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Tetraneopentoxypthalocyanine Langmuir-Blodgett Films:
Spectroscopy at the Air/Water Interface

By

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in

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Tetraneopentoxypthalocyanine Langmuir-Blodgett Films: Spectroscopy
at the Air/Water Interface

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Abstract

A series of tetraneopentoxypthalocyanine (Ag^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+}) compounds are used in the study of Langmuir monolayers at the air/water interface. Isotherm measurements and absorption spectra of the free standing monolayers are presented to discuss the mechanism of monolayer formation with tetraneopentoxypthalocyanines. The MTNPc species form self-assembled domains when the coverage is less than 1 monolayer. Combining exciton coupling theory with the isotherm measurement provides a consistent representation of the orientation angle of the MTNPc units at the air/water interface.

Introduction

Organized monolayers are of very interest for fundamental and technological reasons.¹⁻³ Conventional studies with Langmuir Blodgett (LB) monolayers have focused on amphiphiles with structural partitioning of their hydrophilic/hydrophobic properties. According to the LB technique, amphiphilic compounds are spread at the air/water interface and a monomolecular layer is formed. Upon compression of the monolayer, the molecules are oriented at the interface, with the hydrophilic component on the water surface, and the hydrophobic component sticking out in the air. However, in recent years molecules with completely different structure such as porphyrins,⁴ phthalocyanines,⁵ oligothiophenes⁶ and polycyclic aromatic quinones⁷ have been shown to form organized monolayers. These compounds have become increasingly important because of their improved thermal and mechanical stability, chemical reactivity and interesting physical characteristics, but their mechanism of monolayer formation is still not clear.⁷⁻¹⁰ They are not amphiphiles in the traditional sense, and therefore do not have a separate hydrophobic group attached to a polar hydrophilic region. We report here that molecular aggregation plays an important role in monolayer formation with tetraneopentoxypthalocyanines in these LB experiments.

Since Roberts¹¹ et al. first demonstrated that a tetrasubstituted phthalocyanine can be deposited as a thin film using the LB method, there have been many reports^{5,8,12-18} dealing with phthalocyanine monolayers with varying number and nature of phthalocyanine ring peripheral substituents. Several techniques have been used to characterize the structures of the transferred phthalocyanine monolayers. These include ESR,¹⁸ UV-VIS, X-Ray,^{5a} electron diffraction and high-resolution electron microscopy.¹⁰ However, little attention has been paid to the characteristics of the initial formation of

the phthalocyanine monolayers. Study of the free standing film at the air/water interface, prior to transfer to a substrate, provides information concerning film formation.

Phthalocyanines are well known to aggregate as their solution becomes more concentrated.¹⁹ In the limit, phthalocyanines become totally aggregated in the solid state.²⁰ Molecular aggregation results in characteristic changes in the phthalocyanine absorption spectra.²¹ Exciton coupling theory has been successfully used to explain the electronic absorption spectrum change upon molecular aggregation.²² The theory predicts that the energy shift due to molecular aggregation depends on the angle at which the molecules pack.²³ In forming sub- and monolayers on an LB trough interface, phthalocyanine molecules have only two dimensional degrees of freedom (translational movement); therefore, under these conditions, phthalocyanine molecules may have relatively simple geometric orientations toward one another. Since exciton coupling theory is largely based on the treatment of molecular geometry, a combination of the isotherm and spectroscopic measurements using exciton coupling theory can usefully be applied to LB film study.

Experimental Section

The general procedures for synthesizing metallated tetraneopentoxypthalocyanines (TNPc) have been previously described.²⁴⁻²⁶ For example, NiTNPc was synthesized by heating metal free tetraneopentoxypthalocyanine (H_2 TNPc) (0.040 g) with a large excess of $Ni(OAc)_2$ in a mixture of dimethylformamide (DMF) and 2-N, N'-dimethylaminoethanol (1:2, 3 ml) at about 120° C for 17 hr under a nitrogen atmosphere. Drops of the reaction mixture were taken from time to time to monitor the electronic absorption at 707 nm, due to H_2 TNPc, relative to that at 672 nm, due to NiTNPc. The reaction was stopped when the 707 nm peak had disappeared. The prod-

uct was then purified with flash chromatography through a silica column, with toluene as eluting solvent. The species Fe(II)Pc(SP4C)_2 ($\text{SP4C} = 4\text{-stearylpyridine}$) was synthesized by reaction of iron(II) phthalocyanine with 4-stearylpyridine in chlorobenzene at $160\text{-}180^\circ\text{C}$ for 6.5 hr under nitrogen. Details of characterization and properties of this material will appear else where.²⁷

A home-made Langmuir-Blodgett trough, designed according to information supplied by Van Ryswyk et al,²⁸ was used in the measurements of the surface pressure-area (π -A) isotherm of the monolayers at the air/water interface. The water subphase was double distilled over KMnO_4 and passed through a Barnstead organic removal cartridge and two Barnstead mixed resin ultrapure cartridges (pH 6). $0.1\text{ M Na}_2\text{SO}_4$ was added into the subphase for experiments to study electrolyte effects upon Langmuir monolayers (pH 5). The spreading solutions were usually made with CH_2Cl_2 or toluene with concentrations from 1.0×10^{-5} to $1.0 \times 10^{-4}\text{ M}$ depending on individual experiment. A monolayer was generally compressed at a speed of $1.5\text{ \AA}^2/\text{molecule}/\text{min}$ after the film was allowed time (15-20 min) for self-reorganization and equilibration. Surface pressure was measured using a filter paper Wilhelmy plate as pressure sensor.²⁹

The electronic absorption spectra of solutions were recorded with a Cary 2415 spectrometer. The absorption spectra of monolayers were measured at the air/water interface with a Guided Wave Inc. Model 100-20 optical waveguide spectrum analyzer using a WW100 fiber optic probe. Scheme 1 shows an apparatus configuration for absorption spectrum measurements of the monolayers. The spectrum was taken by light passing through the monolayer with a mirror placed about 1 mm under the water surface reflecting the signal vertically back, via a second pass through the monolayer, to the fiber optic probe.³⁰

Results and discussion

Spectra of MTNPc in organic solvents. The absorption spectra of dilute MTNPc solutions in organic solvent usually consist of a strong narrow $\pi-\pi^*$ absorption between 650 and 710 nm and a weaker vibrationally coupled satellite band at 60 to 70 nm shorter wavelength (Table I). In a progression of spectra from that of lower concentration to higher concentration, a second broader and partially resolved $\pi-\pi^*$ absorption appears with increasing intensity between the first $\pi-\pi^*$ absorption and satellite band. This growth in absorption near 620 nm is typical¹⁹ of phthalocyanine aggregation. The blue shifted Q band ($\pi-\pi^*$) absorption with a broad natural bandwidth is a consequence of molecular association with a cofacial phthalocyanine ring orientation and depends upon the inter-phthalocyanine ring distance and the angle of orientation.

Spectra of MTNPc as spread films (Langmuir monolayers). By dropping a small volume of solution of MTNPc in CH_2Cl_2 onto the subphase surface in the LB trough, the MTNPc formed a monolayer at the air/subphase interface after the volatile CH_2Cl_2 evaporated. An isotherm was recorded by measuring the pressure of the monolayer and the area of the film when the film standing on the subphase surface was compressed by a moving barrier (Figure 1). By extrapolating the upswing part of the isotherm to zero monolayer pressure, the area occupied by a molecule at monolayer coverage could be determined, namely:

68 Å² for Ag(II)TNPc,

71 Å² for Ni(II)TNPc,

87 Å² for Zn(II)TNPc,

120 Å² for Co(II)TNPc.

These values are independent of spreading solvent (toluene or CH_2Cl_2). The

value for Co(II)TNPc is much higher than those of other MTNPc species, although it is still smaller than that of the planar area of tetraneopentoxypthalocyanine ring, estimated to be about $235 \text{ \AA}^2$ by use of a molecular model. Since the measured area occupied by a molecule at monolayer coverage is much smaller than the planar area of the phthalocyanine ring, the phthalocyanine molecules in the monolayer are not sitting flat on the subphase surface, but rather subtend a certain angle to the surface with the molecular planes of the phthalocyanines face to face with each other. The cofacial arrangement arises through preferential molecular aggregation via phthalocyanine ring-ring π -interaction (vide infra).

The electronic spectra (Figures 2, 3) of the monolayers were recorded using the method depicted in Scheme 1. Spectra were recorded over a period of time from the initial film formation to monitor for possible time related changes (e.g. slow re-organisation processes, or oxidation or hydrolysis processes). The spectra of the AgTNPc and NiTNPc were constant from the initial measurement. However, the absorption spectra of CoTNPc and ZnTNPc monolayers developed as a function of time. The spectra measured immediately after spreading the solutions had two broad absorption peaks around 620 and 680 nm. The peak intensities around 620 nm decreased, while the peak intensities around 680 nm increased gradually (Figure 3). After about 15 minutes the spectrum reached its constant equilibrium appearance.

The absorption spectra were also monitored as the monolayers were compressed. Interestingly, for all MTNPc studied, the absorption spectra did not change as the monolayers were compressed once the monolayer was at equilibrium. A closely related experiment involved monitoring the absorption spectra of films of submonolayer coverage at the air/water interface at different locations. For example, the absorption peak

intensities at 620 nm of the absorption spectrum of a NiTNPc surface at 0.5 monolayer coverage were measured at different locations. There were, in fact, two levels of absorption peak intensity, at some locations no absorption could be detected, while at other locations, the same absorption intensity as the full monolayer, was detected. This observation indicated that molecules were not uniformly distributed at the air/water interface, rather they self-assembled and formed many islands at surface coverages less than unity. This is an important observation, since it infers that each molecule experiences the same degree of exciton coupling irrespective of the degree of compression, in other words, the phthalocyanines formed self-assembled oriented domains.³¹ Similar results on monolayers of porphyrin esters have been reported³² and TEM results on Langmuir films containing tetrakis(cumylphenoxy)phthalocyanines support our observation.³³ This is different from monolayer formation with conventional amphiphilic compounds in which the compression is needed to reorient the molecules at the air/water interface. This behavior was found to be independent of whether chloroform or toluene was used as spreading solvent, and of whether the subphase contained electrolyte (0.1 M $\text{Na}_2\text{S}_2\text{O}_4$) or not.

Control experiments with Fe(II)Pc(SP4C)_2 . (SP4C = 4-stearylpyridine) The aggregation of phthalocyanines can be effectively prevented by blocking the metal center. The iron center of Fe(II)Pc(SP4C)_2 is coordinated by two 4-stearylpyridine ligands.²⁷ Data for a Fe(II)Pc(SP4C)_2 monolayer are shown in Figure 4 which illustrates the isotherm and the absorption spectrum, showing a relatively narrow Q band which is indicative of only unaggregated species in the monolayers. The absorption peak at 680 nm was not shifted either by monolayer compression or by changing the spreading solution concentration. In this case it is the stearylpyridine ligands which cause the organization but restrain the phthalocyanine units to be too far apart to display exciton

coupling.

Nature of Canting Angle. The MTNPc species have highly hydrophobic peripheral substituent groups while the complexed metal ion center is much more hydrophilic. There will be some balance between the forces holding the phthalocyanine units close together, and the interaction of the metal center with the water surface. The assembled domains assuming monolayer coverage are canted over the water surface by an angle which can be estimated from the measured area of a molecule at monolayer coverage via the following equation, with results listed in Table II:

$$\theta = \arccos \frac{\text{Area occupied by a molecule at monolayer coverage}}{\text{Planar area of phthalocyanine ring}}$$

These values should be regarded as averages in the sense that the molecules probably adopt a range of similar canting angles from one domain to the next.

It should also be possible to use the electronic spectrum of the monolayer as an independent measure of the canting angle, at least in a qualitative sense. Aggregated phthalocyanine molecules at the air/water interface can be considered as a simple linear chain or array of molecules forming a thread-like polymer.²³ This linear chain polymer model offers the simplest relationship between the molecular aggregation of phthalocyanine and exciton interaction energy and band structure. Since the molecular components in the long chain polymers are translationally equivalent and the single phthalocyanine molecule has a planar structure, the aggregated phthalocyanine complexes can be visualized as a pack of cards or parallel chain polymer as shown in scheme 2a. The angle θ is that between the chain axis and the molecular plane of the phthalocyanine, and can have values from 0 to $\pi/2$. The energies of allowed exciton states, E_k , are related to θ by²³

$$E_k = E^0 + A_k(1 - 3\cos^2\theta)$$

where E^0 denotes the energy of the first excited singlet state of the free or isolated component molecule of the aggregate, and $A_k = M^2/r^3$, is directly proportional to the square of the transition moment and inversely proportional to the cube of the distance between two adjacent molecules.

The selection rules for absorption spectra for the linear chain polymers allow transitions from the ground state to the excited states of higher energy. The energies involved in the transitions are directly proportional to $(1 - 3\cos^2\theta)$. The model (Scheme 2b) predicts a red shift if θ is less than 54.7° , and a blue shift if θ exceeds 54.7° , relative to the monomeric molecular spectrum. An important feature of this model is that for $\theta = 54.7^\circ$, the interaction energy is zero and the absorption peak energy remains unshifted. A blue shift in absorption seen for both AgTNPc and NiTNPc is consistent with their canting angle as determined by the pressure isotherm measurement (Table II). The magnitude of the shift is rather less than that calculated with the appropriate canting angle and assuming a short (minimum) contact distance of about $3.6 \text{ \AA}$ but would be fitted with a slightly longer inter-phthalocyanine distance of about $4.7 \text{ \AA}$. The interaction between the metal center of the phthalocyanine and the water surface may cause an increase in the contact distance of the phthalocyanine molecules. In addition, the distance between adjacent molecules along the stacking direction is larger than the perpendicular distance. It is the distance along the stacking direction which more effectively influences the π orbital overlap between two adjacent phthalocyanine molecules. The large neopentoxyl groups on the phthalocyanine ring could also keep the adjacent phthalocyanine molecules further away. Interestingly the CoTNPc molecules show a canting angle of 59° very close to that of the (magic) angle 54.7° . In agreement, there is essentially no shift in the Q band maximum between the LB film absorption, and the solution absorption (Table I, II). Nevertheless the CoTNPc must be heavily

aggregated since the Q band absorption is still very broad and CoTNPc is known to aggregate markedly in solution.¹⁹

Thus AgTNPc, NiTNPc and CoTNPc show isotherm and spectroscopic data which are consistent with the linear chain model proposed. On the other hand a ZnTNPc molecule occupies $87 \text{ \AA}^2$ and the nominal value of θ is 68° , yet no Q band blue shift was observed for ZnTNPc monolayers at equilibrium. Indeed the ZnTNPc species, at equilibrium, exhibits behaviour very similar to that of the non-aggregated Fe(II)Pc(SP4C)₂ control molecule which specifically shows an unshifted (from solution monomer spectrum) and narrow Q band absorption. Indeed the key lies in this narrow Q band absorption unlike that of the CoTNPc LB monolayer. Zinc phthalocyanine species are known to bind one water molecule strongly.³⁴ Moreover a freshly spread ZnTNPc LB film shows the broad Q band and the 620 nm blue shifted absorption. With time, a water molecule must percolate through the stack, forming (H₂O)ZnTNPc, separating the molecules, reducing the degree of interaction (decreasing the magnitude of A_λ (eqn.2)), thereby narrowing the Q band and shifting the maximum back to the red (unshifted).

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Figure Captions

Figure 1. Surface pressure-molecular area isotherms for MTNPc monolayers. (a) AgTNPc; (b) NiTNPc; (c) ZnTNPc; (d) CoTNPc.

Figure 2. Absorption spectra of MTNPc monolayers at equilibrium. (a) AgTNPc; (b) NiTNPc; (c) ZnTNPc; (d) CoTNPc.

Figure 3. Development of CoTNPc absorption spectra with time. The spectra were measured at several minute intervals after the spreading solution was dropped on the water surface. (a) 2.5 minutes; (b) 5 minutes; (c) 7.5 minutes; (d) 15 minutes.

Figure 4. (a) Surface pressure-molecular area isotherm of $\text{FePc}(\text{SP4C})_2$ monolayer; (b) Absorption spectrum from $\text{FePc}(\text{SP4C})_2$ monolayer at monolayer coverage.

Table I Electronic Absorption Spectra Data (Q-band) of MTNPc in organic solvents

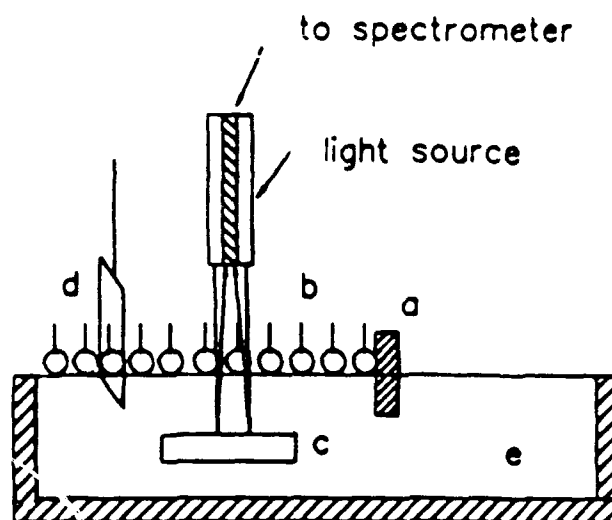
Species	λ_{max} , nm ($\epsilon/10^4$ M ⁻¹ cm ⁻¹)
AgTNPc ^(a)	618(2.12), 685(7.61)
NiTNPc ^(b)	606(2.90), 672(9.26)
ZnTNPc ^(c)	614(4.60), 680(5.09)
CoTNPc ^(d)	614(2.42), 680(8.38)

(a) Fu, G. Y.; Fu, Y. S.; Jayaraj, K.; Lever, A. B. P. *Inorg. Chem.* 1990, 29, 4090, in DCB solution; (b) This work, 1.0×10^{-5} M in CH₂Cl₂; (c) Leznoff, C. C.; Marcuccio, S. M.; Greenberg, S.; Lever, A. B. P.; Tomer, K. B. *Can. J. Chem.* 1985, 63, 623, in CH₂Cl₂; (d) Bernstein, P. A.; Lever, A. B. P. *Inorg. Chem.* 1990, 29, 608, 8.65×10^{-5} M in DCB.

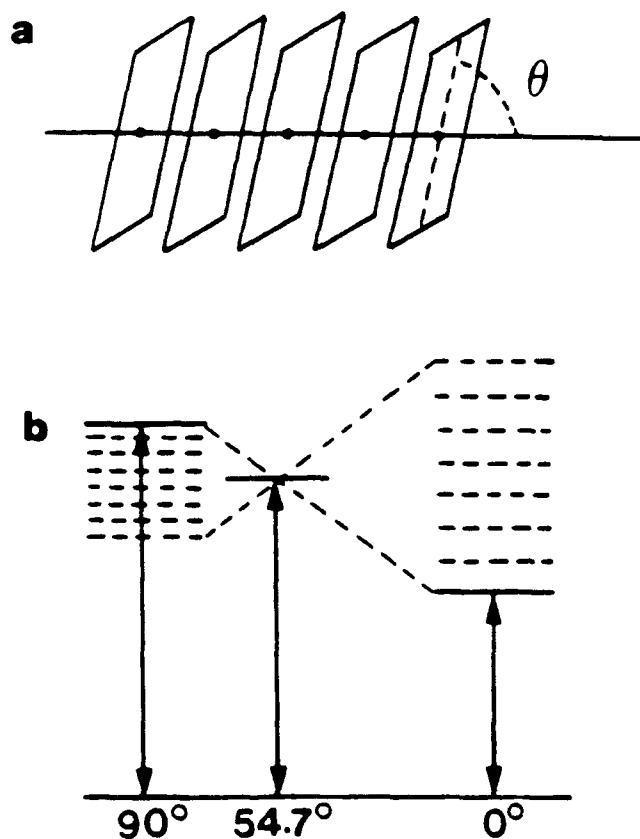
Table II Electronic Absorption Spectra and Isotherm Measurement Results of MTNPc Monolayers

<i>Species</i>	<i>Electronic absorption maxima</i>	<i>Area occupied by a molecule</i>	<i>Calculated θ (a)</i>
<i>AgTNPc</i>	<i>626 nm</i>	<i>68 Å²</i>	<i>73°</i>
<i>NiTNPc</i>	<i>622 nm</i>	<i>71 Å²</i>	<i>72°</i>
<i>ZnTNPc</i>	<i>690 nm</i>	<i>87 Å²</i>	<i>68°</i>
<i>CoTNPc</i>	<i>685 nm</i>	<i>120 Å²</i>	<i>59°</i>

(a) See text for equation.



Scheme 1. Apparatus configuration (not to scale) for absorption spectrum measurements of the monolayers. (a) moving barrier; (b) monolayer; (c) mirror; (d) filter paper Wilhelmy plate; (e) water subphase.



Scheme 2. (a) Molecule-packing model for aggregated phthalocyanine complexes; (b) a qualitative energy diagram for exciton coupling dependence on canting angles of monolayer molecules on water surface (adapted from McRae and Kasha²³).

