Articles

Cooperative Static Quenching of the S_1-S_0 Fluorescence of Tetrasulfonated Aluminum Phthalocyanine by Azaferrocene and an Organic Donor (Imidazole, 4-Aminopyridine)

Janusz Zakrzewski,*,†,‡ Charles Giannotti,§ and Jacques Delaire†

PPSM Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires, CNRS UMR 8531, Ecole Normale Supérieure de Cachan, 94235 Cachan Cedex, France, and Institut de Chimie des Substances Naturelles, CNRS, Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex, France

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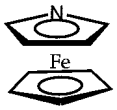
The S_1-S_0 fluorescence of tetrasulfonated aluminum phthalocyanine ($AlPcS_4^{3-}$) is quenched by azaferrocene (AF) by both dynamic and static quenching, the last being due to the complexation of two molecules of AF by the phthalocyanine (presumably to its axial sites). Fluorescence quenching studies revealed that some other nitrogen ligands can cooperate with AF, giving nonfluorescent, mixed hexacoordinate adducts. This leads to "cooperative" static quenching observed for imidazole and 4-aminopyridine.

Introduction

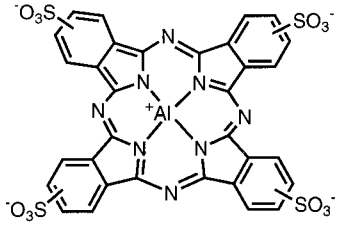
In recent years, considerable effort has been devoted to studies of photophysical and photochemical properties of metallophthalocyanines in homogeneous solutions[1−7] as well as in organized media.[8,9] The closed-shell metal ion phthalocyanines display fluorescence between 600 and 700 nm, with a decay time shorter than 10 ns, which is attributed to the S_1-S_0 transition.[1,2] A weak emission observed in experiments with excitation into the Soret band (360 nm) at around 450 nm is believed to originate from the metallophthalocyanine excited S_2 state.[2] Examples of photoredox reactions involving the metallophthalocyanine S_1 state are scarce. It has been found that this state can be oxidized by methyl viologen, anthraquinone, or anthraquinone 2,6-disulfonate with a rate close to the diffusion-controlled limit[1] and reduced by some amines.[9] We have recently found[10] that the S_1-S_0 fluorescence of tetrasulfonated zinc phthalocyanine is quenched by an organometallic iron(II) complex azaferrocene (hereby denoted as AF).



AF

Because AF behaves as electron donor in many photochemical reactions involving porphyrins, phthalocyanines, and naphthalocyanines[11] and, in particular, it reduces excited tetrasulfonated zinc phthalocyanine $ZnPcS_4^{4-}$ to the corresponding radical anion,[11d] this quenching can be attributed to the electron transfer from AF to the phthalocyanine S_1 state. The Stern−Volmer analysis showed that both dynamic and static quenching (i.e., formation of a nonfluorescent ground-state complex between the phthalocyanine and AF) are observed.

In this paper we report on the fluorescence quenching of closely related tetrasulfonated aluminum phthalocyanine ($AlPcS_4^{3-}$) by AF itself and AF in the presence of some organic



$AlPcS_4^{3-}$

nitrogen bases (imidazole, pyridine, and 4-aminopyridine). We believe that these results shed new light on the axial ligation of these compounds by $AlPcS_4^{3-}$.

† Ecole Normale Supérieure de Cachan.

‡ On leave from Department of Organic Chemistry, University of Lodz, 90-136 Lodz, Narutowicza 68, Poland.

§ Institut de Chimie des Substances Naturelles.

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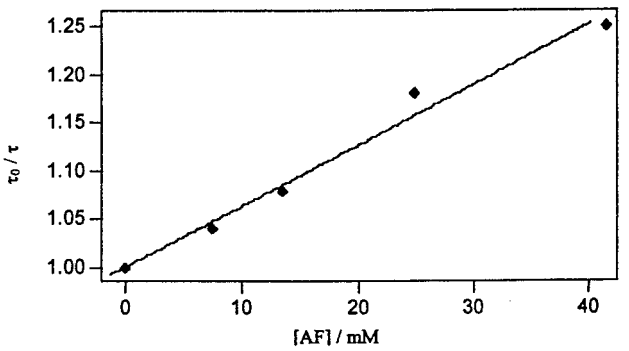


Figure 1. Stern−Volmer plot of the fluorescence lifetimes of $AlPcS_4^{3-}$ in DMSO solutions containing increasing concentrations of AF ($[AlPcS_4^{3-}] = 6 \times 10^{-6}$ M). Irradiation wavelength is 660 nm.

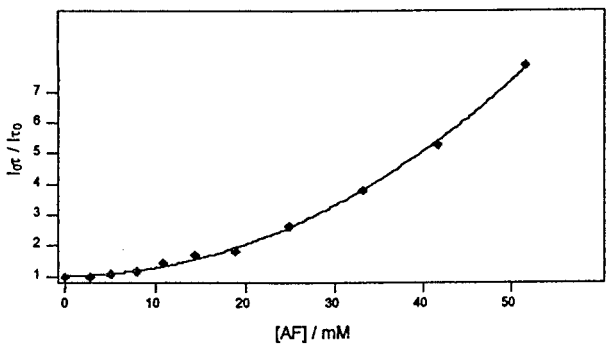


Figure 2. Static quenching of $AlPcS_4^{3-}$ fluorescence by AF, illustrated by plot of $I_0\tau/(I\tau_0)$ vs [AF]. The fluorescence lifetimes are those of Figure 1. The fluorescence intensities have been measured in DMSO solutions ($[AlPcS_4^{3-}] = 6 \times 10^{-6}$ M), with an irradiation wavelength fixed at 660 nm and an analysis wavelength fixed at 691 nm. The curve is fitted according to eq 1.

Results and Discussion

Dynamic Quenching of the S_1-S_0 Fluorescence of $AlPcS_4^{3-}$ by Azaferrocene. The quenching of fluorescence may occur through either dynamic quenching or static quenching. In dynamic quenching, the fluorophore in its excited state and the quencher diffuse toward each other to form the encounter complex and subsequently energy transfer or electron transfer takes place. In static quenching, a ground-state complex is formed between the fluorophore and the quencher that does not emit in the excited state. Such a complex is called a dark complex.

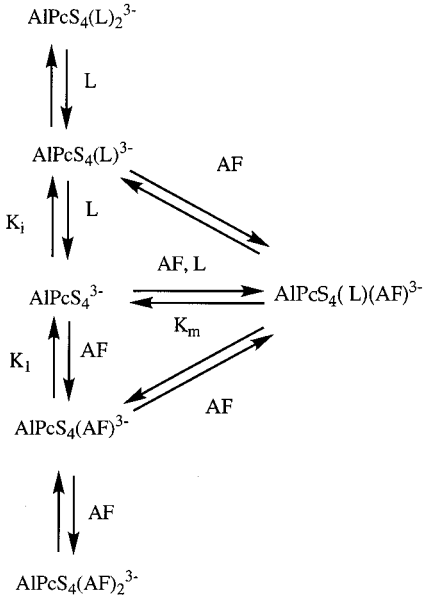
The insight into dynamic quenching of the fluorescence of $AlPcS_4^{3-}$ by AF was provided by the measurements of the fluorescence lifetimes (τ) at various concentrations of this quencher in dimethyl sulfoxide (DMSO) solutions. These measurements were done by using a multifrequency phase-modulation technique. The phthalocyanine concentration was 6×10^{-6} M. It has been checked by the electronic absorption spectra that at this concentration phthalocyanine is mainly monomeric. The measured fluorescence lifetime in the absence of AF ($\tau_0 = 6.4$ ns) is longer than the reported value (5.0 ns, measured in methanol−ethanol at 298 K) and closer to the value reported for nonsulfonated aluminum phthalocyanine (6.8 ns).[1] The Stern−Volmer plot of τ_0/τ as a function of the AF concentration is shown in Figure 1.

The calculated bimolecular rate constant, 10^9 M^{-1} s^{-1}, is about 10 times lower than the value measured for $ZnPcS_4^{4-}$, 1.1×10^{10} M^{-1} s^{-1}.[10] In our opinion, this difference may be due to the higher positive charge of the central ion, which favors solvation of metallophthalocyanine macrocycle by DMSO and therefore decreases the frequency of collisions with the molecules of AF.

Static Quenching of the S_1-S_0 Fluorescence of $AlPcS_4^{3-}$ by Azaferrocene. The measure of the static quenching is the value $I_0\tau/(I\tau_0)$.[12] When only dynamic quenching takes place, $I_0\tau/(I\tau_0) = 1$ and values higher than 1 indicate a contribution of a static quenching. The fluorescence intensities of $AlPcS_4^{3-}$ were measured under steady-state conditions at 691± 1 nm (excitation at 660 nm).

The plot of $I_0\tau/(I\tau_0)$ against AF concentration is shown in Figure 2. This plot points out a predominant contribution of the static quenching at AF concentrations higher than around 20 mM. This means that $AlPcS_4^{3-}$ is able to bind AF presumably to the axial coordination sites of the central metal ion and the resulting complex(es) is (are) nonfluorescent. In fact, there is some evidence in the literature for the formation of coordination complexes of metallophthalocyanines and nitrogen bases, although systematic studies of this phenomenon are still lacking. Undoubtely, such studies are hampered by a very limited solubility of phthalocyanines (especially nonsubstituted ones) and by the fact that axial coordination of nitrogen bases practically leads to no change of the absorption spectra of these macrocyclic systems.[2] Conversely, there is ample evidence that AF behaves as a relatively good ligand for the axial sites of systems closely related to phthalocyanines, such as metalloporhyrins and cobaloximes.[11]

Scheme 1. Complexation Equilibria between $AlPcS_4^{3-}$, Azaferrocene, and Other Nitrogen Ligands



We have considered formation of two complexes between $AlPcS_4^{3-}$ and AF: $(AlPcS_4)(AF)^{3-}$ and $(AlPcS_4)(AF)_2^{3-}$ (Scheme 1). Assuming stationary-state conditions for the S_1 excited states under steady-state illumination, one can express the fluorescence intensity (I) of such a system by the following equation:

$$I = \frac{k_F}{k_S + k_q[AF]} I_{abs} + \frac{k'_F}{k'_S + k_q[AF]} I'_{abs} + \frac{k''_F}{k''_S + k_q[AF]} I''_{abs} \quad (1)$$

where I_{abs}, I'_{abs} and I''_{abs} stand for the rate of light absorption by $AlPcS_4^{3-}$, $AlPcS_4(AF)^{3-}$, and $AlPcS_4(AF)_2^{3-}$, respectively, k_F, k'_F, and k''_F are radiative rate constants for $AlPcS_4^{3-}$,

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$AlPcS_4(AF)^{3-}$, and $AlPcS_4(AF)_2^{3-}$, respectively, k_S, k'_S, and k''_S are rate constants for the decay of the S_1 states of $AlPcS_4^{3-}$, $AlPcS_4(AF)^{3-}$, and $AlPcS_4(AF)_2^{3-}$, respectively, and k_q is the bimolecular rate constant for the dynamic quenching of the S_1 state by AF (we assume that k_q is the same for all phthalocyanine complexes existing in solution because no deviation from the monoexponential decay of fluorescence was observed upon addition of AF).

Because addition of azaferrocene does not change the absorption at the excitation wavelength, the rate of light absorption is proportional to the concentration of the corresponding species with a proportionality coefficient α. The analytical phthalocyanine concentration can be expressed as follows:

$$[AlPcS_4^{3-}]_0 = [AlPcS_4^{3-}] + [AlPcS_4(AF)^{3-}] + [AlPcS_4(AF)_2^{3-}] \quad (2)$$

In the absence of AF,

$$I = I_0 = \frac{k_F}{k_S} I_{abs} = \alpha \frac{k_F}{k_S} [AlPcS_4^{3-}]_0 \quad (3)$$

Because a priori we know nothing about the fluorescent behavior of the above complexes, we considered three hyphotheses.

1. If both complexes are nonfluorescent (dark) ($k'_F = k''_F = 0$), then the fluorescence intensity is

$$I = \alpha \frac{k_F}{k_S + k_q[AF]} [AlPcS_4^{3-}] \quad (4)$$

According to eq 2, it becomes

$$I = I_0 \frac{k_F}{k_S + k_q[AF]} \frac{1}{1 + K_1[AF] + K_2[AF]^2} \quad (5)$$

After introduction of lifetimes τ and τ_0 for the phthalocyanine in the presence and in the absence of AF, respectively, it becomes

$$\frac{I_0\tau}{I\tau_0} = 1 + K_1[AF] + K_2[AF]^2 \quad (6)$$

2. $(AlPcS_4)(AF)^{3-}$ is fluorescent, and $(AlPcS_4)(AF)_2^{3-}$ is dark ($k'_F \neq 0$ and $k''_F = 0$). Assuming $k'_F = k_F$, a similar treatment leads to

$$\frac{I_0\tau}{I\tau_0} = 1 + \frac{K_2[AF]^2}{1 + K_1[AF]} \quad (7)$$

Hence,

$$\frac{1}{\frac{I_0\tau}{I\tau_0} - 1} = \frac{K_1}{K_2[AF]} + \frac{1}{K_2[AF]^2} \quad (8)$$

3. $(AlPcS_4)(AF)_2^{3-}$ is fluorescent, and $(AlPcS_4)(AF)^{3-}$ is dark ($k''_F \neq 0$ and $k'_F = 0$). Assuming that $k''_F = k_F$, a similar treatment leads to

$$\frac{I_0\tau}{I\tau_0} = 1 + \frac{K_1[AF]}{1 + K_2[AF]^2} \quad (9)$$

This equation, however, introduces negative deviations from the straight line $I_0\tau/(I\tau_0) = 1 + K_1[AF]$, which are not observed, and therefore, this hyphothesis will be rejected.

We have obtained a good fitting of $I_0\tau/(I\tau_0)$ by a binomial expression (eq 6) with $K_1 = (7.5 \pm 620) \times 10^{-2}$ M^{-1} and $K_2 = 2540 \pm 120$ M^{-2}. In case 2, the quantity $1/(I_0\tau/(I\tau_0) - 1)$ vs $1/[AF]$ was fitted by a binomial expression to give $K_1 = 4 \pm 20$ M^{-1} and $K_2 = (3.3 \pm 0.3) \times 10^3$ M^{-2}.

It is seen that both models lead to a similar value of $K_2 = (2.9 \pm 0.4) \times 10^3$ M^{-2}, whereas they give only a very rough estimation of K_1, endowed with a large error. Because the calculated values are low, we suggest that within experimental error $K_1 = 0$. We have verified that the acceptable fitting of the experimental data can be obtained assuming $K_1 = 0$ and $K_2 = 2.9 \times 10^3$ M^{-2}. The equilibrium concentration of $AlPcS_4(AF)^{3-}$ is presumably very low (if not equals zero), and the question of whether it is dark or not cannot be addressed.

According to the above data, $AlPcS_4^{3-}$ displays a significant preference for formation of the bisazaferrocene adduct, $AlPcS_4(AF)_2^{3-}$. Such a preference for the formation of bis-ligated complexes is a well-known phenomenon in the coordination chemistry of metalloporphyrins (e.g., iron porphyrins).[13] We have also reported that AF displays an unusual preference for formation of a bis-ligated complex with 5,10,15,20-tetrakis-(pentafluorophenyl)porphyrinatocobalt(II).[14]

Static Quenching of the S_1-S_0 Fluorescence of $AlPcS_4^{3-}$ by Azaferrocene and an Organic Base L (Imidazole, Pyridine, and 4-Aminopyridine). If the static quenching of the $AlPcS_4^{3-}$ fluorescence by AF is due to formation of the ground-state complex(es) between both partners, one could expect that addition of another ligand L that would compete with AF in coordination to $AlPcS_4^{3-}$ and that does not quench the metallophthalocyanine fluorescence will influence the quenching. Therefore, it has been decided to study the quenching by AF in the presence of pyridine, imidazole, and 4-aminopyridine. These organic nitrogen donors are known to form stable complexes with metal macrocyclic systems,[15] and their σ-donor properties (expressed as $pK_A(BH^+)$ values) encompass a relatively broad range (4.5 for AF,[16] 6.65 for imidazole, and 9.29 for 4-aminopyridine[15]).

In control experiments, it has been ascertained that in the absence of AF, none of these compounds quenches the $AlPcS_4^{3-}$ fluorescence even at concentrations as high as 0.5 M. Cyclic voltammetry showed that they are neither oxidized nor reduced between −1 and +1.1 V vs SCE, where the electron-transfer quenching of of the S_1 state of $AlPcS_4^{3-}$ is thermodynamically favorable[1] (AF is oxidized at +0.65V vs SCE[17]). The concentration of AF was then settled at 0.028 M (this results in I_0/I around 1.7), and the observed fluorescence intensity was taken as I'_0 for constructing the Stern−Volmer plots. The results obtained are presented in Figure 3.

As can be seen, the presence of imidazole or 4-aminopyridine markedly influences $I'_0\tau/(I\tau_0)$. In contrast, we have found that

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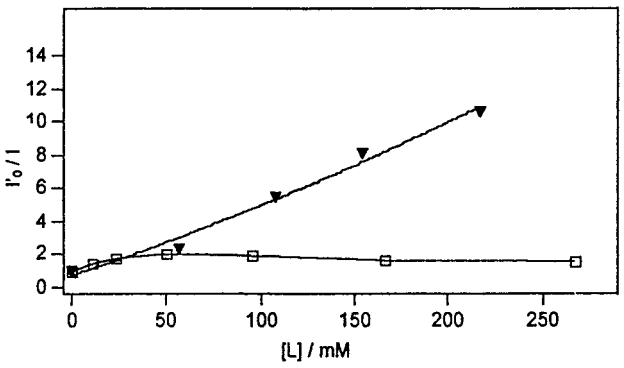

Figure 3. Steady-state fluorescence quenching of $AlPcS_4^{3-}$ by AF and an organic base L (▼, imidazole; □, 4-aminopyridine): $[AlPcS_4^{3-}] = 6 \times 10^{-6}$ M; [AF] = 0.028 M. The reference intensity I'_0 is measured in the presence of AF. The curves are interpolated between the experimental points using a binomial function of [L].

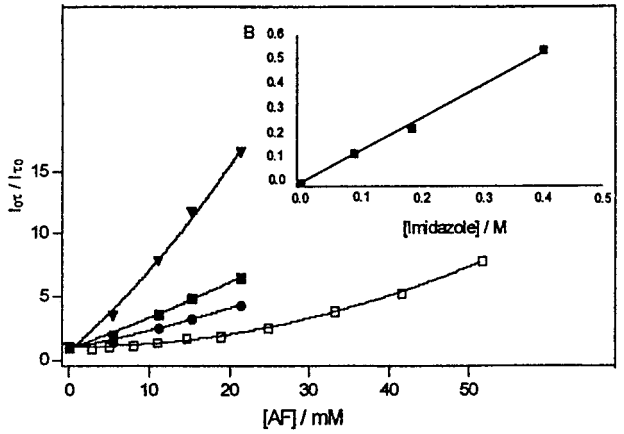

Figure 4. Cooperative static quenching of $AlPcS_4^{3-}$ by AF and imidazole (Im). The different plots correspond to different concentrations of Im (□, [Im] = 0; ●, [Im] = 0.09 M; ■, [Im] = 0.18 M; ▼, [Im] = 0.4 M). The curves are fitted according to a binomial function vs [AF]. The inset is a plot of the linear *B* coefficient vs [Im] (see text).

pyridine does not display the same effect and that $I'_0\tau/(I\tau_0)$ in its presence remains equals 1.00 ± 0.04. For imidazole, Stern−Volmer plots of $I'_0\tau/(I\tau_0)$ as a function of [AF] were also obtained for various concentrations of this organic ligand; they are gathered in Figure 4.

The influence of L on the quenching of the $AlPcS_4^{3-}$ fluorescence by AF can be explained in terms of the coordination equilibria shown in Scheme 1. We assume formation, apart from $AlPcS_4(AF)^{3-}$ and $AlPcS_4(AF)_2^{3-}$, of fluorescent mono- and bis-ligated complexes $AlPcS_4(L)^{3-}$ and $AlPcS_4(L)_2^{3-}$ (these complexes must be fluorescent because L species do not quench the $AlPcS_4^{3-}$ fluorescence) and a dark mixed complex $AlPcS_4(AF)(L)^{3-}$. For such equilibria, the following equation can be derived:

$$\frac{I'_0\tau}{I\tau_0} = 1 + \frac{K_1 + K_m[\mathrm{L}]}{1 + K_i[\mathrm{L}] + K_j[\mathrm{L}]^2}[\mathrm{AF}] + \frac{K_2}{1 + K_i[\mathrm{L}] + K_j[\mathrm{L}]^2}[\mathrm{AF}]^2 \quad (10)$$

In the case of imidazole, a fitting of $I'_0\tau/(I\tau_0)$ by a binomial expression $A + B[\mathrm{AF}] + C[\mathrm{AF}]^2$ showed that the uncertainty of the *C* coefficient is so significant that the values for *C* are useless for discussion of the complexation equilibria in the system $AlPcS_4^{3-}$−AF−imidazole. Besides, it has been found that the linear coefficient *B* is proportional to [L]. This can be explained assuming that equilibrium constants for formation of $AlPcS_4(L)^{3-}$ and $AlPcS_4(L)_2^{3-}$ are small, close to 0. Indeed, under these circonstances and if $K_1 = 0$ (see earlier discussion), the linear coefficient should be equal to K_m[L] (see eq 10). Hence, the K_m value can be calculated (see inset of Figure 4). We have obtained $K_m = (1.4 \pm 0.1) \times 10^3$ M^{-2}.

The K_m value can also be derived from the plot of $I'_0\tau/(I\tau_0)$ against [L] for a fixed concentration of AF as in this case the linear coefficient is K_m[AF]. The value obtained by this way is $K_m = (1.4 \pm 0.5) \times 10^3$ M^{-2}, which nicely corroborates the value gotten from the plot of $I_0\tau/(I\tau_0)$ against [AF].

Finally, when we fitted $I'_0\tau/(I\tau_0)$ versus [AF] with a linear function assuming that the slope is K_m[L], we obtained $K_m = (1.9 \pm 0.2) \times 10^3$ M^{-2}. The fitting in this case was not as good as that with a binomial function, and the value obtained in this way is probably slighty overestimated. In the case of L = 4-aminopyridine, the obtained plot of $I'_0\tau/(I\tau_0)$ against [L] is not a monotonic function (see Figure 3). At low concentrations of this ligand, a slight enhancement of $I'_0\tau/(I\tau_0)$ is observed with a maximum at around 0.05 M and then the value of this expression smoothly drops. In terms of eq 5, this means that in this case K_i and K_j may be comparable with K_m. The maximum of $I'_0\tau/(I\tau_0)$ corresponds presumably to the maximum concentration of the "mixed" bis-ligated dark adduct $AlPcS_4(AF)(L)^{3-}$, which, at higher concentrations of L, is transformed into luminescent adducts $AlPcS_4(L)^{3-}$ and $AlPcS_4(L)_2^{3-}$.

As a conclusion, we think that the influence of L on the fluorescence of the system containing $AlPcS_4^{3-}$, AF, and L is a delicate balance between different equilibria shown in the Scheme 1. For L = pyridine, K_i, K_j, and K_m are small, presumably close to zero, and addition of this ligand does not influence fluorescence observed in the $AlPcS_4^{3-}$−AF system. For L = imidazole, which is a better ligand for metal macrocyclic system, K_i and K_j are still close to zero whereas the K_m value is significantly higher, leading approximately to a proportionality of $I'_0\tau/(I\tau_0)$ with the concentration of imidazole. This result, together with the observed preference for the formation of $AlPcS_4(AF)_2^{3-}$, means that coordination to $AlPcS_4^{3-}$ of either AF or imidazole facilitates binding of the second AF ligand. There is therefore a "cooperation" of these two ligands in static quenching of the $AlPcS_4^{3-}$ fluorescence.

Finally, for L = 4-aminopyridine, all K_i, K_j, and K_m are relatively high (and comparable to each other), which leads to the preferential formation of a luminescent complex $AlPcS_4(L)_2^{3-}$ at high concentrations of this ligand and limits our ability to observe ligand-binding cooperation.

The results obtained in this work are worthy to be put in a more general perspective concerning coordination of axial ligands to metallophthalocyanines. This coordination usually does not result in pronounced changes in electronic aborption spectra of metallophthalocyanines and therefore cannot be studied by visible absorption spectroscopy. We have found that by using a ligand that forms dark complexes with a fluorescescent phthalocyanine, a deep insight into coordination equilibria existing in phthalocyanine solutions can be gained from the steady-state fluorescence studies. In particular, the cooperative effects observed in the system $AlPcS_4^{3-}$−AF−L provide spectacular evidence for the existence of bis-ligated species in this system.

Experimental Section

Materials. AF was prepared and purified according to an earlier published procedure.[18] $AlPcS_4^{3-}$ (Porphyrin Inc.) and DMSO (Aldrich, A.C.S. spectrophotometric grade) were used as received. Organic amines (Aldrich, reagent grade) were purified by standard procedures (distillation, crystallization).

Methods. The fluorescence lifetimes were measured using a multifrequency (0.1−200 MHz) phase modulation fluorometer described earlier,[19] operating according to the principle developed by Gratton and Limkeman.[20] Samples were excited with a 10 mW He−Ne laser (Hughes Aircraft). Fluorescence was detected through a cutoff filter (Schott RG 645). Dilute aqueous suspensions of silica (Ludox HS40 from Dupont) were used as a scattering reference.

The fluorescence intensities were measured on a Spex Fluorolog (Jobin Yvon) spectrofluorometer and were corrected for the wavelength response of the photodetector. The nitrogen-saturated solutions were excited at 660 nm to give the emission spectra with $\lambda_{max} = 690 \pm 1$ nm. All the florescence intensity measurements were carried out at λ_{max}.

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