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Formation and quenching of the photoexcited triplet state of tetrasulfonated zinc phthalocyanine, ZnPcS$_4{}^{4-}$ by azaferrocene and ferrocene

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Abstract

A nanosecond laser flash photolysis study with excitation at 532 nm showed that azaferrocene (AF) quenches the S_1 state of ZnPcS$_4{}^{4-}$ in DMSO solutions giving its T_1 state, which is then quenched itself by the same solute with the rate constant $2.4 \times 10^8\ M^{-1}\ s^{-1}$. Ferrocene (Fc) quenches only the phthalocyanine T_1 state (and not the S_1 state) with the rate constant $4.4 \times 10^8\ M^{-1}\ s^{-1}$. 2,5-DimethylAF does not quench the S_1 state of ZnPcS$_4{}^{4-}$. These differences cannot be accounted for by thermodynamic considerations, but are discussed in terms of the possible oxidation of AF at the nitrogen atom. © 2001 Elsevier Science B.V. All rights reserved.

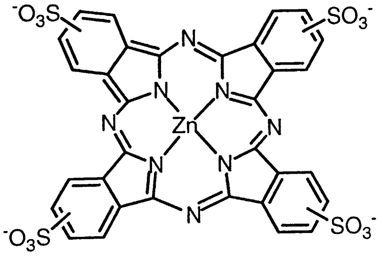
Keywords: Zinc phthalocyanine; Azaferrocene; Quenching

1. Introduction

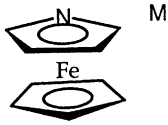
Photophysical and photochemical properties of metallophthalocyanines (MPc) in homogenous solutions as well as in organised media have been extensively studied in the last two decades, mainly due to the possible application in the solar energy conversion and phototherapy of cancer [1–10]. Our interest in this area is connected with the photochemical reduction of various MPc observed when solutions of these species, containing an excess of an organometallic base, azaferrocene (AF), were irradiated with red light (S_0–S_1 excitation of phthalocyanine) [11–15].

The plausible mechanism (Scheme 1) involves a photoinduced electron transfer between MPc and AF, with subsequent irreversible decomposition of the azaferrocenium cation, AF$^+$, which is a very unstable, still putative species [16].

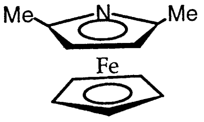
Comparison of the reduction potentials of ZnPcS$_4{}^{4-}$ (1.19 and 0.49 V versus SCE for the S_1 and T_1 states, respectively [2]) with the oxidation potential of AF (0.65 V versus SCE [16]) indicates that the former can be the photoreactive state. Accordingly, we have found that S_1-S_0 fluorescence of ZnPcS$_4{}^{4-}$ and closely related AlPcS$_4{}^{3-}$ is quenched by AF [17,18]. Both static (i.e. involving formation of the ground state dark complex between reactants) and dynamic (i.e. diffusional) quenching were observed.



ZnPcS$_4{}^{4-}$



AF



2,5-diMeAF

AF is closely related to ferrocene (Fc) but is able to bind to metal centres through nitrogen [11–15]. Although it is

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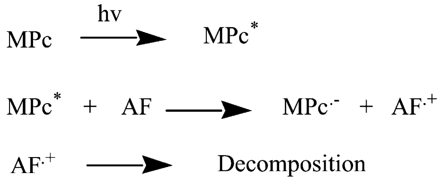

Scheme 1.

known that Fc quenches efficiently excited states of many organic, inorganic and organometallic complexes [19], there is only one report on the quenching of the T_1 state of a MPc by this complex, namely that of AlPcCl in DMSO [20]. It has been explained by an electron transfer mechanism as the energy of the T_1 state of Fc is significantly higher than that of AlPcCl making the energy transfer impossible. The quenching does not produce radical ions since the back transfer is very efficient.

Our earlier experiments [17,18] showed that in contrast to AF, Fc does not quench the S_1 state of $ZnPcS_4{}^{4-}$, in spite of its stronger electron donor properties (redox potential 0.4 V versus SCE). Furthermore, stationary photolysis of $ZnPcS_4{}^{4-}$ in the presence of AF did not result in photoreduction of phthalocyanine. It seemed therefore interesting to compare directly the photobehaviour of $ZnPcS_4{}^{4-}$ in the presence of these two organometallic complexes in a time resolved laser photolysis study.

Here, we report the results of the nanosecond laser photolysis study of $ZnPcS_4{}^{4-}$ in DMSO in the presence of AF and Fc. This study reveals that AF is able to quench efficiently not only the phthalocyanine S_1 state but also its T_1 state. In our opinion, the results obtained cast new light on the electron transfer processes involving photoexcited MPc.

2. Experimental

AF was prepared and purified according to earlier published procedure [21]. $ZnPcS_4{}^{4-}$ (Porphyrin Inc.) and DMSO (Aldrich, A.C.S. spectrophotometric grade) were used as received. A stock solution of $ZnPcS_4{}^{4-}$ was prepared by dissolving an appropriate amount of phthalocyanine in DMSO in the presence of solid $NaHCO_3$, stirring for 1 h and filtering.

The nanosecond laser was a Q-switched Nd:YAG laser manufactured by BM Industries (model BMI 5011 DNS 10), delivering 7–8 ns pulses at 1064 nm. Q-switching was made with a Pockels cell inside the cavity. The giant pulse was frequency doubled in a KDP crystal. The output energy was 10 mJ at 532 nm. This energy was measured with a Gentec pyroelectric detector. The excitation beam and the probe beam generated by a pulsed xenon source were perpendicular to each other inside the 1 cm × 1 cm cell. The analysing beam was spectrally dispersed by a monochromator and converted to an electrical signal by a Hamamatsu R928 PM tube. The electrical signal was recorded by a digital memory oscilloscope (Tektronix TDS 620 B) connected with a PC computer. The transient signals were analysed by a home made routine using Igor® procedure. Every decay and given rate constant are the mean value of at least 10 different measurements.

The fluorescence intensities were measured on a Spex Fluorolog (Jobin Yvon) spectrofluorimeter and were corrected for the wavelength response of the photodetector. The nitrogen-saturated solutions were excited at 532 nm in a cell with an optical path length of 1 mm to give the emission spectra with $\lambda_{max} = 690 \pm 1$ nm.

3. Results and discussion

The excitation of phthalocyanines to their S_1 state is usually achieved by irradiation into the Q-band (around 650–670 nm) [1,2]. However, as laser facility was not available in this domain, we have decided to work at the excitation wavelength 532 nm. The photon energy at this wavelength is too low to populate the phthalocyanine S_2 state, so we have not expected photochemical processes resulting from it. However, as the ground-state absorption of $ZnPcS_4{}^{4-}$ at 532 nm is rather weak we had to use solutions of concentrations 7×10^{-4} M in DMSO to generate an observable amount of the excited state (the optical density at this wavelength was around 0.7 for an optical path length of 1 cm). The solutions displayed strong fluorescence and electronic absorption spectrum indicating that phthalocyanine is present mostly in the monomeric form [1,2]. In agreement with our recent work [17,18], we have found that addition of AF brings about quenching of the phthalocyanine fluorescence with yields

$$1-\frac{I}{I_0}$$

(where I and I_0 stand for the fluorescence intensity in the presence and in the absence of quencher, respectively) reaching 0.5 at the AF concentration 13.6 mM. The corresponding Stern–Volmer plot is shown in Fig. 1.

The nonlinearity of the plot may be due to the increased static quenching, as now we use more concentrated $ZnPcS_4{}^{4-}$ solutions in comparison to those described in our earlier works [17,18].

The irradiation at 532 nm with the nanosecond laser pulse of a nitrogen-saturated 0.7 mM solution of $ZnPcS_4{}^{4-}$ in DMSO produces an intermediate whose absorption spectrum is shown in Fig. 2 (note that because of rather high phthalocyanine concentration, a window in which we were able to measure transient absorption was limited to around 450–560 nm). This intermediate had a relatively long lifetime (>100 μs) which enabled its identification as the $ZnPcS_4{}^{4-}$ T_1 state [10]. It is known that S_1 state of $ZnPcS_4{}^{4-}$ in DMSO has a lifetime of 3.1 ns [17], which is too short to be observed this state in a nanosecond scale experiment. Accordingly, at the end of the pulse, we observed

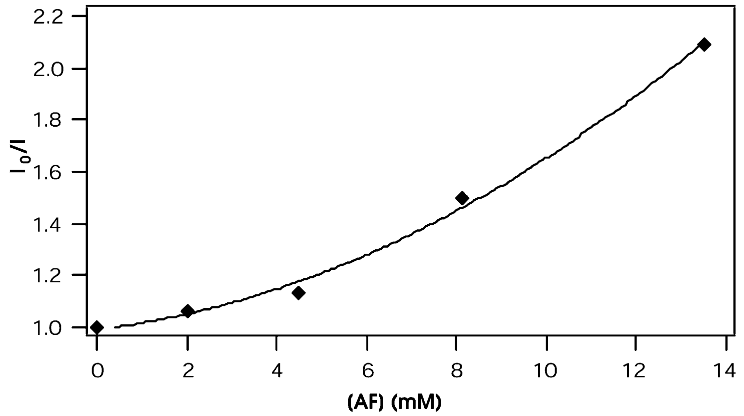

Fig. 1. Steady-state fluorescence quenching of $\mathrm{ZnPcS_4}^{4-}$ (7×10^{-4} M in DMSO, nitrogen-saturated) by AF.

a spectrum displaying only the broad $T_1 \rightarrow T_n$ absorption with the maximum at 490 nm [10].

The time evolution of the transient absorption at 490 nm observed in the absence and the presence of AF are shown in Fig. 3a.

It is seen that in spite of the significant quenching of the fluorescence (e.g. quenching yield equals 0.5 for [AF] = 13.6 mM) the concentration of the T_1 state observed at the end of the pulse does not depend on the concentration of AF. This means that quenching of the phthalocyanine S_1 state leads to the T_1 state. We suggest here a mechanism expressed by Eqs. (1)–(3):

$$^{1}\mathrm{ZnPcS}_4^{4-} + \mathrm{AF} \rightarrow {}^{1}(\mathrm{ZnPcS}_4^{5\bullet-}, \mathrm{AF}^{\bullet+}) \tag{1}$$

$$^{1}\mathrm{ZnPcS}_4^{5\bullet-}, \mathrm{AF}^{\bullet+} \rightarrow {}^{3}(\mathrm{ZnPcS}_4^{5\bullet-}, \mathrm{AF}^{\bullet+}) \tag{2}$$

$$^{3}(\mathrm{ZnPcS}_4^{5\bullet-}, \mathrm{AF}^{\bullet+}) \rightarrow {}^{3}\mathrm{ZnPcS}_4^{4-} + \mathrm{AF} \tag{3}$$

First, a photoinduced electron transfer from AF to the $\mathrm{ZnPcS_4}^{4-}$ S_1 state takes place forming a singlet ion pair (Eq. (1)). This step is expected to be exergonic by $0.65 - 1.19 = -0.54$ eV. It is followed by the intersystem crossing leading to the triplet ion pair (Eq. (2)), which should be facilitated by enhanced spin–orbit coupling in iron compounds [20]. Finally, this ion pair recombines to the T_1 state of $\mathrm{ZnPcS_4}^{4-}$ and AF (Eq. (3)). This back electron transfer should be exergonic by $-(0.65–0.49) = -0.16$ eV. It is worth noting that the AF-mediated intersystem crossing $S_1{-}T_1$ has to proceed with a high efficiency since the observed recovery of the T_1 state is practically quantitative. Presumably, it occurs in the caged ion pairs.

It is also seen from Fig. 3a that AF efficiently quenches the phthalocyanine T_1 state. The calculated quenching rate constant is $2.4 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$. The system totally relaxes in around 4–5 μs for the AF concentration range 3.6–13.6 mM, indicating that there is no significant irreversible formation of the phthalocyanine radical anion (presumably the quantum yield of this process is too low). For obvious reasons, the quenching rate constant of the triplet state is lower than that of the $\mathrm{ZnPcS_4}^{4-}$ S_1 state, $1.1 \times 10^{10}\ \mathrm{M^{-1}\,s^{-1}}$ [17], which can be considered as diffusion limited.

The time evolution of the transient absorption signal at 490 nm of solutions of $\mathrm{ZnPcS_4}^{4-}$ containing Fc observed are shown in Fig. 3b. Similarly to AF, Fc also quenches the

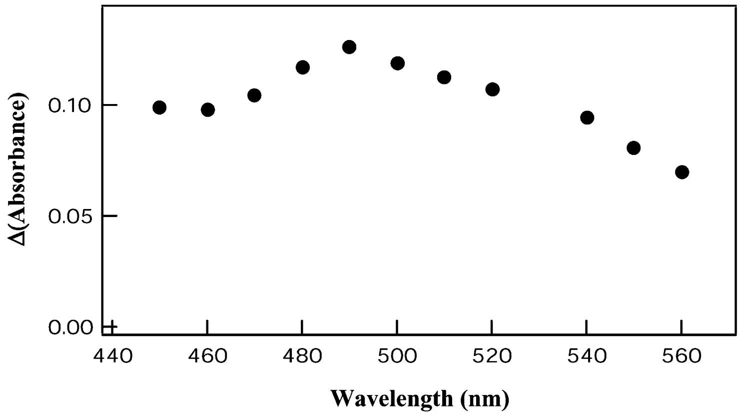

Fig. 2. Transient absorption spectrum observed at the end of a 10 ns pulse of a Nd:YAG laser (excitation wavelength 532 nm) in a $\mathrm{ZnPcS_4}^{4-}$ solution in DMSO (concentration 7×10^{-4} M, nitrogen-saturated).

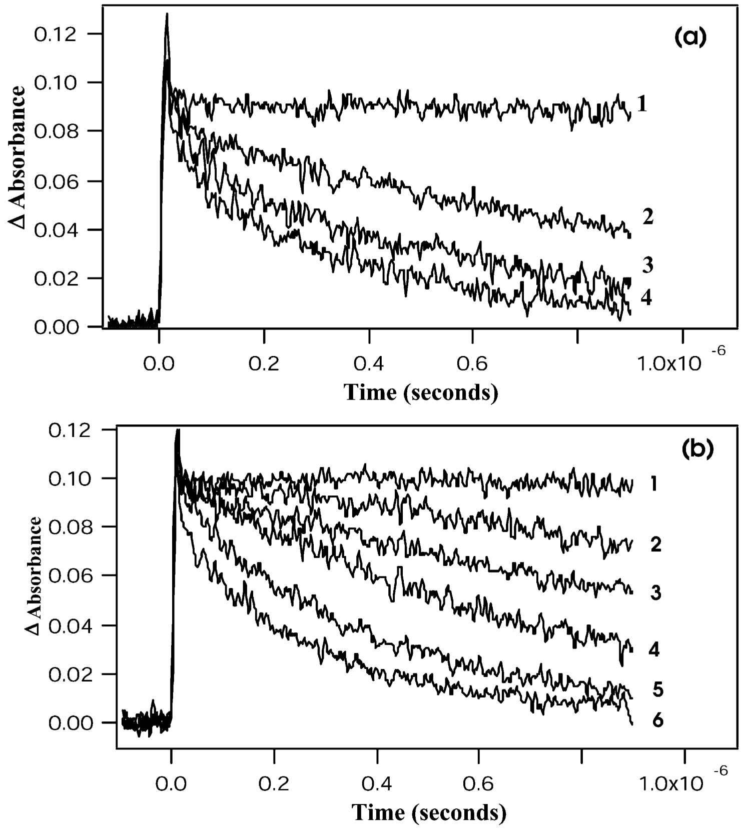

Fig. 3. Time evolution of the absorbance at 490 nm in a solution of $ZnPcS_4^{4-}$ (7×10^{-4} M in DMSO) in presence of (a) azaferrocene: [AF] = 0 M (curve 1), 3.6×10^{-3} M (curve 2), 6.6×10^{-3} M (curve 3), 1.3×10^{-2} M (curve 4) and (b) ferrocene: [Fc] = 0 M (curve 1), 5.9×10^{-4} M (curve 2), 1.18×10^{-3} M (curve 3), 2.36×10^{-3} M (curve 4), 4.71×10^{-3} M (curve 5), 9.41×10^{-3} M (curve 6).

T_1 state of $ZnPcS_4^{4-}$. The calculated quenching constant $4.4 \times 10^8\,M^{-1}\,s^{-1}$ is higher than that of AF, in agreement with the lower oxidation potential of Fc. It is also worth noting that our value that we found is close to that measured for the quenching of the T_1 state of AlPcCl by Fc in DMSO ($6.6 \times 10^8\,M^{-1}\,s^{-1}$) [20].

The results obtained in this work, together with the earlier ones, generate some questions concerning the nature of the interaction of the MPc excited state with AF and Fc. The first question is why is the S_1 state quenched by AF, whereas the stronger electron donor, Fc, is nonactive? We think that it could be a fundamental difference between electron removal from AF and Fc. The former may act as N-donor, whereas the latter is typical Fe-donor. The oxidation of the nitrogen atom in AF may be faster as it can get in closer contact with the photoexcited macrocycle than does the iron atom in Fc. Furthermore, the overlap of the macrocycle π-orbitals with the nitrogen lone pair orbital in AF can be more efficient than the overlap with iron-centered Fc orbitals, increasing in this way the rate of the electron transfer. To confirm this hypothesis we have studied the effect of 2,5-dimethylazaferrocene (2,5-diMeAF) on the S_1-S_0 fluorescence of $ZnPcS_4^{4-}$. This derivative of AF is even somewhat stronger reductant as the parent complex ($E_{1/2}$ = 0.6 V versus SCE) [22], but the nitrogen atom is sterically protected by two methyl substituents and it cannot get in so closed contact with the excited macrocycle as can nitrogen in unsubstituted AF. In fact, we have found that 2,5-diMeAF does not quench the fluorescence of $ZnPcS_4^{4-}$, at concentrations up to 0.1 M and it is not able to photoreduce this phthalocyanine under stationary photolysis conditions, comparable to those under which there is efficient formation of phthalocyanine radicals from $ZnPcS_4^{4-}$ and AF [14].

The idea that AF possesses two redox active sites at nitrogen and iron atoms has been recently put forward on the basis of the ^{57}Fe Mossbauer study of the products of oxidation of some AF derivatives by iodine [22], although for this reaction a different trend was observed (AF was oxidised by iodine at iron, whereas 2,5-diMeAF underwent oxidation at nitrogen). Apparently both reactions do not have the same steric requirements, iodine oxidation being more sensitive to electronic factors.

The second question to be answered is that of the quenching of the T_1 state of $ZnPcS_4^{4-}$ by AF. This reaction is formally endergonic by 0.16 eV, but proceeds with a rate only slightly lower that of the quenching of the same state by Fc which is slightly exergonic (by 0.09 eV). However, both reactions proceed at rates lower than diffusion limit. These results can be accounted for by the Hush–Marcus theory of electron transfer processes. Indeed, according to this theory, endergonic reactions may occur, but their rate constants will be below the diffusion limit by one or two orders of magnitude, depending on the value of the solvent reorganisation energy [23].

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