50 to 150 mV s^{-1} gave data with a dispersion of only 2% for the effective area, the diffusion coefficients of ferricyanide and ferrocyanide being taken as 6.93 and 6.56 $cm^2\ s^{-1}$, respectively.[37]

The hydrodynamic behavior of the rotated RVC electrode was tested as follows: after pretreatment the rotated electrode was maintained in a large volume of background solution (50 cm^3) at a controlled potential corresponding to the oxidation of ferrocyanide till the background current reached a steady state and then an aliquot of stock solution of ferrocyanide was injected and the current jump rapidly measured in order to avoid ferrocyanide consumption. The electrode rotation frequencies ranged from 200 to 3000 rpm. A variable-speed Tacussel EDI motor with a Tacussel CONTROVIT controller was used to rotate the electrode.

(4) Immobilized Protein Assays. Hydrolysis of native LDH and fluorimetric assays of the amino groups were used as standards. For hydrolysis, 50-μL aliquot of a 4 mg cm^{-3} stock solution were added to 2-cm^3 samples of 6 M hydrochloric acid and the resulting solutions were held at 99 °C for 5 h (or various durations as shown in Figure 2) in closed test tubes. The assay of immobilized LDH is of interest only if the corresponding electrode area is known. Therefore we proceded as follows: RVC cylinders 7 mm high were weighed before gluing and their areas were determined as described above. A typical result was 450 $cm^2\ g^{-1}$. After immobilization the electrode was rinsed thoroughly (final rinsing with water). Cylinders 3 mm high were cut at the bottom of each electrode, dried during one night, and weighed. The RVC areas were deduced from the weights. Hydrolysis of each piece was carried out in 200 μL of 6 M hydrochloric acid under the same conditions as with native LDH. After being cooled the solution was neutralized with 100 μL of 12 M sodium hydroxide; 50 μL of hydrolysate (i.e., between 1 and 10 pmol of LDH) and 1.5 cm^3 of 0.2 M borate buffer pH 9 were introduced in a test tube. After rapid addition of 0.5 cm^3 of fluorescamin solution (14 mg in 50 cm^3 of acetone) and vigorous mixing, the fluorescence was measured.

Fluorimetric assays[27] were performed with a JY 3 JOBIN-YVON spectrofluorimeter (excitation wavelength 366 nm; emission 470 nm). For standardization we used a solution of quinine sulfate (0.1 mg L^{-1}) in 0.1 M sulfuric acid. Due to the high sensitivity of the method, extra precautions were essential for cleaning glassware and filtering solutions (on 0.22-μm MILLIPORE membranes).

(5) Spectrophotometric Measurements. The absorbance due to the production of NADH was measured at 340 nm ($\epsilon_{NADH,340}$ = 6220 $M^{-1}\ cm^{-1}$) in order to determine the enzymatic activity. Typically the reaction mixtures contained initially 3.8 cm^3 of 0.1 M glycine buffer at pH 9 plus 0.1 M KCl plus 5 mM NAD^+ plus lactate at various concentrations. The rotated electrode dipped only in the top region of the solution. We used a HEWLETT-PACKARD (type 8450 A) absorption spectrophotometer, and the measurements were not altered by light from the surroundings.

In order to assay enzymatically active NAD^+ in the presence of lactate and pyruvate, we had to operate according to a procedure avoiding lactate and pyruvate interferences. Therefore we used a reagent consisting of alcohol dehydrogenase (2 units cm^{-3}) and ethanol (1%) in glycine-buffered background. Under such conditions more than 95% of the enzymatically active NAD^+ is transformed into NADH in 10 min, and the total amount of NADH can then be deduced from the absorbance of the solution at 340 nm.

(6) Electrochemical Measurements. The reference electrode was a saturated KCl calomel electrode and the counter electrode was a platinum foil. Both were put into different compartments communicating with the working electrode compartment through glass frits. Cells with two distinct working electrode compartment volumes were used: 2.7 cm^3 for recycling experiments and 50 cm^3 for other purposes. The water-jacketed cells were thermostated at 25 °C. Electrochemical measurement of immobilized enzyme activity was realized as already described in the case of a disk electrode (Figure 7 and ref 10), but due to the lack of hydrodynamic model, comparisons can be established only at fixed rotation frequency (in general 1700 rpm).

(7) Chemicals. NAD^+ and NADH (grade III), LDH (type XI), alcohol dehydrogenase (A 3263), and 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide methoxy *p*-toluene sulfonate (C 1011) were obtained from SIGMA. Fluorescamin, 1-lactate, and pyruvate were obtained from FLUKA. Other reagent grade chemicals were from CARLO ERBA. All chemicals were used as received.

Registry No. LDH, 9001-60-9; NAD^+, 53-84-9; NADH, 58-68-4.

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Molecular Association and Monolayer Formation of Soluble Phthalocyanine Compounds

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Abstract: This paper reports on synthesis, association in solution, and Langmuir–Blodgett monomolecular layer formation of H_2, Mg, Co, Ni, Cu, Zn, Pd, Pt, Bi, and Pb phthalocyanine compounds with cumylphenoxy peripheral substitution on each benzo ring at either the 2- or 3-position (tetracumylphenoxy-substituted isomer mixture). The degree of association is dependent on the identity of the complexed ion and varies from monomeric for the Pb compound to tetrameric for the Pt phthalocyanine as determined by vapor pressure osmometry measurements on 10^{-2}–10^{-3} M toluene solutions. The phthalocyanine compounds form stable Langmuir–Blodgett monomolecular layers to film pressures greater than 20 mN/m. The force–area curves indicate that the phthalocyanine units are densely packed with a cofacial orientation. Electronic spectra of solutions and X-ray diffraction patterns from bulk solids indicate that the phthalocyanine rings are cofacially oriented within an aggregate structure. The complexed metals (Ni, Pd, Pt) inducing the highest degrees of association in solution also yield correspondingly larger areas per phthalocyanine unit in the monolayer.

Phthalocyanine compounds continue to be the subjet of increasing research activity.[1] As thin films, these compounds display properties of particular current interest such as electrical conductivity,[2] electrical switching between conducting states,[3] photovoltaic effects,[4] oxidative catalytic activity,[5] and electrochromism,[6] which can be modified by interactions with chemical vapors,

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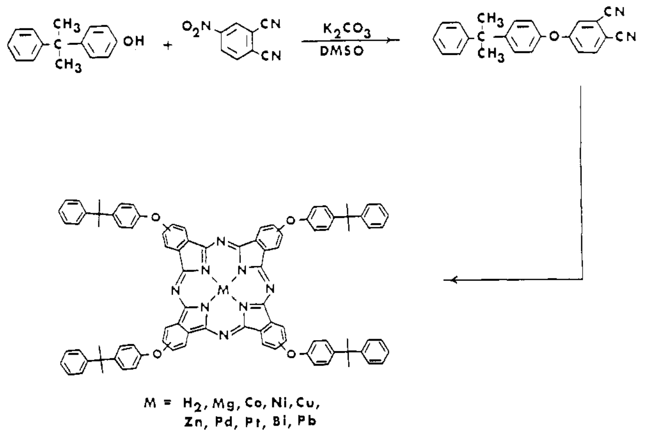

Figure 1. General synthesis and structure of $MPcX_4$ compounds.

electromagnetic radiation, or an electrical potential. Techniques for application of phthalocyanine thin films include vacuum sublimation, spraying of a fine suspension, dispersion in a polymeric binder, and mechanical rubbing, all of which involve procedures of questionable reproducibility. Variables difficult to control are thickness and uniformity of films and size and distribution of crystallites. An alternative approach, based on the Langmuir–Blodgett technique of monomolecular layer formation and transfer, offers potential for circumventing these difficulties and for controlling the orientation and packing of the phthalocyanine units within the film. However, full utilization of the Langmuir–Blodgett technique requires soluble phthalocyanine compounds, the ability to modify them chemically, and a knowledge of their solution and solid-state molecular aggregation.

In the present work the objective is to prepare a series of soluble phthalocyanine compounds containing a variety of complexed metal ions and to investigate their potential for forming stable Langmuir–Blodgett films. Noting that peripherally unsubstituted phthalocyanine compounds are insoluble in organic solvents (with the exception of Mg and Li phthalocyanine which are soluble but form unstable[7] or poorly transferable[8] monolayers), the approach of solubilizing the phthalocyanine ring with aryloxy groups substituted at the periphery appeared promising. The solubility of this series of compounds facilitates characterization of intermolecular ordering in solution by spectroscopy and vapor pressure osmometry (VPO) measurements. Such measurements have been useful in distinguishing dimerization from aggregation in the closely related porphyrin system.[9] In this report we describe the synthesis of ten members of a series of tetrakis(cumylphenoxy)-substituted phthalocyanines, their degrees of association in solution and their monolayer forming properties at the water/air interface. Our new findings are that the degree of association is dependent on the identity of the ion in the phthalocyanine cavity and that these phthalocyanine aggregates form stable monomolecular films whose packing densities at the air/water interface relate to the degree of association.

Results

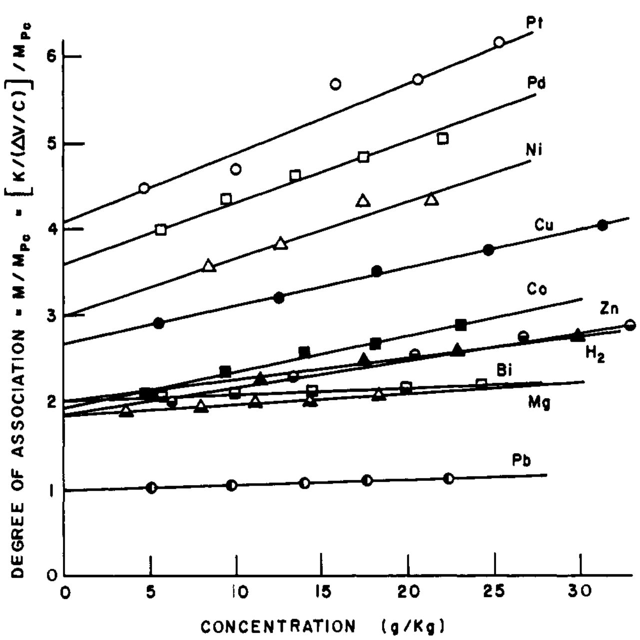

Figure 2. Number-average degree of association (vapor pressure osmometry molecular weight divided by monomeric molecular weight) of $MPcX_4$, compounds in toluene solution at 65 °C.

Synthesis. The tetrakis(cumylphenoxy)phthalocyanine compounds, $MPcX_4$, were synthesized according to the scheme in Figure 1. With the exception of H_2PcX_4, the procedure for conversion of phthalonitrile to metallophthalocyanine is analogous to that developed by Linstead and co-workers for unsubstituted phthalocyanines.[10a] This procedure yields a mixed isomer product with a cumylphenoxy group at either the 2- or 3-position of each benzo ring in the phthalocyanine molecule. The cumylphenoxy groups dominate the solubility properties of these compounds. These compounds are soluble in aromatic, chloroalkane, and cyclic ether solvents and were purified by column chromatography on neutral alumina. Geometric isomers were not separated by the chromatography. Elemental analysis and spectroscopic data (^1H NMR, ESR, infrared, and electronic) are consistent with the assigned structures. With the exceptions of Pd- and $PtPcX_4$, parent molecular ions were detected by fast atom bombardment mass spectrometry.[10b]

Molecular Association. Molecular aggregation in Langmuir–Blodgett solid-state monolayers and molecular associations in solution are closely related in that molecular chemistry, geometry, and intermolecular forces of attraction are largely the determining factors. Only in the Lamgmuir–Blodgett films is the ordering further influenced by the preferential adsorption of hydrophilic groups at the interface. It is apparent that a knowledge of the molecular association in solution would aid in understanding ordering in Langmuir–Blodgett films. Molecular association in solution can be measured directly by classical molecular weight measurements or by spectroscopic measurements. Determination of the surface induced molecular ordering in solid-state Langmuir–Blodgett transfer films is generally much less definitive, requiring information from a variety of techniques such as diffraction, polarized light, and ESR spectroscopies, and will not be considered in this paper.

The number-average degree of association of the $MPcX_4$ compounds in toluene solution was measured by vapor pressure osmometry[11] as the apparent molecular weight divided by the molecular weight calculated from the assigned structure (Figure 2). The linearity of the plot indicates that the degree of association does not significantly vary over the concentration range 3×10^{-3} to 2×10^{-2} M. Most of the $MPcX_4$ compounds (M = H_2, Mg, Co, Zn, Bi) are dimeric complexes in solution. The exceptions

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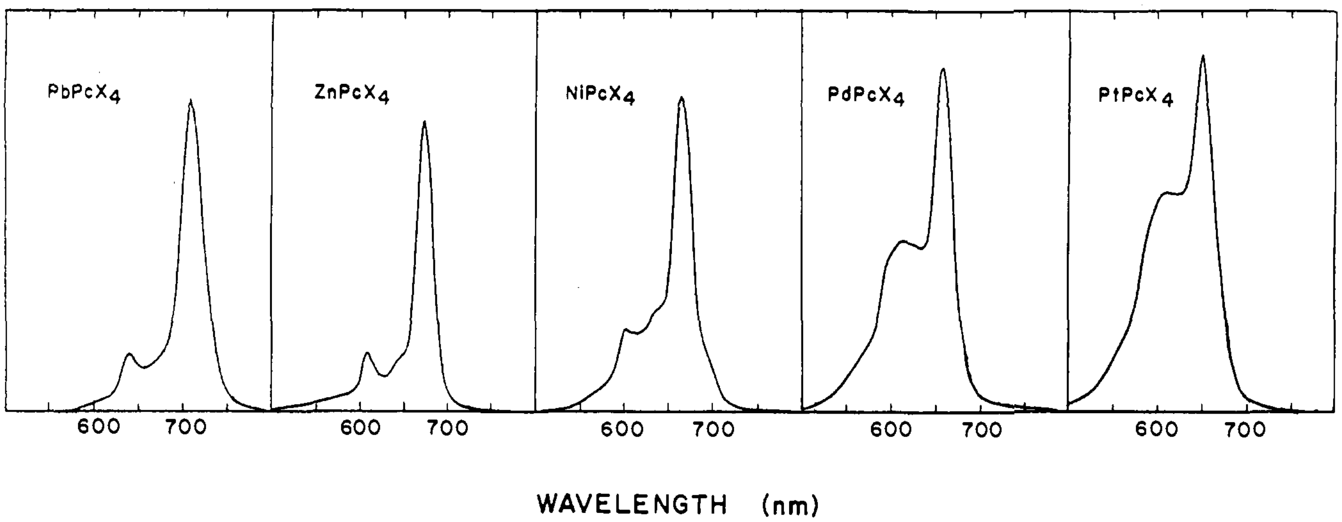

Figure 3. Electronic spectra of monomeric $PbPcX_4$, dimeric $ZnPcX_4$, and progressively higher order (Ni, Pd, Pt) $MPcX_4$ complexes.

are $PbPcX_4$, which is unimolecular, and the Cu, Ni, Pd, and Pt phthalocyanines, which form progressively higher order complexes.

The association of phthalocyanine compounds may also be observed by electronic and ESR spectroscopies although absorptions of species having different degrees of association are only partially resolved. Visible spectra of Pb-, Zn-, Ni-, Pd-, and $PtPcX_4$ in 10^{-5} M dioxane solutions are presented in Figure 3 and are representative of $MPcX_4$ compounds that associate as monomers, dimers, and higher order complexes under conditions of the VPO measurement. The spectra consist of a strong narrow $\pi-\pi^*$ absorption between 650 and 710 nm accompanied by a weaker vibrationally coupled satellite band at at 60- to 70-nm shorter wavelength. In a progression of spectra from that of the monomeric $PbPcX_4$ to that of the highly associated $PtPcX_4$, a second broader and partially resolved $\pi-\pi^*$ absorption appears with increasing intensity between the first $\pi-\pi^*$ absorption and satellite band. In previous studies, the narrow longer wavelength absorption has been attributed to a monomeric phthalocyanine compound, and the broad partially resolved absorption has been attributed to a dimer complex.[12,13] Only the $PbPcX_4$ electronic spectrum follows Beer's law, which would be expected since it is monomeric at the higher concentration of the VPO measurement and can exhibit no complex equilibria. The other $MPcX_4$ compounds' spectra have a nonlinear dependence on concentration, and the relative intensity of the shorter wavelength $\pi-\pi^*$ absorption is favored at higher concentrations. The ESR spectra of $CoPcX_4$ and $CuPcX_4$ in 10^{-3} M toluene solution consist of singlet signals due to exchange effects from the close approach of Co or Cu ions in the phthalocyanine oligomer complexes. When these compounds are mixed in a 10-fold quantity of H_2PcX_4 or dissolved in concentrated sulfuric acid, ESR spectra with resolved hyperfine and superhyperfine structure are observed as documented in the literature for these complexes ions.[8f,1,9c]

Monolayer Formation. Monomolecular films of the $MPcX_4$ compounds, where M = H_2, Co, Cu, Ni, Pd, and Pt, were spread at the water/air interface from benzene solution.[14] Each of the phthalocyanine compounds was discovered to form stable, reproducible films to film pressures of 20 mN/m or higher (Figure 4). These films compressed and expanded reversibly with application and withdrawal of film pressure. Two outstanding features of the resulting force–area curves are, first, that the complexing metals have a pronounced effect on the area occupied per phthalocyanine molecule and, second, that all the phthalocyanine derivatives occupy areas that are remarkably small. The effect of the metal ions on phthalocyanine packing in the monolayer relates to the degree of association given in Figure 2. The phthalocyanines giving dimeric association in solution, Co, H_2, and also Cu, also occupy effective surface areas consistent with dimer formation. The metals giving the highest degree of association, Ni, Pd, and Pd, occupy larger areas/molecule at equivalent film pressures and in the same order. The correlation indicates that the electronic interactions giving rise to the different degrees of associations in solution are also operative in the monolayer regime.

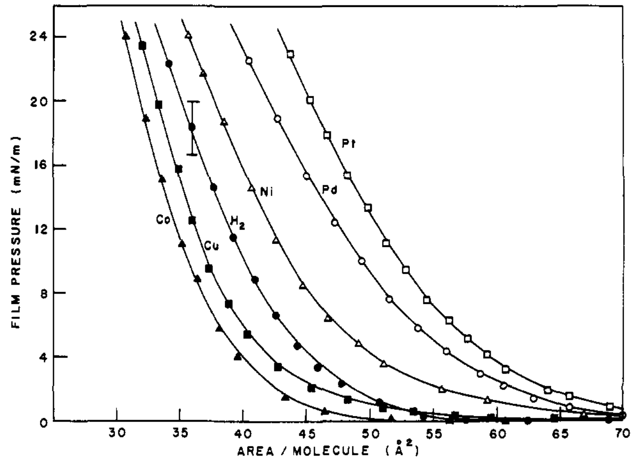

Figure 4. Langmuir–Blodgett force–area curves of $MPcX_4$ compounds at air–water interface.

Discussion

Two results of immediate importance are that the degree of $MPcX_4$ association in solution is dependent on the identity of the complexed ion and that the packing efficiency of the phthalocyanine units in a Langmuir–Blodgett monolayer correlates with the size of the phthalocyanine aggregate in solution. The phthalocyanine aggregate is an equilibrium distribution of mo-

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nomer, dimer, and oligomer phthalocyanine complexes which will be dependent on concentration, solvent quality, and possibly nature of the peripheral substituent group in addition to identity of the complexed metal ion. The VPO measurement of aggregate size is nicely complemented by spectroscopic techniques which provide additional information about the aggregate structure. The VPO measurement samples a higher concentration range (10^{-3}–10^{-1} M) than electronic spectroscopy (10^{-7}–10^{-4} M) or ESR (10^{-4}–10^{-2} M) and does not require assignment and deconvolution of overlapping spectral absorptions. Both characterization techniques are particularly useful for interpreting the Langmuir–Blodgett monolayer formation data.

Previous work on phthalocyanine association has involved electronic and ESR spectroscopic studies of sulfonate- or sulfamide-substituted phthalocyanine compounds in aqueous[12] and organic[13] solvents. The systems studied have included H_2, Cu, Co, Zn, Fe, and VO phthalocyanines, and the possibility of complexes larger than dimers was not quantitatively considered with the exception of one report investigating a metal-free system.[12m] In these studies, phthalocyanine solubilization was achieved by sulfonation at the 2- or 3-positions on the benzo rings, $MPc(SO_3Na)_4$,[12] and by conversion of the sulfonate to the *n*-octadecylsulfamide, $MPc(SO_2NHC_{18}H_{37})_4$,[13] for the respectively aqueous and organic systems. It should be noted that these substituents are strong hydrogen-bonding functional groups and may contribute to molecular association (for example, see ref 12k). By comparison, the cumylphenoxy ether substituent of this work should have a much smaller influence on molecular association. The electronic and ESR spectroscopic studies have attributed the concentration and solvent polarity dependencies of the spectra to a phthalocyanine monomer–dimer equilibrium.[12,13] The visible spectroscopic observation is a narrow monomer π–π^* absorption between 650 and 700 nm overlapped by a broad dimer π–π^* absorption with a partially resolved maximum at a shorter wavelength. This π–π^* transition shift with a broader natural bandwidth is a consequence of molecular association with a cofacial phthalocyanine ring orientation. This effect has been demonstrated in a study of monodisperse oxygen-bridged silicon phthalocyanine monomer, dimer, and trimer compounds where a coafacial phthalocyanine ring orientation is forced.[15] Although the concentration ranges differ by 2 to 3 orders of magnitude, the VPO data of Figure 2 and visible spectra data of Figure 3 correlate in that this "dimer" or "oligomer" π–π^* absorption becomes progressively more intense as the $MPcX_4$ tendency to aggregate becomes stronger. In ESR studies, the spectroscopic observation for aggregation is an exchange narrowing and loss of hyperfine structure resulting from close positioning of paramagnetic ions in an aggregate complex. The interpretation of Cu phthalocyanine electronic and ESR spectra as a dimer[13c,16] has been disputed in favor of a higher complex on the basis of a more comprehensive ESR study.[12l] The VPO result of this work supports the latter position.

The VPO data of Figure 2 indicate that, within the concentration range investigated, the dimer complex is the predominant aggregate for five of the ten $MPcX_4$ compounds. For the other five $MPcX_4$ compounds, specific metal ion effects superimpose on this association equilibria. In the case of $PbPcX_4$, the large size of the plumbus ion (1.20-Å ionic radius) appears to be a factor in promoting the monomer as the predominant species. Spectroscpic and crystallographic data on unsubstitued PbPc indicate that the lead ion is displaced 0.4 Å from the plane of the phthalocyanine ring.[17,18] This structural distortion of symmetry may disrupt the attractive forces between phthalocyanine rings. On the other hand, Ni-, Pd-, and $PtPcX_4$ stand out for their formation of aggregates with a significantly higher degree of association than dimer complexes. While this enhanced aggregative bonding is not currently understood, there are features that uniquely correlate with this group of phthalocyanine compounds. Specific to these ions is a d^8 electronic configuration. In a phthalocyanine molecular orbital diagram, complexes ions with this configuration fill all of the bonding and nonbonding levels but none of the antibonding levels.[19] In comparison with other phthalocyanines, the π–π^* transition of this group is at a significantly shorter wavelength,[20] and, within the group, it increases in energy in the order Ni < Pd < Pt, which is also the order of increasing association. Finally, this group of phthalocyanine compounds displays a remarkably intense ESR signal at a free electron *g* value.[21] An oxygen–phthalocyanine interaction is known to modify the ESR signal intensity of this "diamagnetic" phthalocyanine group,[22] but the source of the paramagnetism is still unresolved.

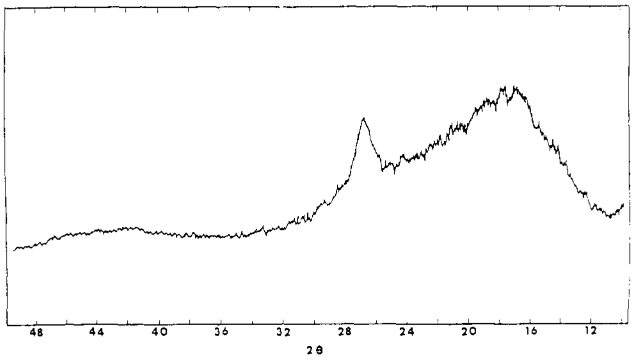

Figure 5. X-ray diffraction spectrum of H_2PcX_4.

Regarding the structure of the $MPcX_4$ aggregates, a large volume of spectroscopic data supports a structural representation as an association of cofacially oriented rings. The change in the π–π^* transition of the visible spectra resulting from association is analogous to that observed in a series of silicon phthalocyanine monomer, dimer, and trimer compounds where the rings in the dimer and trimer are cofacially linked through an oxygen bridge.[15] The exchange narrowing of the ESR spectra requires a close approach of the complexed paramagnetic ions which would be best accommodated by a cofacial association. For the specific case of H_2PcX_4, the cavity protons are a sensitive probe of the phthalocyanine ring current strength as detected by ^1H NMR spectroscopy. Formation of a cofacially oriented dimer complex reinforces the ring current of the monomer and shifts the cavity proton resonance to an extraordinarily high upfield value. As an example, a cavity proton resonance at δ −8.1 has been recently reported for a covalently bonded face-to-face porphyrin dimer while that for the corresponding monomer is δ −3.8.[23] This N–H resonance shift was also observed to a lesser extent in a porphyrin monomer–dimer equilibrating system.[24] The chemical shift of the H_2PcX_4 N–H resonance is δ −6.4 in $CDCl_3$ which we attribute to the dimer. While we have not determined conditions for observing the monomer resonance, variations in structure of the solubilizing group X, which may affect the phthalocyanine interplanar distance, correlate with N–H chemical shift in the following order: neopentoxy[25] δ −5.2 < cumylphenoxy δ −6.4 < phenoxy[26] δ −8.0. An interplanar separation distance ranging from 3.4 to 5 Å for a variety of phthalocyanine complexes has been

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calculated from thermodynamic,[12d] ESR,[12f] and electronic[27] spectroscopic data. In a polymeric phthalocyanine system where the phthalocyanine rings are constrained to a face-to-face orientation through a bridging oxygen atom, it has been shown by careful extrapolation from the crystal structure of a model trimer compound that an intense reflection in the X-ray powder diffraction pattern correlated well with a 3.3–3.8-Å interplanar ring separation distance.[28,29] In a recent X-ray analysis of a nonpolymeric octasubstituted phthalocyanine liquid crystal system, a columnar stacked structure was reported with one of two large angle reflections assigned to a 3.8-Å spacing between rings.[30] We find that an X-ray powder diffraction spectrum of H_2PcX_4 consists of a single sharp reflection at a 3.4-Å *d* spacing (Figure 5). Noting that this compound is an isomeric mixture, that the cumylphenoxy group is not conducive to efficient crystalline packing, and that no metal atoms are present, it appears reasonable to correlate the reflection with a stacked coplanar association of phthalocyanine rings independent of metal ion induced ordering. Polymorphs attributable to dimer structures, which are distinct from the commonly encountered α and β phthalocyanine forms, have also been proposed for CuPc[16] and H_2Pc.[27]

Since the early work of Alexander[7] force–area curves of phthalocyanines and related planar macrocyclic compounds have been interpreted as indicating some degree of cofacial packing of the molecules at the water–air interface. Their degree of cofacial packing and their orientation with respect to the interface will be strongly influenced by the molecular composition and structure, especially by the presence of hydrophobic pendant groups such as the cumylphenoxy at the periphery of the phthalocyanine macrocycle. The extrapolation of structural relationships in solution to a surface film is always risky due to replacement of the solvent environment by the strong unsymmetrical forces present at the interface. Even though correlations have been made between the behavior of specific metal-complexes phthalocyanines in solution and the same compounds adsorbed at the water/air interface, the aggregation and orientation of the molecules at the surface have not been confirmed. In a subsequent study, the monolayer morphology of the adsorbed metal-complexed phthalocyaniines will be investigated.

Experimental Section

All reagents and solvents were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted. Molecular weight measurements were obtained from toluene solutions at 65 °C on a Wescan 232A vapor pressure osmometer calibrated with specially purified benzil provided by the manufacturer. Spectroscopic data were obtained with the following associated instruments: electronic, Cary 118c; infrared, Perkin-Elmer 267; ^1H NMR, Varian EM390 (90 MHz); ESR, JEOL JES-ME-3X (X-band); X-ray, Philips XRG-2600 (Ni filtered Cu Kα radiation). Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory and in house by atomic emission analysis. Melting points are uncorrected.

4-(Cumpylphenoxy)-4-phthalonitrile (I). I was prepared by K_2CO_3-catalyzed nitro displacement of 4-nitrophthalonitrile (Eastman) by cumylphenol (Aldrich) in Me_2SO. In a nitrogen atmosphere, 19.56 g (0.141 mol) of finely ground anhydrous K_2CO_3 was added to a solution of 19.08 g (0.090 mol) of 4-cumylphenol and 15.57 g (0.090 mol) of 4-nitrophthalonitrile in 150 mL of dry Me_2SO by 1–2-g additions at $^1/_2$- to 1-h intervals over an 8-h period. The mixture was stirred for 24 hours at 20 °C under nitrogen. The reaction was worked up by filtering the undissolved salt and slowly adding the filtrate to a rapidly stirred 400-mL volume of water. The suspension was neutralized with HCl, and the crude products werre taken up into 100 mL of methylene chloride and combined with two subsequent 50-mL extractions. The methylene chloride solution was then extracted with 100 mL of 5% Na_2CO_3 to remove unreacted phenol, washed, and dried and solvent stripped to yield 21.3 g (70%) of I. The crude product was recrystallized twice from methanol yielding large platelets; MP 90 °C; IR (KBr) 3082 w, 3059 w, 3038 w, 2976 m, 2956 w, 2872 w, 2238 m, 1531 s, 1563 m, 1502 s, 1487 s, 1313 s, 1303 s, 1288 s, 1278 s, 1255 s, 1210 s, 1176 m, 1018 m, 901 m, 861 s, 769 m, 704 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (s, 6 H, methyl), 7.27 (m, 12 H, aromatic); mass spectrum, *m/e* 338 (calcd 338). Anal. Calcd for $C_{23}H_{18}N_2O$: C, 81.65; H, 5.32; N, 8.23. Found: C, 81.86; H, 5.28; N, 8.23. On standing for several weeks the platelet crystals turn light green which is associated with the presence of a trace quantity of occluded methanol. Recrystallization from hexane proceeds with difficulty but yields needle-shaped crystal, mp 90 °C, which remain colorless indefinitely. Anal. Found: C, 81.72; H, 5.41; N, 8.33.

Tetrakis(cumylphenoxy)phthalocyanine Syntheses. With the exception of the metal-free derivative, the procedures for the metallophthalocynines are very similar and analogous to those reported by Linstead and coworkers[10a] for unsubstituted metallophthalocyanines. Since the solubility properties of the phthalocyanine products are determined by the cumylphenoxy groups, the workup and purification procedures are also very similar. The general reaction and purification procedures are as follows except where departures are specified.

To a 10 × 75 mm tube fitted with an 8-mm Teflon-coated magnetic stirring bar were added the prescribed quantities of I and coreactant. The mixture was carefully fused under vacuum (less than 0.1 torr) to remove residual methanol occluded in I and sealed under vacuum. The entire tube was heated with stirring for the designated time and temperature. The crude product was purfied by column chromatography (neutral Woelm, activity 1) using toluene as a loading solvent and dioxane as an elution solvent. The dioxane solution was concentrated to a 2–3-mL volume, and the phthalocyanine was precipitated by dropwise addition into a stirred volume of 200 mL of methanol. The flocculent blue precipiate was filtered into the thimble of a micro Soxhlet extractor, extracted with methanol to ensure complete removal of unreacted I, and extracted into benzene. The benzene solution was concentrated to a 3-mL volume and added dropwise to 200 mL of stirred petroleum ether. The flocculent product was collected and vacuum dried (180 °C/0.1 torr).

Metal-Free Tetrakis(cumylphenoxy)phthalocyanine (II). A mixture of 1.00 g (2.96 mmol) of I and 0.081 g (0.74 mmol) of hydroquinone (purified by sublimation) was fused by gentle heating to the melting point without vacuum, cooled, sealed under vacuum, and reacted at 180 °C for 16 h: yield 0.49 g (49%); UV–vis (dioxane) λ_{max} 286, 341, 390, 602, 635, 663, 697 nm; IR (supported film on NaCl) 3290 w (N–H), 3093 w, 3062 w, 3040 w, 2977 m, 2940 w, 2877 w, 1607 m, 1508 s, 1477 s, 1237 s, 1176 m, 1093 m, 1017 s (H_2Pc specific band[31]), 932 m, 830 m, 766 m, 747 s, 701 s cm^{-1}; ^1H NMR ($CDCl_3$) δ −6.4 (br s, 2 H, internal N–H), 1.73 (s, 12 H, methyl), 7.32 (m, 24 H, aromatic); mass spectrum *m/e* 1355 (P + 1). Anal. Calcd for $C_{92}H_{74}N_8O_4$: C, 81.51; H, 5.50; N, 8.27. Found: C, 81.61; H, 5.62; N, 8.43.

[Tetrakis(cumylphenoxy)phthalocyanine]copper (III). A mixture of 0.676 g (2.00 mmol) of I and 0.245 g (4.00 mmol) of copper bronze (Creslite) was reacted at 270 °C for 12 h: yield 0.302 g (43%); UV–vis (dioxane) λ_{max} 280, 347, 606, 674 nm; IR (supported film on NaCl) 3097 w, 3063 w, 3042 w, 2988 m, 2943 w, 2879 w, 1607 s, 1508 s, 1408 m, 1447 m, 1242 s, 1182 m, 1126 m, 1100 m, 969 m, 832 m, 768 m, 752 s, 704 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (br s, 12 H, methyl), 7.25 (br s, 24 H, aromatic); ESR (1:10 $CuPcX_4$:H_2PcX_4, toluene) g = 2.34, 2.21, 2.04 (hfs), 1.96 (hfs)[13c]; mass spectrum, *m/e* 1416 (P + 1).

Anal. Calcd for $C_{92}H_{72}N_8O_4Cu$: C, 78.00; H, 5.12; N, 7.91; Cu, 4.48. Found: C, 78.19; H, 50.01; N, 7.99; Cu 4.61.

[Tetrakis(cumylphenoxy)phthalocyanine]nickel (IV). A mixture of 0.676 g (2.00 mmol) of I and 0.245 g (4.00 mmol) of nickel powder (HCl etched, washed, and dried) was reacted at 280 °C for 44 h: yield 0.534 g (76%); UV–vis (dioxane) λ_{max} 290, 340, 600, 667 nm; IR (supported film on NaCl) 3096 w, 3063 w, 3039 w, 2978 m, 2940 w, 2878 w, 1608 s, 1508 s, 1477 s, 1417 m, 1242 s, 1181 m, 1127 m, 1099 m, 1021 m, 963 m, 830 m, 768 m, 756 s, 703 s cm^{-1}; ESR (toluene) g = 2 (s, ΔHpp = 6 G); mass spectrum, *m/e* 1411 (P + 1).

Anal. Calcd for $C_{92}H_{72}N_8O_4Ni$: C, 78.23; H, 5.14; N, 7.93; Ni, 4.16. Found: C, 78.00; H, 5.23; N, 7.82; Ni, 3.96.

[Tetrakis(cumylphenoxy)phthalocyanine]palladium (V). A mixture of 0.676 g (2.00 mmol) of I and 0.088 g (0.50 mmol) of $PdCl_2$ (Alfa) was reacted at 290 °C for 48 h: yield 0.109 g (15%); UV–vis (dioxane) λ_{max} 283, 329, 612, 660 nm; IR (supported film on NaCl) 3093 w, 3064 w, 3038 w, 2977 m, 2938 w, 2880 w, 1608 s, 1508 s, 1455 s, 1409 m, 1242 s, 1172 m, 1131 m, 1110 m, 832 s, 767 m, 751 m, 702 s cm^{-1}; ESR (toluene) g = 2 (s, ΔHpp = 8 G).

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Anal. Calcd for $C_{92}H_{72}N_8O_4Pd$: C, 75.68; H, 4.97; N, 7.76; Pd, 7.29. Found: C, 75.94; H, 4.99; N, 7.35; Pd, 7.25.

[Tetrakis(cumylphenoxy)phthalocyanine]platinum (VI). A mixture of 1.00 g (2.96 mmol) of I and 0.20 g (0.75 mmol) of $PtCl_2$ (Alfa) was reacted at 290 °C for 48 h: yield 0.263 g (23%); UV–vis (dioxane) λ_{max} 278, 394, 605, 651 nm; IR (supported film on NaCl) 3096 w, 3063 w, 3040 w, 2978 m, 2940 w, 2878 w, 1608 s, 1508 s, 1475 s, 1411 m, 1242 s, 1174 m, 1136 m, 1111 m, 831 m, 768 m, 753 m, 702 s cm^{-1}; ESR (toluene) $g = 2$ (s, ΔHpp = 4 G).

Anal. Calcd for $C_{92}H_{72}N_8O_4Pt$: C, 71.35; H, 4.69; N, 7.24; Pt, 12.60. Found: C, 72.31; H, 4.65; N, 7.75; Pt, 11.94.

[Tetrakis(cumylphenoxy)phthalocyanine]magnesium (VII). A mixture of 0.50 g (1.48 mmol) of I and 0.14 g (5.92 mmol) of Mg powder (lightly etched with dilute HCl) was reacted at 280 °C for 70 h: yield 0.072 g (14%); UV–vis (dry dioxane) λ_{max} 282, 380, 615, 680 nm; IR (supported film on NaCl) 3091 w, 3061 w, 3039 w, 2976 m, 2940 w, 2878 w, 1606 s, 1508 s, 1488 s, 1237 s, 1178 m, 1085 m, 1049 m, 952 m, 832 m, 702 s cm^{-1}; mass spectrum, *m/e* 1377 (P + 1).

Anal. Calcd for $C_{92}H_{72}N_8O_4Mg$: C, 80.19; H, 5.27; N, 8.13; Mg, 1.76. Found: C, 80.70; H, 5.22; N, 7.48; Mg, 1.42.

[Tetrakis(cumylphenoxy)phthalocyanine]cobalt (IX). A mixture of 0.676 g (2.00 mmol) of I and 0.236 g (4.00 mmol) of Co powder (HCl etched, washed, and dried) was reacted at 280 °C for 12 h: yield 0.249 g (35%); UV–vis (dioxane) λ_{max} 275, 342, 603, 669 nm; IR (supported film on NaCl) 3093 w, 3063 w, 3041 w, 2987 m, 2941 w, 2879 w, 1608 s, 1509 s, 1476 s, 1413 s, 1242 s, 1182 m, 1137 m, 1102 m, 1063 m, 1020 m, 963 m, 831 m, 767 m, 756 s, 702 s cm^{-1}; ESR (1:10 $CoPcX_4$:H_2PcX_4, toluene, −90 °C) $g = 2.9$ (eight lines[32]); mass spectrum, *m/e* 1412 (P + 1)).

Anal. Calcd for $C_{92}H_{72}N_8O_4Co$: C, 78.23; H, 5.14; N, 7.93; Co, 4.17. Found: C, 77.77; H, 5.13; N, 7.92; Co, 4.07.

[Tetrakis(cumylphenoxy)phthalocyanine]zinc (X). A mixture of 0.676 g (2.00 mmol) of I and 0.262 g (4.00 mmol) of Zn powder (HCl etched, washed, dried) was reacted at 280 °C for 70 h: yield 0.397 g (56%); UV–vis (dioxane) λ_{max} 281, 350, 609, 674 nm; IR (film supported on NaCl) 3093 w, 3063 w, 3040 w, 2988 m, 2940 w, 2879 w, 1607 s, 1508 s 1493 s, 1476 s, 1402 m, 1361 m, 1240 s, 1179 m, 1122 m, 1092 m, 1050 m, 1021 m, 952 m, 832 m, 767 m, 750 s, 703 s cm^{-1}, mass spectrum *m/e* 1417 (P + 1).

Anal. Calcd for $C_{92}H_{72}N_8O_4Zn$: C, 77.87; H, 5.11; N, 7.90; Zn, 4.61. Found: C, 77.86; H, 4.85, N, 7.86; Zn, 4.58.

[Tetrakis(cumylphenoxy)phthalocyanine]lead (XI). A mixture of 0.500 g (1.48 mmol) of I and 0.250 (1.12 mmol) of PbO (Fisher, yellow) was reacted at 210 °C for 14 h: yield 0.280 g (49%); UV–vis (dioxane) λ_{max} 244, 270, 339, 360 sh, 383 sh, 638, 710 nm; IR (film supported on NaCl) 3092 w, 3063 w, 3042 w, 2986 m, 2938 w, 2877 w, 1606 s, 1525 m, 1508 s, 1487 s, 1392 m, 1344 m, 1238 s, 1180 m, 1083 m, 1050 m, 950 m, 832 m, 768 m, 750 m, 702 s cm^{-1}; mass spectrum, *m/e* 1561 (P + 1).

Anal. Calcd for $C_{92}H_{72}N_8O_4Pb$: C, 70.80; H, 4.65; N, 7.18; Pb, 13.27. Found: C, 70.74; H, 4.89; N, 7.46; Pb, 13.03.

[Tetrakis(cumylphenoxy)phthalocyanine]bismuth (XII). A mixture of 0.676 g (2.00 mmol) of I and 0.84 (4.0 mmol) of Bi powder (HNO_3 etched, washed, dried) was reacted at 290 °C for 150 h: yield 0.164 g (21%); UV–vis (dioxane) λ_{max} 287, 343, 663, 696 nm; IR (film supported on NaCl) 3093 w, 3062 w, 3040 w, 2979 m, 2940 w, 2880 w, 1606 s, 1508 s, 1478 s, 1390 m, 1330 m, 1238 s, 1179 m, 1079 m, 1020 m, 947 m, 832 m, 768 m, 743 m, 702 s cm^{-1}; mass spectrum, *m/e* 1562 (P + 1).

Anal. Calcd for $C_{92}H_{72}N_8O_4Bi$: C, 70.71; H, 4.64; N, 7.17; Bi, 13.37. Found C, 72.96; H, 5.06; N, 7.74; Bi, 12.42, 14.22.

Preparation of Monolayers of (Cumylphenoxy)phthalocyanines. A Teflon-coated Pyrex trough (11 cm × 40 cm × 0.5 cm) was used as the film balance tray for preparing monolayers of the metal-free and metal-substituted (cumylphenoxy)phthalocyanine and for determing their monolayer properties. Teflon-coated glass rods (15 cm × 0.4 cm × 0.6 cm) were used as barriers to compress the films adsorbed at the water surface and to sweep the water surface of adsorbed contaminants. A Wilhelmy plate was used to measure changes in the surface tension. The plate was of platinum, 2.0 cm × 1.5 cm × 0.005 cm. It was attached to a Statham UC 2 strain gauge and, via an appropriate resistance bridge circuit, to a strip chart recorder. The system can be calibrated to easily detect film pressures of 0.05 mN/m. The movable Teflon barriers were coupled with a variable speed motor drive to permit continuous controlled compression of an adsorbed film. The rate of compression was maintained sufficiently slow so that the resulting surface tension vs. film pressure curves were independent of compression rate. The film balance system was enclosed in a Lucite box to maintain a relatively dust-free environment during the course of a run. The measurements were carried out at room temperature, 25 ± 2 °C.

Solutions of metal-free and metal-containing (H_2, Cu, Ni, Co, Pt, Pd) (cumylphenoxy)phthalocyanines were prepared in benzene. All glassware was acid cleaned, rinsed profusely with distilled water, and dried prior to use. Solutions were delivered to the water surface from a micrometer syringe. In these initial studies the substrate used was 0.01 N HCl.

Prior to a run the film balance was washed with a detergent, rinsed with distilled water, drained, and filled with substrate. The surface was cleaned by appropriate sweeping with the film barriers until no changes in film pressure were observed when the surface was compressed to within 0.5 cm of the Wilhelmy plate mounted 2 cm from the end of the trough. The spreading solution was added dropwise to the surface and allowed to equilibriate while the solvent evaporated, usually 10–15 min. The Wilhelmy plate was cleaned by flaming to red heat, cooled, and lowered until it just touched the surface and was wet by the substrate. The film was then compressed slowly, and the film pressure vs. area/molecule curves were recorded. The film balance was also equipped with a motor driven dip coater to transfer Langmuir–Blodgett films to solid surfaces by lowering and raising the solid substrates through the monolayer-covered interfaces.

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Registry No. I, 83482-57-9; II, 83484-76-8; III, 91083-47-5; IV, 91083-48-6; V, 91083-49-7; VI, 91083-50-0; VII, 91083-51-1; IX, 91083-52-2; X, 91083-53-3; XI, 91083-54-4; XII, 91083-55-5; 4-nitrophthalonitrile, 31643-49-9; cumylphenol, 22239-54-9; hydroquinone, 123-31-9.

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