a SnO_2 surface.

Spectral shifts, such as those shown here, are similar to those seen in porphyrin^{19–22} or phthalocyanine^{23–25} dimers or oligomers and in thin films^{12,17} and monolayers.^{13c,14,15a,c} In most of these cases, a blue-shift instead of a red-shift of the Soret band was observed. Recently, Whitten et al.²⁶ have reported a similar blue-shift aggregate formation with a variety of squaraine^{26a,b} and fatty acid derivatives of diphenylpolyenes.^{26c,d} In contrast to these results, Bardwell et al.^{13b,c} and Dick et al.¹⁸ observed a consistent red shift, compared to the corresponding monomeric species in the solution, with increasing aggregation of the tritolylporphyrin chromophores. Similar bathochromic shifts were reported for face-to-face double-decker and triple-decker cerium octaethylporphyrin^{27a} and vanadyl phthalocyanine^{27b} aggregates. Similarly, in the present study, by allowing the tritolylporphyrin chromophore to form an aggregate in a close to face-to-face fashion, we observed a substantial red-shift, which is directly proportional to the degree of molecular aggregation.

The variety of results observed for different chromophores may arise from variations in the nature of the film and nature of the chromophores and can be explained in terms of the molecular exciton model²⁸ for excited-state resonance interactions in weakly coupled electronic systems. The system of study in all the *blue-shifted* aggregates reported earlier were varied from spin-coated¹⁶ and sublimed^{16,17} thin films to Langmuir–Blodgett multilayers.²⁶ In a multilayer, the surrounding environment

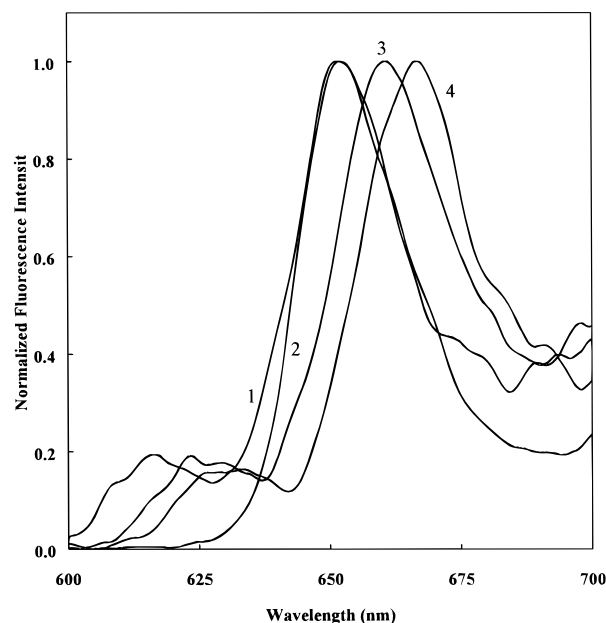


Figure 5. Corrected fluorescence spectra. Numbers correspond to their samples shown in Figure 4. The samples were excited at the peak of the B band. Spectra are normalized to their maximum fluorescence intensity at λ_f .

of a chromophore is very similar to that of a single crystal and very different from that in a monolayer because of the presence of an effective interlayer interaction ($\pi-\pi^*$), which in turn may reflect the change in environment on going from monomer to multimer. In our system, probably the absence of interlayer interaction ($\pi-\pi^*$) is causing a bathochromic shift.^{26d} A similar explanation for the red-shift in vanadyl phthalocyanine aggregates was given by Law^{27b} on the basis of theoretical calculations.^{27c}

In the monolayers of all compounds, the full width at half-maximum (fwhm) of the Soret band became narrower as the degree of order increased and is close to that observed for the face-to-face zinc porphyrin dimer described by Leighton et al.,²¹ suggesting that its local environment is quite well-ordered.²⁹

The pattern of spectral shifts that emerges in the progression from curves 1 to 4 in Figure 3 and along the columns of the λ_{max} values in Table 1 can be summarized as follows: the Soret band is progressively red-shifted as the degree of order of porphyrin rings increases in the monolayer films; the red shift is consistently smaller when the surface texture of the substrate was changed from smooth to a rough one. From these patterns and from the surface pressure–area isotherm data given earlier, we conclude that these spectral shifts are an indication of the increasing degree of order along this progression.

Fluorescence Spectra and Fluorescence Quantum Yields (ϕ_f). Figure 5 shows the fluorescence spectra of the same solutions and monolayer films as those in Figure 3. The fluorescence spectrum of P–A in chloroform solution (curve 1) was taken in a $1.00 \times 1.00 \text{ cm}^2$ cell using the same front face apparatus and conditions as those for the monolayers. Table 1 shows the fluorescence characteristics for all the model compounds on different substrates. The fluorescence fluorescence wavelengths (λ_f) also followed the trend of red shift on both the substrates, as was observed for their Soret bands, except that the shifts are much less than those for the Soret band, and there is no significant difference between the

(19) (a) Chang, C. K. *J. Heterocycl. Chem.* **1977**, *14*, 1285. (b) Chang, C. K. *Adv. Chem. Ser.* **1979**, No. 173, 162.

(20) Collman, J. P.; Anson, F. C.; Barnes, C. E.; Bencosme, C. S.; Geiger, T.; Evitt, E. R.; Kreh, R. P.; Meier, K.; Pettman, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 2694 and references therein.

(21) (a) Leighton, P.; Cowan, J. A.; Abraham, R. J.; Sanders, J. K. M. *J. Org. Chem.* **1988**, *53*, 733. (b) Tollin, G.; Salamon, Z. *Photochem. Photobiol.* **1993**, *58*, 730.

(22) Boxer, S. G. *Biochim. Biophys. Acta* **1983**, *726*, 265 and references therein.

(23) Ciliberto, E.; Doris, K. A.; Pietro, W. J.; Reisner, G. M.; Ellis, D. E.; Fragala, I.; Herbststein, F. H.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7748.

(24) Kobayashi, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1987**, *109*, 7433.

(25) (a) Kobayashi, N.; Lam, H.; Nevin, W. A.; Janda, P.; Leznoff, C. C.; Koyama, T.; Monden, A.; Shirai, H. *J. Am. Chem. Soc.* **1994**, *116*, 879. (b) Fujiki, M.; Kurihara, T. *J. Phys. Chem.* **1988**, *92*, 1281. (c) Chau, L. K.; Osburn, E. J.; Armstrong, N. R.; O'Brien, D. F.; Parkinson, B. A. *Langmuir* **1994**, *10*, 351.

(26) (a) Kim, Y. S.; Liang, K.; Law, K. Y.; Whitten, D. G. *J. Phys. Chem.* **1994**, *98*, 984. (b) Chen, H.; Herkstroeter, W. G.; Perlstein, J.; Law, K. Y.; Whitten, D. G. *J. Phys. Chem.* **1994**, *98*, 5138. (c) Spooner, S. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1994**, *116*, 1240. (d) Song, X.; Geiger, C.; Furman, I.; Whitten, D. G. *J. Am. Chem. Soc.* **1994**, *116*, 4103.

(27) (a) Buchler, J. W.; Ciani, A. D.; Fischer, J.; Kihn-Botulinski, M.; Paulus, H.; Weiss, R. *J. Am. Chem. Soc.* **1986**, *108*, 3652. (b) Law, K. Y. *J. Phys. Chem.* **1988**, *92*, 4226. (c) Schaffer, A. M.; Gouterman, M.; Davidson, E. R. *Theor. Chim. Acta* **1973**, *30*, 9.

(28) (a) Davydov, A. S. *Theory of Molecular Excitons*, translated by Dresner, S. B.; Plenum Press: New York, 1971. (b) Yan, X.; Holten, D. *J. Phys. Chem.* **1988**, *92*, 409. (c) Kasha, M. In *Spectroscopy of the Excited State*; Di Bartolo, B., ed.; Plenum Press: New York, 1976.

(29) See, for example: Suto, S.; Uchida, W.; Yashima, M.; Goto, T. *Phys. Rev. B* **1987**, *35*, 4393.

Table 2. Comparison of Surface Pressure–Area Isotherm and Fluorescence Emission Quantum Yield (ϕ_f) on Different Substrates and Estimated Rate of Electron Injection (k_{et}) in SnO₂ for Porphyrin Model Compounds^a

compound	area/ molecule (Å ² molecule ⁻¹)	ϕ_f (rel) ^b quartz	ϕ_f (rel) ^b SnO ₂	$\Delta\phi_f$ (rel) ^c	$k_{et} \times 10^7$ (s ⁻¹)
P–A	79.7 ± 0.5	0.417 ± 0.001	0.388 ± 0.001	0.029	1.5
P–Me–A	70.6 ± 0.4	0.363 ± 0.004	0.332 ± 0.006	0.031	2.1
P–Et–A	61.4 ± 0.4	0.307 ± 0.007	0.282 ± 0.006	0.025	1.2
P–Pr–A	39.3 ± 0.3	0.264 ± 0.002	0.202 ± 0.002	0.062	6.9
P–Gly–A	24.8 ± 0.3	0.238 ± 0.003	0.167 ± 0.004	0.071	10.9
P–Glyco–A	74.7 ± 0.3	0.221 ± 0.007	0.380 ± 0.004	0.159	0
P–Ace–A	87.0 ± 0.4	0.383 ± 0.003	0.173 ± 0.006	0.210	20.4

^a Measurements carried out at 22 ± 2 °C. ^b All ϕ_f were calculated relative to P–A solution³⁰ in CH₂Cl₂. ^c $\Delta\phi_f = \phi_f$ (rel) (quartz) – ϕ_f (rel) (SnO₂).

red shifts on quartz versus those on SnO₂. A measure of the relative quantum yield of fluorescence $\phi_{f,rel}$ of the monolayer films relative to the known quantum yield of P–A in dichloromethane solution ($\phi_f = 0.13 \pm 0.1$)³⁰ was then obtained by comparing the integrated fluorescence intensities of the monolayers of all the model porphyrin compounds to that of P–A in dichloromethane solution.

The fluorescence spectra shown in Figure 5 were corrected for the instrumental response and were normalized at the Soret band to the absorbance of the corresponding samples. Since the peak absorbances of these monolayer films (and those to be discussed below) are typically >0.05, the ratio of the amount of light absorbed by a reference to that absorbed by a sample is given by the Beer–Lambert law expression³¹

$$N = (1 - 10^{-A_{i,r}})/(1 - 10^{-A_{i,s}}) \quad (1)$$

where $A_{i,r}$ and $A_{i,s}$ are the measured absorbances at wavelength λ of the reference and sample spectra, respectively. N is needed to compare quantitatively the fluorescence from different monolayer films of the absorption spectrum with the corresponding fluorescence spectrum. All samples were excited at the peak of the Soret band. Table 2 includes the relative fluorescence quantum yields for all the monolayers on quartz and SnO₂ surfaces and the surface pressure–area isotherms. The fluorescence of a porphyrin dimer, solid film or monolayers, is usually assumed^{19,22} to be quenched relative to that of the monomer. Although quenching is a common result of interchromophore interactions,^{12,13c,15a,24} there have been several reported systems where a dimer is either unquenched^{22,26c} or actually emits more strongly²² than the constituent monomers. In the solid state, for example, ϕ_f for naphthalene single crystals is equal to its ϕ_f in solution,^{8b} while for anthracene single crystals the ϕ_f is increased relative to that in solution.^{8b,32,33} Quenching seems to be the rule for any system involving a flexible linkage between the chromophores.²² This can be understood as contributing to an increase in the number of available vibrational modes leading to an enhanced rate of internal conversion. Orientational disorder in the solid state can presumably have a similar effect.

The results in Figure 5 and Table 2 show that increasing the order of the monolayer film leads to a large decrease in the fluorescence efficiency. On the quartz surface, the least ordered P–A monolayer film fluoresces ~43% more efficiently than the most ordered P–Gly–A monolayer

film and only ~8% more efficiently than the P–Ace–A monolayer film. The P–Ace–A film has a quantum yield for fluorescence comparable to that of the solution species (curve 1, Figure 5). Both P–Ace–A and P–Glyco–A possess a comparable surface pressure–area isotherm, but a difference of almost 57% in fluorescence yield was observed between them. This may be due to the lone pair of electrons on the central oxygen atom of P–Glyco–A, which enhances the deactivation of the excited state. Because of differences in reflection effects and film thickness (~1 cm for solution, versus a few micrometers for the monolayer films), it is difficult to make an exact comparison of quantum yields. However, in all monolayer films of model porphyrin compounds examined, a decrease in fluorescence efficiency with increased order of the film (as seen by a red shift and broadening of the Soret band) has always been observed. Thus, fluorescence quenching of monolayer films, at least in the case of tritolylporphyrins, is not a necessarily a consequence of but rather is a function of the disordered environment.

Semiconductor surfaces are known to quench the fluorescence of porphyrins.²⁹ A quenching of 5–15% for the porphyrins on indium titanium oxide (ITO) substrate has been reported.²⁹ SnO₂ substrates were used because of our ultimate goal to investigate the photoelectron-transfer properties of these films. A strong influence of the SnO₂ surface on the fluorescence yields was observed (Table 2). All the monolayer films, except that of P–Glyco–A, showed a quenching of the order of 7–55% on changing the substrate from quartz to SnO₂. A steady increase in quenching was observed by increasing the degree of order of the porphyrin rings in the monolayer films. This may be the consequence of increased electron injection behavior of the long chain porphyrins, which leads to an enhanced deactivation of the singlet (S_1) excited state. As discussed earlier, the SnO₂ surface results in more disorder of the porphyrin monolayer films due to its rough surface, and so less quenching and a higher fluorescence yield are expected. Hence, it may be concluded that SnO₂ contributes to considerable quenching by the electron injection process, which overcomes the decreasing quenching effect by the increasing film disorder. For the monolayer film of P–Glyco–A, no quenching was observed, rather an increase in fluorescence yield was recorded. This could be due to its inability to carry out an efficient electron injection, and an increased fluorescence yield is contributed by the increased disorder of the monolayer film on SnO₂ surface. As the deactivation process on SnO₂ surface is a combined effect of both quenching and the electron injection process, we were not able to account for them separately. Thus, we conclude that the additional fluorescence quenching on a SnO₂ surface arises primarily from the electron injection process

(30) Siemiarczuk, A.; McIntosh, A. R.; Ho, T. F.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 7224.

(31) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968.

(32) Wright, G. T. *Proc. Phys. Soc., Ser. B* **1955**, *68*, 241.

(33) Jortner, J.; Bixon, M. *Mol. Cryst. Liq. Cryst.* **1969**, *9*, 213.

from the excited state of porphyrin to the conduction band of the SnO_2 semiconductor.

As discussed in the previous paragraph, a substantial increase in the fluorescence yield ($\sim 50\%$) was observed for P-Glyco-A, due to its inability to carry out an efficient electron injection to the semiconductor and increased disorder of the monolayer film on SnO_2 surface. Assuming that electron injection is not significant for the monolayer of P-Glyco-A, we can say that all the fluorescence quenching is contributed by aggregation only. If the other model compounds also do not undergo an electron injection mediated deactivation of the excited state, then they are expected to show an increased fluorescence yield on the SnO_2 surface, almost to the extent of the increase that was observed for P-Glyco-A. As no such increase in the fluorescence yield is observed, we assume that the excited singlet state deactivation in these compounds arises from an electron injection process. Hence, using P-Glyco-A as a reference, in which the rate constant of electron injection has been assumed to be zero ($k_{\text{et}} \approx 0$), k_{et} for the other model compounds can be estimated.

The estimated k_{et} values for all the model compounds are tabulated in Table 2. A general increase in the electron injection rate was observed as one goes from P-A to P-Pr-A, which indicates that an increased alkane chain contributes to an enhanced electron transfer. An unusual result was observed for P-Et-A, as it does not follow the increasing trend of the compounds with increasing alkane chain. An increasing k_{et} clearly indicates that as we increase the length of the alkane chain, electron transfer is facilitated. This may be due to the presence of some kind of interaction between the orbitals of neighboring atoms, which helps in an enhanced electron tunneling, resulting in increased k_{et} . For P-Gly-A and P-Ace-A a very high electron-transfer rate was observed. This must be due to their electron-rich chains, which facilitates the electron transfer. Hence from the trend of k_{et} for all the model compounds, it is obvious that through bond electron tunneling is a leading cause of the deactivation of the excited state for the compounds with electron-rich linkage systems.

Conclusions

The model porphyrin compounds examined here exhibit a significant variation in their surface-pressure-area isotherms, which appears to arise from the nature of the different side chains attached to the porphyrin ring. The compounds with longer side chains were found to possess a smaller area per molecule, as compared to those with

shorter chains. This is perhaps due to the presence of greater conformational flexibility of the porphyrin ring, which allows them to compact into a tight arrangement in the monolayer and hence occupy a smaller area. Thus P-A, where there is no side chain, possesses a higher surface area per molecule, and P-Gly-A, where the side chain is considerably longer, occupies a very small surface area.

The nature of the packing of these porphyrin compounds is also reflected in the absorption characteristics of their monolayers deposited onto quartz and SnO_2 surfaces, respectively. An increasing red shift in λ_{max} was observed, as the attached chain length was increased, which probably arises from the increasing compactness of the porphyrin structure in the monolayer. With change of the substrate from quartz to SnO_2 , a blue shift was observed for λ_{max} of the monolayers of all the compounds. This probably arises from the rough surface of SnO_2 , on which the compounds cannot make a perfectly compact matrix as they can do on the smooth quartz surface. The more "open" monolayer on SnO_2 thus leads to a blue shift of λ_{max} for monolayers on SnO_2 , as compared to λ_{max} on a quartz surface.

The fluorescence quantum yield data indicate a considerable quenching of the excited state for all the monolayers on a quartz surface. The degree of quenching was found to be directly related to the extent of molecular aggregation of the molecules in the monolayer. Hence, compounds with a long side chain, such as P-Pr-A, show a very high fluorescence quenching on a quartz surface. On a SnO_2 surface, a smaller quenching effect was expected for all the compounds, as the molecular packing is not as good as it is on a quartz surface. Instead, an enhanced quenching was observed. We have postulated that this is due to the occurrence of isoenergetic electron transfer from the excited singlet state of the porphyrin to the conduction band of the semiconductor. This process serves as an additional deactivation pathway of the excited singlet state and results in an enhanced fluorescence quenching. P-Ace-A and P-Gly-A showed the maximum quenching due to the presence of an electron-rich chain system, which resulted in a higher isoenergetic electron transfer and more quenching of the excited state for these molecules.

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