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Effects of Ligands, Solvent, and Variable Sulfonation on Dimer Formation of Aluminum and Zinc Phthalocyaninesulfonates

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The absorption spectra and emission spectra in aqueous solution of three types of phthalocyaninesulfonates of aluminum are compared: IA, a trisulfonate formed by sulfonation of aluminum phthalocyanine, shows no evidence for dimerization in water with changing pH or ionic strength. IIA, a tetrasulfonate prepared by metalation of the tetrasulfonated free base using Al(acac)$_3$, when added to water immediately shows spectra characteristic of a "contact dimer". IIIA, a tetrasulfonate prepared by condensation of sulfophthalic acid around AlCl$_3$, also shows dimer-like spectral changes, but they develop over 4 h. This "slow-forming dimer", like the "contact dimer", shows no emission but has a sharper red band. Comparison is made to similarly prepared phthalocyaninesulfonates of zinc: IZ, IIZ, IIIZ. Again, there is little dimer formation by IZ, although somewhat more than by IA. The zinc phthalocyaninetetrasulfonates, IIZ and IIIZ, show large amounts "contact dimer" but no "slow-forming dimer" spectrum, which is attributed to formation of a binuclear μ-oxo aluminum phthalocyaninetetrasulfonate.

Introduction

Phthalocyanines were first discovered at a Scottish dye works in 1928.[4] Since their initial use as dyes, there has been a variety of other applications including electrocatalysis, photovoltaics, photoxerography, photocatalysis, and chemical sensors.[4] More recently, medical diagnostic[5,6] and therapeutic uses[7-10] of phthalocyanines have begun to emerge.

Many applications of phthalocyanines require water-soluble derivatives. The most common water-soluble metallophthalocyanines are sulfonates. Most sulfonated metallophthalocyanines are highly aggregated in water.[11-13] The state of aggregation greatly affects the photophysical properties of phthalocyanines in solution: notably, dimerization and aggregation quench their usually strong fluorescence. This diminishes the performance of these species in various applications, often rendering the interpretation of their role in a given process difficult.

Darwent et al.[14] reported that they could find no evidence for the dimerization of sulfonated aluminum phthalocyanines. We have examined three aluminum phthalocyaninesulfonates prepared by three different synthetic procedures: IA shows no dimer spectra in water in agreement with Darwent; however, IIA shows spectral changes that occur immediately in water and that we attribute to "contact dimers" customarily observed with phthalocyanines. In contrast, IIIA develops a dimer-like spectrum over 4 h. In this paper, we present the kinetics and spectral characteristics of this "slow-forming dimer". We also report on similarly prepared zinc phthalocyanine complexes, IZ, IIZ, and IIIZ, which show only contact dimer formation. This contrasting behavior is used to support the hypothesis that the slow-forming dimer is a binuclear μ-oxo aluminum phthalocyaninetetrasulfonate.

Table I. Nomenclature

species	method of prepn	identification[a]
IA	ClAlPc sulfonation	trisulfonate/hydroxide
IIA	H$_2$TsPc + Al(acac)$_3$	tetrasulfonate/acetylacetonate
IIIA	AlCl$_3$ + sulfophthalic acid	tetrasulfonate/hydroxide
IZ	ZnPc sulfonation	trisulfonate
IIZ	H$_2$TsPc + Zn(acac)$_2$	tetrasulfonate
IIIZ	ZnSO$_4$ + sulfophthalic acid	tetrasulfonate

[a] The fifth ligand on the aluminum is presumed from the synthetic method.

Phthalocyanine Electronic Spectra

The absorbance of a photon by the phthalocyanine causes the transition from the ground state, $^1S_0$, to a singlet excited state, either ^1Q or ^1B, as explained by the four-orbital model.[15] Chloroaluminum phthalocyanine (ClAlPc) has a sharp Q(0,0) band, with a full width at half-maximum (fwhm) of 19 nm in methanol. The addition of four sulfonate groups, on the periphery of the fused benzene rings, causes the peak to broaden to 25 nm (fwhm), as the 4-fold symmetry of the molecule is lost.

Phthalocyanine monomers, either free base or with light central atom closed-shell metals, are highly fluorescent. The emitted photons, for the phthalocyanines studied in this paper, have a peak wavelength around 680 nm, the Q(0,0) band. The fluorescent spectra exhibit associated vibronic bands, which occur at wavelengths longer than that of the Q(0,0) band.

Dimers of some phthalocyanines are detected by the presence of visible absorbance peaks, Q_d, blue-shifted in relation to the Q(0,0) band of the monomer.[9,11] A similar observation has been made for the Soret band of the μ-oxo dimers of scandium octaethylporphyrin and tetraphenylporphyrin and has been attributed to exciton coupling.[16] Lever and co-workers[17-19] have investigated the dimerization properties of mononuclear, binuclear, and tetranuclear neopentyl-substituted free-base, zinc, and cobalt phthalocyanines in organic solvents.

Experimental Section

Synthesis and Purification. Chloroaluminum phthalocyanine (ClAlPc) and zinc phthalocyanine (ZnPc) were purchased from Kodak. Free-base phthalocyaninetetrasulfonate (H$_2$TsPc) was obtained from Porphyrin Products, Logan, UT.

IA and IZ were prepared by sulfonation of ClAlPc and ZnPc, respectively. Solid metallophthalocyanine was treated with chlorosulfuric

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acid, and the mixture was heated to 150 °C for 2 h. The resultant slurry was quenched over ice. A deep blue solid was isolated by suction filtration and hydrolyzed to yield sulfonated aluminum or zinc phthalocyanine. Elemental analysis revealed an average of three sulfonate groups per phthalocyanine macrocycle.

IIA was made by metalation of the free base of phthalocyaninetetrasulfonate (H_2TsPc). This starting material is prepared at Porphyrin Products via a proprietary method, which produces only a tetrasulfonated product.[20] To a solution of the metal-free phthalocyaninetetrasulfonate in dimethylformamide was added 10 molar equiv of aluminum acetylacetonate. The solution was stirred at room temperature, and the reaction progress was monitored by absorption spectroscopy. After 4 h, the metalation was judged to be completed and the reaction mixture was diluted with methylene chloride to precipitate the product. The crude product was collected by filtration and washed with methylene chloride to remove excess aluminum acetylacetonate. The product was isolated in 92% yield. IIZ was prepared with an identical procedure utilizing zinc acetylacetonate as the metal source.

IIIA and IIIZ were prepared by the urea process according to the procedure of Weber and Busch.[21] The starting sulfonic acid was obtained from Aldrich as a 3:1 mixture of 4- and 3-sulfophthalic acids. The metal sources were aluminum trichloride for IIIA and zinc sulfate for IIIZ.

For convenience of the reader, we have summarized the notation for the three species studied in Table I, where we indicate the presumed fifth ligand on the aluminum.

Instrumentation. All electronic absorption spectra were recorded on a Beckman Instruments Model DU-70 single-beam spectrophotometer. All excitation and emission scans were taken on a Perkin-Elmer Model MPF-66 fluorescence spectrometer with a red-sensitive photomultiplier tube (Hamamatsu R-928). The photosignal reported by this instrument is corrected for intensity fluctuations of the lamp with time. A rhodamine B quantum counter corrects the excitation spectra for photon flux variations of the lamp with wavelength. The quantum counter is not effective for excitation wavelengths longer than 630 nm. As a result, the Q(0,0) bands in the excitation spectra appear weaker than they should.

Unless noted otherwise, all spectra were recorded in 1-cm^2 quartz cuvettes at room temperature.

Quantum Yields. The quantum yields presented in this paper were calculated relative to that of IA in distilled water. Fluorescence spectra were excited in the Soret band after diluting by 100-fold the solutions reported in absorption using the same solvent. Each sample was allowed to equilibrate for at least 1 h prior to recording a spectrum. Brannon and Magde[22] reported a quantum yield of 0.58 for ClAlPc in chloronaphthalene. We compared the emission yields of ClAlPc and IA in methanol and found them to be identical. A quantum yield of 0.6 shall therefore be used for IA in distilled water. The relative quantum yield (RQY) can then be calculated for similar compounds via the formula

$$\mathrm{RQY} = (I/I')[(A_S' - A_b')/(A_S - A_b)]\mathrm{QY}' \qquad (1)$$

where I is the fluorescence intensity, A_S is the absorbance of the Soret band, A_b is the background absorbance, and QY is the quantum yield. The primes signify the value of the IA standard. All spectra reported herein have nearly identical emission maxima, so there was no need to correct for PMT response in the evaluation of relative quantum yields.

Kinetic Analysis. For the kinetic experiments, the change in intensity of the 648-nm Q_d peak of IIIA is followed.[23] We assume this peak is due to a dimer-like species. We define DA(t), the change in absorption due to formation of Q_d, by the equation

$$\mathrm{DA}(t) = A(t) - A_1 \qquad (2)$$

where $A(t)$ is the absorbance at time t and A_1 is the absorbance of the solution if it were completely monomeric.

The kinetics experiment consists of placing monomeric IIIA in a high ionic strength solution and observing Q_d absorbance with time by recording repeated absorbance scans of the sample in a sealed cuvette. This experiment was repeated with IIA and with IIIZ. Their dimers formed by the time we did the first scan, i.e. within 1 min.

The slow dimer formation of IIIA was assumed to follow the reaction model

$$2\mathrm{Pc} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (\mathrm{Pc})_2 \qquad (3)$$

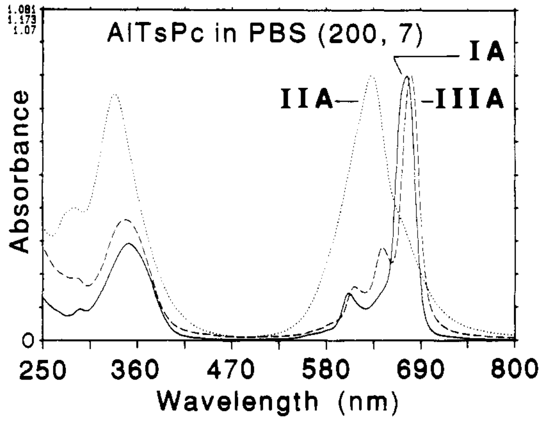

Figure 1. Comparison of the visible absorbance spectra for IA (solid), IIA (dotted), and IIIA (dashed) in PBS(200,7) at approximately 10^{-5} M for IIA and about half that for the other two. The maximum ordinate values are 1.173, 1.081, and 1.07, respectively.

If the reaction does indeed follow eq 3, then the absorbance variable DA(t) can be shown to follow the equation[23]

$$\mathrm{dDA}/\mathrm{d}t = k_f'\mathrm{DA}_d - (2k_f' + k_r)\mathrm{DA} + (k_f'/\mathrm{DA}_d)(\mathrm{DA})^2 \qquad (4)$$

DA_d is the value DA would have if the solution were pure dimer and

$$k_f' = k_f C_0 \qquad (5)$$

where C_0 is the phthalocyanine concentration if the solution were completely monomeric.

Equation 4 was integrated by computer and the solution applied to the absorbance at 648 nm, the principal dimer band. DA(t) can then be plotted versus time, assuming values for DA_d, k_f', and k_r, and the resulting curve compared to the experimental data. The actual curve was fit to the data by manual iteration of the three parameters in eq 4.

Results

In Figure 1 we contrast the optical absorption spectra for the three aluminum phthalocyaninesulfonates in pH 7, ionic strength 200 mM phosphate buffered saline, which we denote PBS(200,7). The concentration of each solution was adjusted so that they all had comparable absorbances at their red maximum, which are normalized in Figure 1. The samples were allowed to equilibrate for 24 h prior to recording these spectra. The spectra in Figure 1 show a great difference in relative absorbance of the Q_d band: IA shows no Q_d band, while IIA shows mostly the Q_d peak at 635 nm. In contrast, IIIA shows a sharp Q_d peak at 646 nm, representing roughly 20% of the material.

Our studies indicate that as the Q_d band increases relative to the far-red band, the quantum yield of fluorescence on Soret band excitation decreases. Table II summarizes emission yields. Although these were taken on solutions diluted 100-fold from those for the absorbance spectra, emission quenching persists. For comparison, Table II also includes data for ClAlPc and ZnPc in methanol and ethanol, respectively.

The Q_d bands observed in aluminum phthalocyanines are nonfluorescent. Figure 2 demonstrates this. Here we show the absorbance, emission, and excitation spectra of IIIA in the aqueous solution PBS(200,11). The Q_d peak is absent in the excitation spectra, and the quantum yield of Soret excitation is less than that of monomeric IA in water (Table II).

A previous study[13] indicated that copper phthalocyaninesulfonates exhibit aggregation properties that are a function of concentration, temperature, pH, ionic strength, and solvent. We investigated some of these effects on IIIA. Figure 3 shows that, in PBS(200,11), increasing phthalocyanine concentration enhances the Q_d band. Figure 4 shows the effect of pH on Q_d band formation. The ionic strength is equal to that reported in Figure 3, and the IIIA concentration is 2×10^{-6} M. We see that the intensity of the Q_d band is larger at extremes in pH. The effect of ionic strength on Q_d band intensity is shown in Figure 5. Here IIIA has been solvated in neutral distilled water and in pH 11 PBS at two ionic strengths: 20 and 200 mM. The Q_d intensity is clearly enhanced by increased ionic strength.

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Table II. Peak Positions of Phthalocyaninesulfonates[a]

molecule	solvent	B(0,0) ABS	Q_d ABS	Q(0,0) ABS	Q(0,0) EM	QY
ClAlPc	methanol	353	*b*	670	675	0.65
IA	water	350	*b*	673	682	0.60
IA	PBS(2,3)	351	*b*	675	682	0.59
IA	PBS(2,7)	349	*b*	673	681	0.63
IA	PBS(2,11)	349	*b*	673	680	0.62
IA	PBS(200,3)	350	*b*	675	682	0.62
IA	PBS(200,7)	349	*b*	674	681	0.64
IA	PBS(200,11)	348	*b*	672	677	0.59
IIA	water	336	636	667	684	0.15
IIIA	water	349	646	677	686	0.53
IIIA	PBS(0.2,11)	348	647	677	684	0.55
IIIA	PBS(2,3)	349	649	680	684	0.43
IIIA	PBS(2,7)	350	648	677	684	0.50
IIIA	PBS(2,11)	350	648	677	684	0.50
IIIA	PBS(20,11)	348	644	676	684	0.51
IIIA	PBS(200,3)	343	644	679	686	0.36
IIIA	PBS(200,7)	345	644	678	685	0.44
IIIA	PBS(200,11)	340	641	675	679	0.37
ZnPc	ethanol	342	*b*	666	672	0.40
IZ	water	343	*c*	670	678	0.23
IZ	PBS(200,7)	343	636	669	679	0.21
IIZ	water	338	636	666	684	0.09
IIZ	PBS(200,7)	337		665	685	0.01
IIIZ	water	338	636	673	683	0.19
IIIZ	PBS(200,7)	338		672	683	0.03

[a] See Table I for the definitions of IA, IIA, IIIA, IZ, IIZ, and IIIZ. PBS(*x*,*y*) stands for phosphate-buffered saline at *x* mM ionic strength and pH *y*. [b] No dimer peak. [c] Dimer peak not clearly resolved.

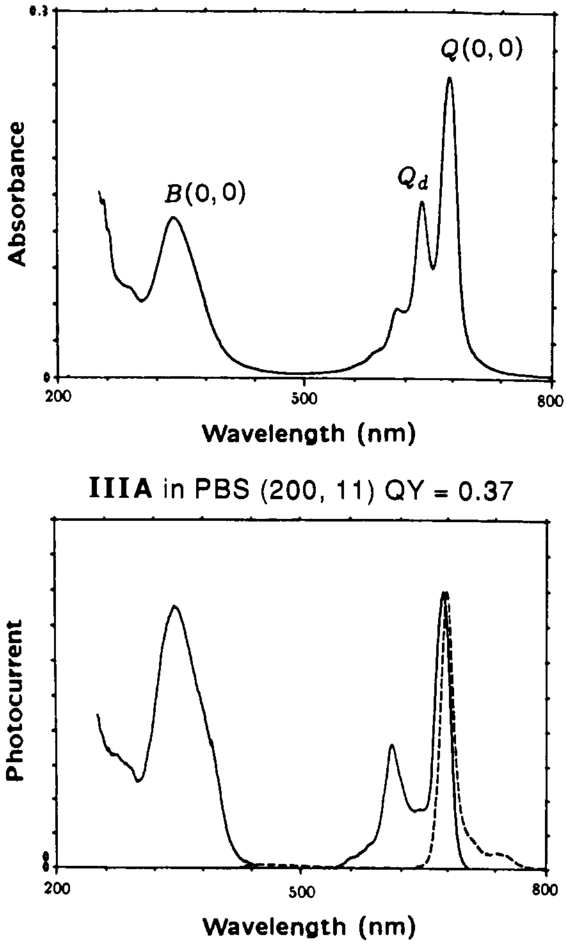

Figure 2. IIIA in PBS(200,11). The top of the figure is the absorbance spectrum. The bottom half consists of an overlay of the emission (dashed) and excitation (solid) spectra. The dimer band is denoted as Q_d.

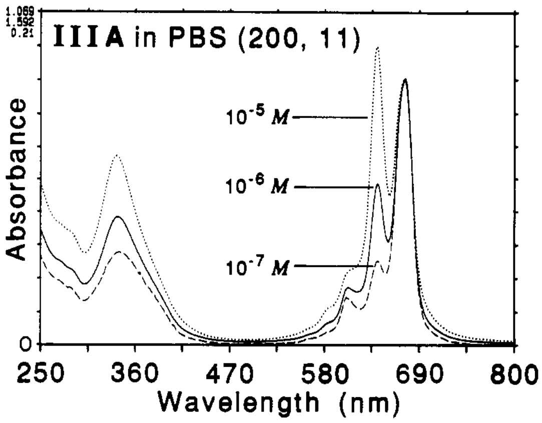

Figure 3. IIIA in PBS(200,11) at three different concentrations: 1 × 10^{-5} M in 1 mm path length cell (dotted); 1 × 10^{-6} M in 1 cm path length cell (solid); 1 × 10^{-7} M in 1 cm path length cell (dashed). The maximum ordinate values are 1.069, 1.592, and 0.21, respectively.

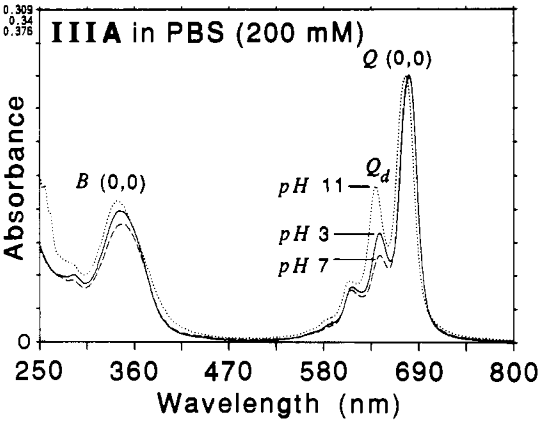

Figure 4. Overlay of the absorbance spectra of IIIA in PBS(200,3) (solid), PBS(200,7) (dashed), and PBS(200,11) (dotted). The spectra are normalized to the red envelope. The maximum ordinate values are 0.34, 0.376, and 0.31, respectively.

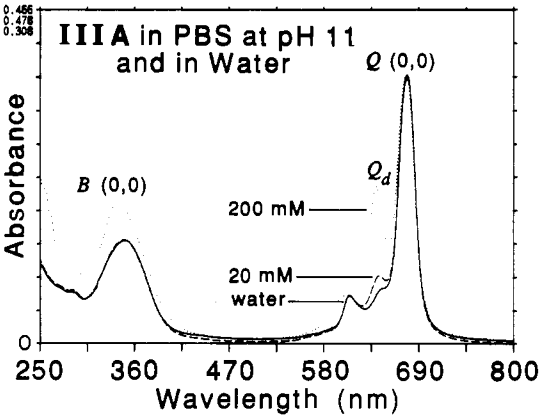

Figure 5. Overlay of the absorbance spectra of IIIA in water (solid), PBS(20,11) (dashed), and PBS(200,11) (dotted). The spectra are normalized to the red envelope. The maximum ordinate values are 0.466, 0.478, and 0.308, respectively.

Figure 6 compares the visible absorption of IIIA and IIIZ at similar concentrations in distilled water at neutral pH. We note from the figure that while IIIA shows essentially no Q_d band, this band contains most of the red absorbance in IIIZ. In Figure 7 we examine a subtle difference between the Q_d bands of IIIA and IIIZ in a 0.2 M NaCl solution. The Q_d band of IIIA is much sharper than that of IIIZ. This suggests that the species responsible for the Q_d band in IIIA has more constrained geometry than the species causing the band in IIIZ.[24]

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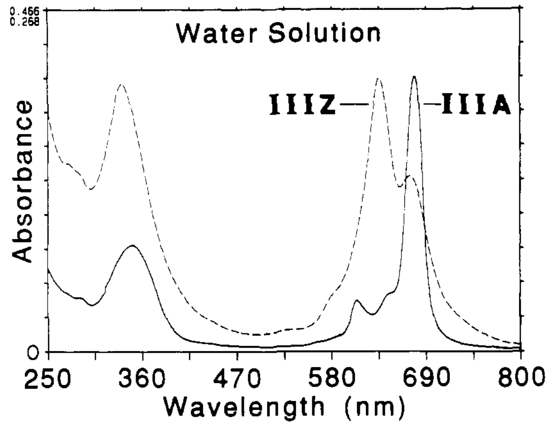

Figure 6. Overlay of the absorbance spectra of IIIA (solid) and IIIZ (dashed) in water at similar concentrations. The maximum ordinate values are 0.466 and 0.2, respectively.

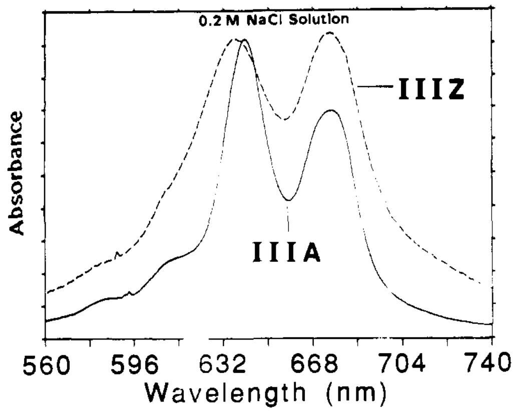

Figure 7. Overlay of the red regions of the absorbance spectra of IIIA (solid) and IIIZ (dashed) in 0.2 M NaCl solution. The maximum ordinate values are 0.466 and 0.268, respectively.

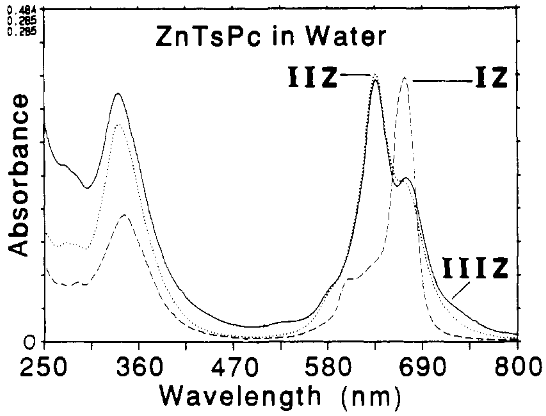

Figure 8. Comparison of the visible absorbance spectra for IZ (dashed), IIZ (dotted), and IIIZ (solid) in distilled water at neutral pH. The maximum ordinate values are 0.285, 0.484, and 0.285, respectively.

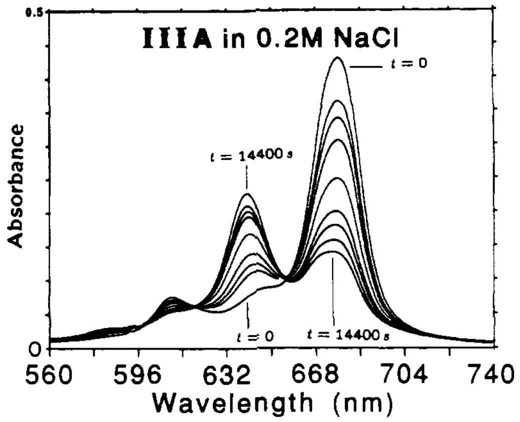

Figure 9. Overylay of the absorbance spectra of dimerizing IIIA in 0.2 M NaCl. The spectrum with the maximum absorbance at 680 nm is that of IIIA in pure water. The others occur at t = 12, 80, 285, 625, 1200, 1800, 3600, and 14400 s after the addition of solid NaCl. Note the isosbestic points at 598, 619, and 656 nm.

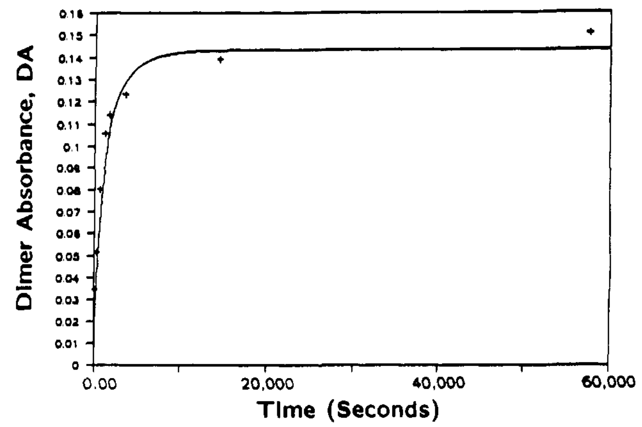

Figure 10. Change in the Q_d absorbance at 648 nm with time for IIIA in water after adding solid NaCl. The final ionic strength is 0.2 M. Plus signs are data points. The solid line is a fit of eq 4. (See text for parameters.) DA defined in eq 2.

The emission yield data for the zinc compounds are also included in Table II. Like the case of aluminum phthalocyanine dimers, excitation in the Q_d band of the zinc phthalocyanine compounds gives no detectable luminescent emission. Unlike the aluminum-based phthalocyanines, zinc phthalocyanines require organic solvents or micellular solutions to remain monomeric.

Figure 8 compares the visible absorption spectra for the three zinc phthalocyaninesulfonates: IZ, IIZ, and IIIZ. Since these molecules have a higher tendency toward aggregation, neutral distilled water was chosen as the solvent environment. IIZ and IIIZ show simiarly intense Q_d bands, while IZ shows only a little dimerization.

Figure 9 is an overlay of the absorbance spectra observed after the addition of solid NaCl to an aqueous solution of IIIA to reach a salt concentration of 0.2 M. The presence of isosbestic points shows that only two absorbing substances are present in solution and also supports the model given in eq 3. The appearance of the Q_d band was also observed for IIA under similar conditions. However, in this case the band is apparent in the first spectrum taken within 1 min of mixing.

Figure 10 is a plot of the absorbance of the Q_d band observed in Figure 9 versus time after the addition of solid NaCl. Also, we have an overlay of the mathematical model given in eq 4. As shown, equilibrium required 4 h. The solid line was plotted for values of $k_f' = 0.09$ s^{-1}, $k_r = 0.004$ s^{-1}, and $DA_d = 0.175$ in eq 4. The agreement between the experimental data and analysis by eqs 3 and 4 gives good support to a dimerization model.

Discussion

The addition of sulfonate groups to the phthalocyanine ring renders the compound water soluble. The three synthetic methods reported above all produce water-soluble sulfonated aluminum phthalocyanines. Compounds IA and IZ differ from the others in having, on the average, only three sulfonate groups per ring; compounds IIA and IIZ may differ from IIIA and IIIZ in the position of the sulfonate groups. Additionally, IIA and IIIA may differ by the fifth ligand on the aluminum.

We have shown that there are very different behaviors with regard to Q_d band formation among the six compounds studied. In water, trisulfonated IA and IZ show very little Q_d and strong emission, suggesting little dimerization or aggregation. However, the tetrasulfonated IIZ and IIIZ derivatives in water show more than 50% of their red absorbance in the Q_d band, which forms immediately. We interpret this as forming "contact dimers".

Similar behavior in water is shown by the tetrasulfonate IIA, which shows a broad intense Q_d band immediately on addition to water. The band is enhanced with incresed ionic strength.

The tetrasulfonate IIIA, however, shows very different behavior. Its Q_d band forms slowly over 4 h when ionic strength is increased and is substantially narrower than that observed in the other cases. We would like to interpret this "slow dimer formation" as formation of the binuclear μ-oxo species:

$$2HOAlTsPc = [AlTsPc]_2O + H_2O \qquad (6)$$

Why are IIA [formed by H_2TsPc plus $Al(acac)_3$] and IIIA [formed by $AlCl_3$ and sulfophthalic acid] so different? There is some evidence that the acetylacetonate ligand is not displaced by a hydroxo ligand. However, attempts to establish the presence of an acetylacetonate ligand by mass spectrometry and by NMR and FTIR spectroscopy gave ambiguous results. Both IIA and IIIA are tetrasulfonates, so we believe that a tightly bound ligand is the reason for their different behaviors rather than some subtle difference in the isomer types contained in each sample.

Our results closely parallel those of Wagner et al.,[9b] who reported on the photochemical activity of selectively sulfonated gallium phthalocyanines. The found that more highly sulfonated phthalocyanines have greater tendency to dimerize and have lower photochemical quantum yields. They did not report on any kinetics for dimer formation, and their spectra suggest that the gallium phthalocyanines form contact dimers rather than μ-oxo binuclear species.

Finally, assuming that the Q_d band of IIIA is indeed due to a binuclear μ-oxo species, we wish to compare its excited-state properties and likely structure to those of the closely related silicon phthalocyanines. An X-ray structure for $[Al(Pc)]_2O$ has been reported by Wynne.[25] This shows that the phthalocyanine rings are eclipsed and separated by 4.27 Å. The Al atoms are 0.459 Å above the least-squares plane of the ring. We note that the monomer peak of IIIA is at 677 nm and the Q_d peak at 648 nm, a shift of 660 cm^{-1}. In the very comparable dimer $[Si(Pc)OR]_2O$ with $R = Si[C(CH_3)_3](CH_3)_2$, studied by Marks and co-workers,[26] the Si atoms are planar within the phthalocyanine rings. The rings are also somewhat staggered and separated by 3.33 Å. In this case, the dimer peak is at 635 nm and the monomer peak at 670.5 nm, a shift of 830 cm^{-1}. This larger shift is consistent with a smaller ring-ring separation in the Si dimer. In both dimers, the M-O-M (M = Al or Si) axis is essentially linear and perpendicular to the ring planes. Wheeler et al.[27] have reported that $[Si(Pc)OR]_2O$ does not fluoresce, as in our study.

The quenching of fluorescence in these dimers is important for their uses as fluorescence monitors and as photochemical sensitizers. Thus, the report here on the effect of variable sulfonation on the dimerization of aluminum phthalocyaninesulfonates should be valuable to research workers who wish to use the molecules for photochemical purposes. It also poses a challenge to isolate and study the binuclear μ-oxo aluminum tetrasulfonate species suggested by our kinetic spectroscopic observations.

Registry No. IA, 131582-87-1; IIA, 134418-66-9; IIIA, 134391-41-6; IZ, 61569-02-6; IIZ, 61586-86-5; ClAlPc, 14154-42-8; ZnPc, 14320-04-8; $Al(acac)_3$, 13963-57-0; $Zn(acac)_2$, 14024-63-6; H_2TsPc, 7790-94-5; $AlCl_3$, 7446-70-0; $ZnSO_4{}^+$, 7733-02-0; sulfophthalic acid, 26657-75-0.

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Synthesis and Properties of Trimeric Ortho-Chelated (Arenethiolato)copper(I) Complexes

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Neutral (arenethiolato)copper(I) complexes $[CuSC_6H_3(CH(R')NMe_2)\text{-}2\text{-}R''\text{-}3]_3$ (R' = H, R'' = H, Cl; R' = Me, R'' = H) with an intramolecularly coordinating ligand have been prepared and characterized. Crystals of $[CuSC_6H_4(R\text{-}CH(Me)NMe_2)\text{-}2]_3\cdot THF$ are hexagonal, space group $P6_3$, with $a = 13.743$ (1) Å, $b = 11.248$ (1) Å, $V = 1839.8$ (3) Å^3, $Z = 2$, and final $R = 0.054$ for 1448 reflections with $I \geq 2.5\sigma(I)$ and 140 variables. The crystals are triboluminescent. The structure contains a Cu_3S_3 six-membered ring in a chairlike conformation with alternating copper and sulfur atoms, and on each sulfur atom the $C_6H_3(R\text{-}CH(Me)NMe_2)\text{-}2$ group is bonded equatorially with respect to this ring. Coordination of the nitrogen atoms of the o-CH(Me)NMe$_2$ substituents to the copper atoms (Cu-N = 2.077 (7) Å) provides three six-membered CuSCCCN chelate rings. The bridge bonding of the arenethiolate has striking structural features, an acute Cu-S-Cu angle of 79.63 (7)°, Cu-S bond lengths of 2.231 (2) Å and 2.186 (2) Å, and a short Cu···Cu distance of 2.828 (1) Å. These features reflect an electron-deficient two-electron three-center Cu_2S bond in which there is interaction of a sulfur sp^2 hybrid orbital with a bonding combination of empty orbitals on the two copper atoms. In solution the $[CuSC_6H_3(CH(R')NMe_2)\text{-}2\text{-}R''\text{-}3]_3$ complexes remain trimeric but exist as two conformers that are in equilibrium through inversion at the bridging sulfur atoms. ^1H and ^{13}C NMR studies reveal that the ratio of these two conformers can be influenced by changing R' and R'' in the arenethiolate ligand. The low free activation energy barrier ($\Delta G^{‡} = \pm 50$ kJ/mol) for sulfur inversion is explained by a new mechanism which is based on a rotation (wagging) process around the axis through the sp^2 hybrid orbital in the electron-deficient Cu_2S unit. Evidence for the occurrence of separate intermolecular exchange processes is presented.

Introduction

Investigations of (thiophenolato)copper(I) complexes[1] in the solid state show them to be polynuclear and to usually contain anionic units of the type $[Cu_n(SAr)_{n+m}]^{m-}$.[2-4] The structural features of copper(I) alkanethiolates are quite similar to those of copper(I) arenethiolates.[4] In general, copper(I) thiolates in

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(1) In this paper (thiophenolato)copper(I) complexes are referred to as copper(I) arenethiolates.

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