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Journal of Photochemistry and Photobiology A: Chemistry 112 (1998) 205–207

Journal of Photochemistry and Photobiology A:Chemistry

Fluorescence quenching of tetrasulfonated zinc phthalocyanine by azaferrocene

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Accepted 15 September 1997

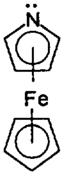
Abstract

It has been found that azaferrocene efficiently quenches the fluorescence from the S_1 state of a sulfonated zinc phthalocyanine $ZnPcS_4$ in DMSO. Both static and dynamic quenching take place. These results are relevant to the high reactivity of azaferrocene observed earlier towards excited states of phthalocyanines or porphyrins.

Keywords: Azaferrocene; Tetrasulfonated zinc phthalocyanine; Fluorescence

1. Introduction

The photochemistry of metallophthalocyanines continues to attract considerable attention because of its relevance in the photoreduction of water to dihydrogen and other visible-light driven conversion processes [1–4] and to the photodynamic therapy of cancer [5,6]. Both phthalocyanine photooxidation and photoreduction can be achieved by the irradiation of the macrocycle in the presence of electron donor or electron acceptor respectively [1]. The electron donors frequently used for the photoreduction of phthalocyanines are organic amines (triethylamine, triethanoloamine, EDTA, etc.) [7–9]. We have recently reported that an *organometallic* amine, azaferrocene (AF) displays especially high electron donor properties towards photoexcited phthalocyanines and naphthalocyanines [10–12].


AF

For example, this donor enabled the photoreduction of tetrasulfonated Zn phthalocyanine, $ZnPcS_4$, in water on irradiation with the red light [11], despite the well-established aggregation of the phthalocyanine, which was believed to destroy any photoredox activity. Organic amines proved completely inactive as electron donors under the same conditions. They are active only in organic solvents and under irradiation into the Soret band [9].

The comparison of redox potentials of the singlet S_1 and triplet T_1 excited states of $ZnPcS_4$ (1.19 and 0.49 V vs. SCE, respectively), with that of the ground state of azaferrocene (0.65 V vs. SCE) [10] suggests that the reductive quenching of the T_1 state is unlikely and therefore, the S_1 state becomes the first candidate for the reactive state (the higher excited states are excluded as photoreduction occurs at irradiation into the Q-band). Obviously, one cannot exclude another possibility—that metallophthalocyanine and azaferrocene form a ground state complex in which redox potentials of both components are changed. It is known that amines are ligated by metallophthalocyanines, practically without changing their absorption spectra, which makes detection of such a ligation extremely difficult [9].

To shed light on the origins of the unusually high electron donor reactivity of azaferrocene towards photoexcited phthalocyanines, we decided to study the influence of AF on the fluorescence resulting from the lowest singlet excited state (S_1) of $ZnPcS_4$. This excited state is populated by irradiation into the phthalocyanine Q-band ($\lambda_{max} = 675$ nm). The experiments were carried out using dilute solutions of $ZnPcS_4$ in dimethylsulfoxide, i.e., conditions under which the phthalo-

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1010-6030/98/$19.00
PII S1010-6030(97)00289-X

cyanine was mainly monomeric. This was confirmed by the electronic absorption spectra exhibiting a strong band at 675 nm characteristic for monomeric $ZnPcS_4$.

2. Results and discussion

The diluted solutions of $ZnPcS_4$ in DMSO contain mainly monomeric phthalocyanine. This can be checked by the presence of the strong Q-band at 675 nm and a weak absorption at ~630 nm, attributed to aggregates as already published [11]. Such solutions (excited into the Q-band) display strong fluorescence centered at 690 nm, originating from the S_1 state [1]. The reported lifetime of this state is 2.9 ns [13]. We have found that the intensity of this fluorescence is markedly reduced in the presence of azaferrocene (Table 1).

The corresponding Stern–Volmer plot is shown in Fig. 1.

The absorption of azaferrocene at the excitation wavelength is negligible and a possibility that this complex acts as internal filter, reducing the intensity of the excitation light, seem very unlikely. However, to exclude this possibility we conducted control experiments in which azaferrocene was replaced by ferrocene (both complexes display practically the same absorption spectra in the region of interest). We have found that there is no quenching of the excited state of $ZnPcS_4$ by ferrocene ($F_0/F = 0.96$ at ferrocene concentration 6.0×10^{-3} mol dm^{-3}). This means that azaferrocene *really quenches the S_1 state of $ZnPcS_4$*. To gain further insight into the nature of the quenching, we have measured the lifetime of this state in DMSO in the absence and presence of AF, using a multifrequency phase-modulation fluorimetry technique [14,15]. The results obtained are shown in Table 2.

Table 1
The fluorescence quenching of $ZnPcS_4$ by azaferrocene (AF) in DMSO

10^3 [AF] (mol dm^{-3})	F_0/F
–	1.00
1.28	1.35
4.49	1.57
6.84	1.84
11.44	2.28

[$ZnPcS_4$] = 2.8×10^{-6} mol dm^{-3}. Excitation at 660 nm.

Table 2
The fluorescence lifetimes of $ZnPcS_4$ in DMSO in the absence and presence of AF

10^3 [AF] (mol dm^{-3})	τ (ns) [a]	τ_0/τ	χ^2 [b]
–	3.10 ± 0.02	1.00	1.12
4.06	2.86 ± 0.02	1.08	1.26
7.92	2.42 ± 0.06	1.28	–

[a] Fluorescence data were analysed according to a first order kinetics. Multiexponential analysis never improved the fitting.

[b] Reduced χ^2 is given with the following standard deviations: 0.06 for the modulation and 0.4 for the phase. Values are given for 20 runs at different frequencies.

The fluorescence lifetime of $ZnPcS_4$ in the absence of AF determined by us (3.1 ns) corroborates well the value reported in the literature (2.9 ns [13]). The results in Table 2 show that the fluorescence lifetimes of $ZnPcS_4$ decrease in the presence of azaferrocene, which suggests a dynamic quenching mechanism. The bimolecular rate constant can be evaluated as equal to 1.1×10^{10} dm^3 mol^{-1} s^{-1}, which is close to the diffusion limit. However, the decrease of the lifetime is markedly weaker than the decrease of the fluorescence intensity (Fig. 1). This means that another

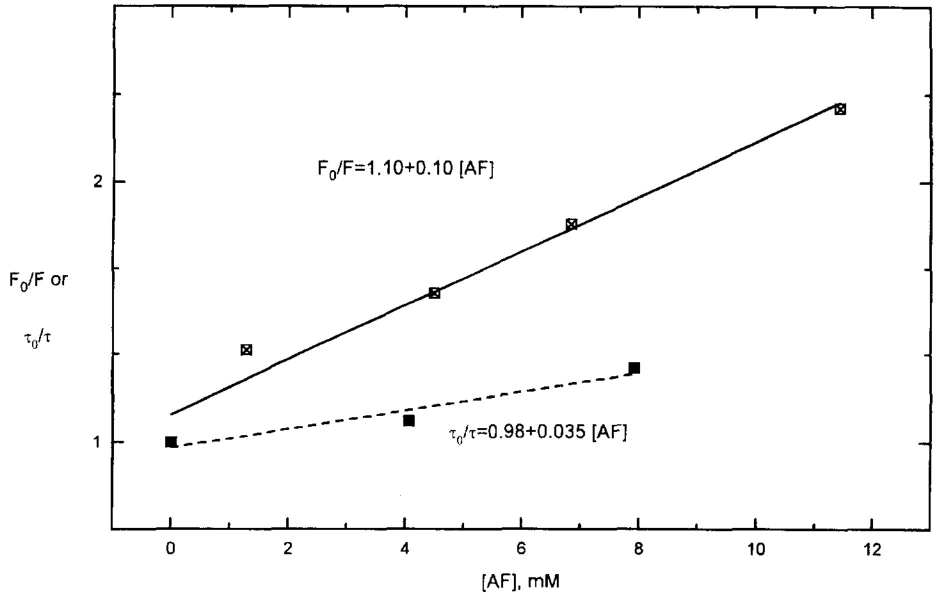

Fig. 1. The Stern–Volmer plots of fluorescence intensities (solid line) and lifetimes (dashed line).

mechanism must operate, presumably a static quenching in the preformed phthalocyanine–azaferrocene adduct. It is known that zinc phthalocyanine coordinate amines, but unfortunately this does not affect their electronic absorption spectra. We were unable to find any evidence of coordination of azaferrocene to $ZnPcS_4$ from the electronic absorption spectra. As azaferrocene displays relatively high coordinating ability towards macrocyclic complexes [10], the formation of a complex phthalocyanine–AF seems very likely.

In the current literature there is an opinion that the photoredox reactions of metallophthalocyanines can originate from either S_1 or T_1 excited states. However, the evidence for the reductive quenching of the S_1 state does not exist. In Ref. [9], Kaneko et al. state that the S_1 fluorescence of $ZnPcS_4$ is not quenched by amines. We fully confirm this statement. In control experiments we did not see any quenching in the presence of imidazole or triethylamine, even at concentrations as high as 10^{-1} mol dm^{-3}. The organic amines are inert at the excitation into the S_1 state of $ZnPcS_4$ and phthalocyanine photoreduction occurs only in the excitation of the Soret band (when higher excited states are populated) [9].

The behavior of azaferrocene is, therefore, completely different and, to our knowledge it is the only amine donor reacting with the S_1 state.

3. Experimental

Azaferrocene was prepared and purified according to an earlier published procedure [16]. $ZnPcS_4$ (Porphyrin Inc.) and DMSO (SDS, analytical purity) were used as received.

The fluorescence intensities were measured on a Spex Fluorolog spectrofluorimeter. The emission spectra were corrected for the wavelength dependent response of the photodetector. The decay times were measured with a multifrequency (0.1–200 MHz) phase-modulation fluorimeter described earlier [14], operating according to the principle developed by Gratton and Limkeman [15]. The samples were excited with a 10 mW He–Ne laser (Hughes Aircraft). Fluorescence was detected through a cut-off filter (Schott RG 645). Dilute aqueous suspensions of silica (Ludox HS40 from Dupont) were used as scattering reference.

Acknowledgements

The authors would like to thank Prof. B. Valeur from PPSM for the use of the phase-modulation fluorimeter and J.P. Lefevre for running the lifetime measurements and data analyses.

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