

UV light and red light chemistry of metallophthalocyanine: wavelength-dependent photochemical reduction of tetrasodium salts of Zn(II) and Cu(II) tetrasulphonatophthalocyanines with amines

Yuji Kaneko ^a, Yoshinobu Nishimura ^{a*}, Tatsuo Arai ^a, Hirochika Sakuragi ^a,
Katsumi Tokumaru ^a, Daisaku Matsunaga ^b

^a Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

^b Chemical Research Laboratories, Nippon Kayaku Co. Ltd., Shimo, Kita-ku, Tokyo 115, Japan

Received 14 September 1994; accepted 10 January 1995

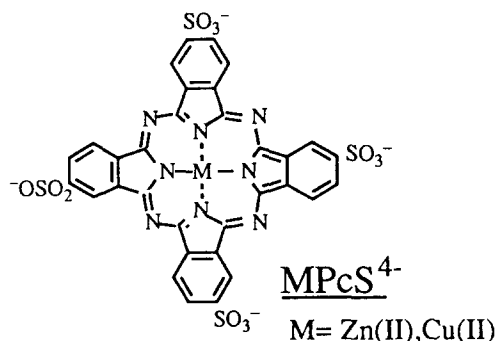
Abstract

Irradiation of tetrasodium salts of zinc(II) ($\text{Na}^+_4\text{ZnPcS}^{4-}$) and copper(II) ($\text{Na}^+_4\text{CuPcS}^{4-}$) tetrasulphonatophthalocyanine in the presence of triethanolamine, triethylamine or ethylenediaminetetraacetic acid in degassed aqueous acetonitrile (1:1 by volume) with red light at 656 nm exciting their Q band did not induce any reaction but that with UV light at 365 nm exciting their Soret band led to their reduction. The reciprocal quantum yields for photoreduction of ZnPcS^{4-} and CuPcS^{4-} on 365 nm excitation increased with increasing concentration of the amines. The mechanism of the reaction was discussed and participation of a higher excited state of the phthalocyanines was suggested.

Keywords: UV Light; Red light; Metallophthalocyanines

1. Introduction

Metallophthalocyanines have long been used as durable dye pigments for various purposes (for example, Ref. [1]) and have recently received attention from photodynamic therapy (for example, Ref. [2]). However, one of the present authors (D.M.) and his collaborators noticed that tetrasodium salts of zinc(II) and copper(II) tetrasulphonatophthalocyanine ($\text{Na}^+_4\text{ZnPcS}^{4-}$ and $\text{Na}^+_4\text{CuPcS}^{4-}$) (Structure 1) were faded in polymer matrices on exposure to light, particularly when air was excluded. This finding prompted us to investigate photochemical behaviour of the phthalocyanines in solution. We found that their irradiation in the presence of triethanolamine (TEOA) in aqueous acetonitrile (1:1 by volume) with visible light to excite the Q band induced no detectable reactions but that with UV light to excite their Soret band resulted in their reduction [3]. Photoinduced electron transfer of phthalocyanines particularly with electron acceptors [4–7] and behaviour



of the resulting radical ions [8,9] have been investigated. However, attention has scarcely been paid to effects of light wavelength. We report here a wavelength-dependent photochemical reduction of ZnPcS^{4-} and CuPcS^{4-} with amines and discuss the mechanism of reaction.

2. Experimental details

2.1. Materials

$\text{Na}^+_4\text{ZnPcS}^{4-}$ and $\text{Na}^+_4\text{CuPcS}^{4-}$ were supplied by Nippon Kayaku Co. Ltd. Amines employed were

* Present address: Department of Chemical Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan.

commercial products and purified by ordinary procedures.

2.2. Spectroscopy

Absorption and fluorescence spectra were recorded with a JASCO Ubest 55 spectrophotometer and a Hitachi F-4000 spectrofluorimeter respectively.

2.3. Cyclic voltammetry

In cyclic voltammetry, nitrogen-bubbled *N,N*-dimethylformamide (DMF) solutions of $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ MPcS^{4-} ($M = \text{Zn, Cu}$) containing 0.1 mol dm^{-3} Bu_4NClO_4 (Nacalai Tesque) as a supporting electrolyte were examined by employing a platinum electrode against an $\text{Ag}^+/\text{NO}_3^-/\text{Ag}$ electrode with a Hokuto HA-201 potentiostat-galvanostat combined with a Hokuto HB-104 function generator.

2.4. Quantum yields of photoreduction

Quantum yields Φ_r for photoreduction of MPcS^{4-} ($M = \text{Zn, Cu}$; $1.0 \times 10^{-5} \text{ mol dm}^{-3}$) were determined in degassed aqueous acetonitrile solutions (1:1 by volume) on irradiation of $365 \pm 25 \text{ nm}$ light filtered by Toshiba UVD-36B and L-35 glass filters by use of chemical actinometry of acridine in methanol [10]. Photoreduction was also attempted by irradiating with $656 \pm 5 \text{ nm}$ light extracted through a bandpass filter (Melles Griot 03FIR006) from a 300 W xenon arc lamp.

2.5. Transient spectroscopy

Transient absorption was determined as previously reported [11] with 308 nm pulses from an XeCl excimer laser (Lambda Physik LPX-100) and with 670 nm pulses from a dye laser (Lambda Physik FL-3002; 10 ns full width at half-maximum, oxazine 720 dye) pumped by the 308 nm excimer laser. The monitoring light was oriented perpendicularly to the exciting laser beam, passed through a grating monochromator (JASCO CT-25C), and detected with a photomultiplier (Hamamatsu Photonix R928) and a storage oscilloscope (Iwatsu TS-8123). The system was computer controlled and the data were analysed by a personal computer (NEC PC-9801vm).

2.6. Quantum yields of emission of ZnPcS^{4-}

Quantum yields Φ_F of S_1 and S_2 emissions of ZnPcS^{4-} with maxima around 680 nm and 450 nm respectively were determined in aqueous acetonitrile (1:1 by volume) by use of rhodamine B ($\Phi_F = 0.42$) [12] as a reference on excitation at 390 nm and 589 nm.

2.7. Two-colour pulsed laser excitation

Two-colour pulsed laser excitation was performed with 623 nm and 500 nm laser pulses with an appropriate delay time. The 623 nm and 500 nm lasers were supplied from excimer laser pumped dye lasers (Lambda Physik LPX100-FL3002 (rhodamine 101) and Lambda Physik EMG101-home-made dye laser (coumarine 307) respectively.

3. Results

3.1. Absorption spectra

ZnPcS^{4-} exhibited absorption maxima of the Soret band at 340 nm and of the Q band at 635 and 667 nm in aqueous solution. The absorptions at 667 nm and 635 nm were assigned respectively to monomeric and dimeric species of ZnPcS^{4-} ; the later results from hydrophobic interaction [13]. In a very dilute solution ($1 \times 10^{-6} \text{ mol dm}^{-3}$), the absorption intensity was much higher at 667 nm than at 635 nm; however, with increase in ZnPcS^{4-} concentration, the intensity at 667 nm was reduced and that at 635 nm was increased with an isosbestic point; both absorptions finally led to comparable intensities at $8 \times 10^{-6} \text{ mol dm}^{-3}$. Addition of acetonitrile to the aqueous solution increased the intensity at 667 nm and reduced that at 635 nm by hydrophobic interaction between the phthalocyanine nucleus and acetonitrile. Fig. 1 shows absorption spectra of ZnPcS^{4-} ($1 \times 10^{-5} \text{ mol dm}^{-3}$) in water and a 1:1 by volume mixture of acetonitrile and water. This figure indicates that ZnPcS^{4-} at $1 \times 10^{-5} \text{ mol dm}^{-3}$ mostly exists as a monomeric form in the mixture of acetonitrile and water. Addition of TEOA to an aqueous solution

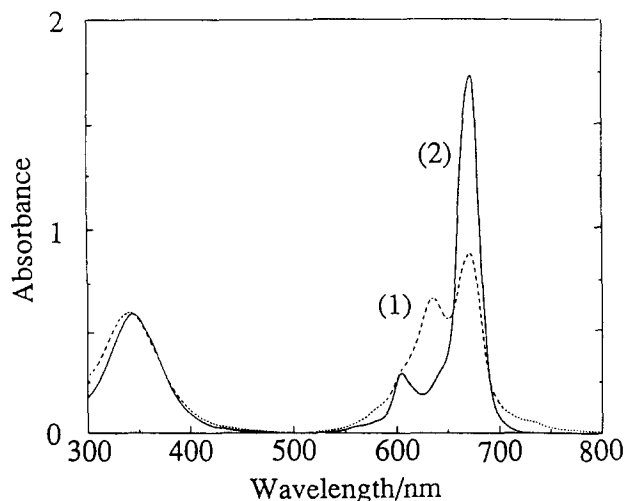


Fig. 1. Absorption spectra of ZnPcS^{4-} ($1 \times 10^{-5} \text{ mol dm}^{-3}$) in water (spectrum 1) and aqueous acetonitrile (1:1 by volume) (spectrum 2).

of ZnPcS^{4-} had a similar effect on the absorption spectrum to the addition of acetonitrile.

CuPcS^{4-} exhibited essentially the same features of the absorption spectrum as ZnPcS^{4-} with the maxima at 345 and 670 nm in aqueous acetonitrile (1:1 by volume).

To determine the equilibrium constant $K = [(\text{ZnPcS}^{4-})_2]/[\text{ZnPcS}^{4-}]^2$ for dimerization of ZnPcS^{4-} in aqueous solution at ambient temperature, the absorption spectra were determined in varying concentrations of ZnPcS^{4-} from 2×10^{-8} to 2×10^{-4} mol dm^{-3} . Fig. 2 shows plots of apparent molar absorption coefficients ϵ at 635 nm (ϵ_{635}) and 670 nm (ϵ_{670}) against $\log[\text{ZnPcS}^{4-}]$, and shows that the ϵ values increased at the former wavelength and decreased at the latter wavelength with increasing concentration of ZnPcS^{4-} .

3.2. Emissions of ZnPcS^{4-}

In analogy with several metallophthalocyanines exhibiting a weak violet fluorescence as well as the well-recognized strong red emission from the lowest excited singlet state (S_1) [7,14–16], ZnPcS^{4-} displayed, in addition to the reported fluorescence at 680 nm from S_1 [17], a very weak emission around 450 nm from S_2 in aqueous acetonitrile on 360 nm excitation as illustrated in Fig. 3. The quantum yields for fluorescence emission from S_1 and S_2 were determined as 0.31 and 0.038 on excitation at 589 nm and 390 nm respectively.

3.3. Electrochemical potentials

The cyclic voltammetry afforded electrochemical potentials $E_{1/2}(\text{ZnPcS}^{4-}/\text{ZnPcS}^{5-})$ and $E_{1/2}(\text{ZnPcS}^{3-}/\text{ZnPcS}^{4-})$ of -0.63 V and $+0.76$ V respectively vs. saturated calomel electrode (SCE) and $E_{1/2}(\text{CuPcS}^{4-}/\text{CuPcS}^{5-})$ as -0.56 V in DMF in the presence of Bu_4NClO_4 (0.1 mol dm^{-3}). The oxidation potential $E(\text{TEOA}^+/\text{TEOA})$ of TEOA was also determined as $+0.81$ V vs. SCE in DMF.

3.4. Stationary light irradiation

Irradiation of ZnPcS^{4-} (1×10^{-5} mol dm^{-3}) in degassed aqueous acetonitrile (1:1 by volume) in the presence of TEOA with 656 nm light led to no change in the absorption spectrum. However, irradiation with 365 nm light under otherwise the same conditions reduced the absorption of ZnPcS^{4-} at 670 nm and increased that at 580 nm; this is attributable to production of ZnPcS^{5-} by one-electron reduction of ZnPcS^{4-} as illustrated in Fig. 4 for a 0.8 mol TEOA dm^{-3} solution. After the irradiation was over, introduction of air to the solution completely removed the new absorption at 580 nm and the absorption due to ZnPcS^{4-} was regained.

CuPcS^{4-} behaved similarly to ZnPcS^{4-} . Excitation of CuPcS^{4-} with 365 nm light in the presence of TEOA reduced the absorption of CuPcS^{4-} and increased that due to CuPcS^{5-} at 580 nm, whereas excitation with 656 nm light induced no spectral change. The observed spectral profile of CuPcS^{5-} at 580 nm agreed with that produced from irradiation of CuPcS^{4-} in polymer matrices with light of wavelength longer than 300 nm [18].

The production of one-electron reduced species of metallotetrasulphonatophthalocyanines (MPcS^{5-}) was confirmed by comparing the present spectra with those reported for electrochemical reduction of MPcS^{4-} [19] and those obtained by treatment of MPcS^{4-} with sodium hydrosulfite in aqueous buffer (pH 11) solution, which afforded their ϵ_{580} ($\text{mmol}^{-1} \text{cm}^2$) as 2.4×10^4 and 1.6×10^4 for $\text{M} = \text{Zn}$ and Cu respectively.

Among the amines examined, TEOA, triethylamine (TEA), and ethylenediaminetetraacetic acid (EDTA) photoreduced ZnPcS^{4-} on 365 nm irradiation; however, 1,4-diazabicyclo[2.2.2]octane (DABCO), *N,N*-dimethylaniline (DMA) and pyridine were inactive. Furthermore, cystein reduced ZnPcS^{4-} on both 365 and 656 nm irradiations.

3.5. Quantum yields for photoreduction

The quantum yield Φ_r for photoreduction of ZnPcS^{4-} was 1.3×10^{-3} in the presence of 0.8 mol dm^{-3} TEOA

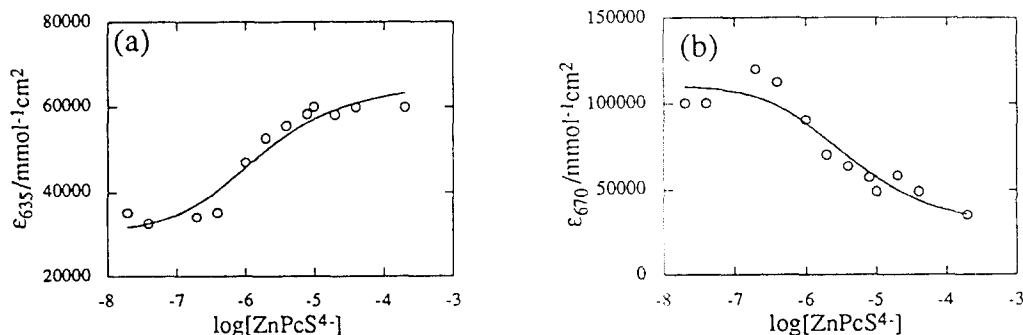


Fig. 2. Plots of the apparent molar absorption coefficients (a) ϵ_{635} and (b) ϵ_{670} against the concentration of ZnPcS^{4-} in aqueous solution.

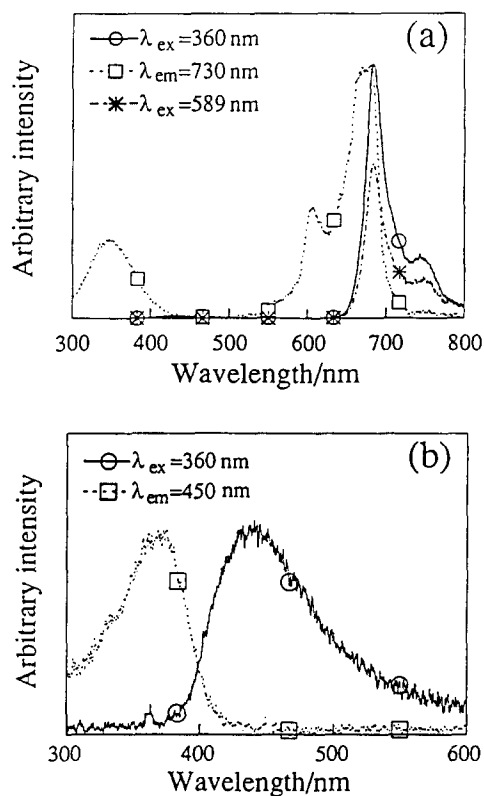


Fig. 3. (a) Fluorescence spectra (—, ○; ---, *) of $ZnPcS^{4-}$ on excitation at 360 nm and 589 nm respectively, and a fluorescence excitation spectrum (···, □) monitored at 730 nm in aqueous acetonitrile. (b) A fluorescence spectrum (—, ○) of $ZnPcS^{4-}$ on excitation at 360 nm and a fluorescence excitation spectrum (···, □) monitored at 450 nm in aqueous acetonitrile.

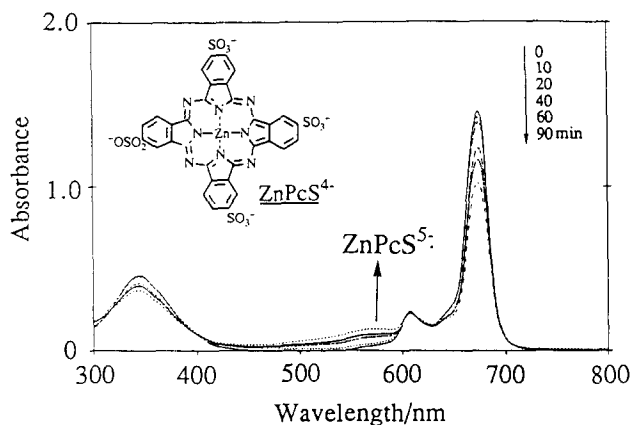


Fig. 4. Spectral change of $ZnPcS^{4-}$ under irradiation with 365 nm light in degassed aqueous acetonitrile (1:1 by volume) in the presence of TEOA (0.8 mol dm^{-3}).

or TEA in aqueous acetonitrile on 365 nm excitation. $CuPcS^{4-}$ exhibited nearly the same order of quantum yield, 1.1×10^{-3} for its reduction with 0.8 mol dm^{-3} TEOA in aqueous acetonitrile. The Φ_r values of $ZnPcS^{4-}$ and $CuPcS^{4-}$ increased with increasing concentration of amines. Fig. 5 shows plots of the reciprocal quantum yield ($1/\Phi_r$) for $ZnPcS^{4-}$ reduction against

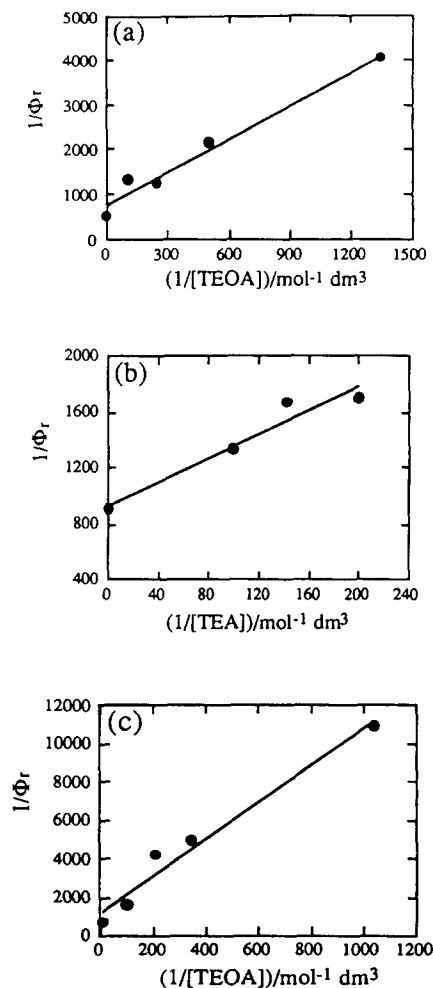


Fig. 5. Plots of the reciprocal quantum yields for photoreduction of $ZnPcS^{4-}$ ($8 \times 10^{-6} \text{ mol dm}^{-3}$) against the reciprocal concentrations of (a) TEOA and (b) TEA and (c) that of $CuPcS^{4-}$ ($1.6 \times 10^{-5} \text{ mol dm}^{-3}$) against the reciprocal concentration of TEOA in degassed aqueous acetonitrile.

the reciprocal TEOA or TEA concentration and that for $CuPcS^{4-}$ reduction against the reciprocal concentration of TEOA. The Φ_r values of $ZnPcS^{4-}$ with cystein (0.01 mol dm^{-3}) in aqueous acetonitrile were 7.4×10^{-4} and 5.7×10^{-4} on 365 nm and 656 nm irradiation respectively.

3.6. Transient absorption

Excitation of $ZnPcS^{4-}$ with 670 nm laser in aqueous acetonitrile in the presence of 0.8 mol dm^{-3} TEOA afforded only the T-T absorption of $ZnPcS^{4-}$ with $\lambda_{max} = 490 \text{ nm}$, which decayed with a lifetime of nearly $100 \mu\text{s}$ and accompanied a depletion of the ground state absorption as shown in Fig. 6(a). On the contrary, as depicted in Fig. 6(b), excitation with 308 nm laser resulted in a new absorption at 580 nm due to formation of $ZnPcS^{5-}$ in addition to the T-T absorption of $ZnPcS^{4-}$ decaying with the same lifetime of nearly 100

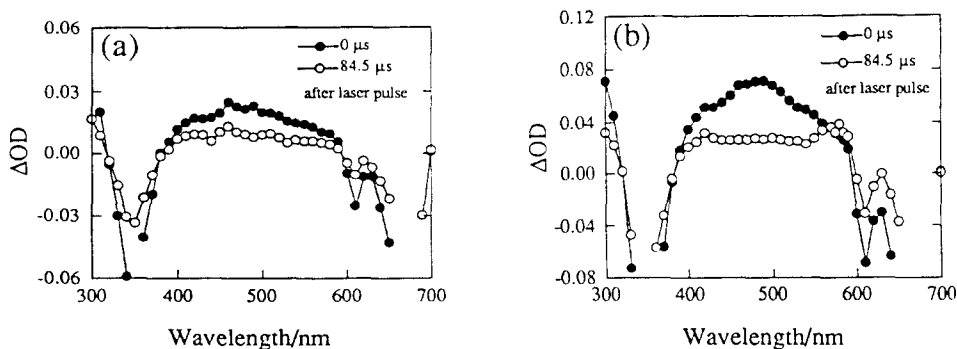


Fig. 6. Transient absorption spectra observed on excitation of ZnPcS^{4-} in degassed aqueous acetonitrile in the presence of TEOA (0.8 mol dm^{-3}) with (a) 670 nm and (b) 308 nm laser pulses.

μs as determined on excitation with the 670 nm laser; the decay rate was not affected at all with the added TEOA.

3.7. Two-colour pulsed laser excitation

To examine a possibility of participation of a higher excited triplet state in the reaction in aqueous acetonitrile in the presence of 0.8 mol dm^{-3} TEOA, ZnPcS^{4-} ($2 \times 10^{-5} \text{ mol dm}^{-3}$) was excited with a 623 nm laser pulse and then 10 μs after the first pulse with a 500 nm laser pulse. The first laser populates the T_1 state, and the second laser subsequently excites T_1 to a higher excited state. The two-colour laser excitation was repeated. Fig. 7 depicts the absorption spectra measured before and after the two-colour laser excitation repeated 1000 times. Two-colour laser excitation resulted in the same spectral change as the steady state irradiation of 365 nm light. Control runs to excite a solution with either 623 or 500 nm laser pulses gave no spectral change.

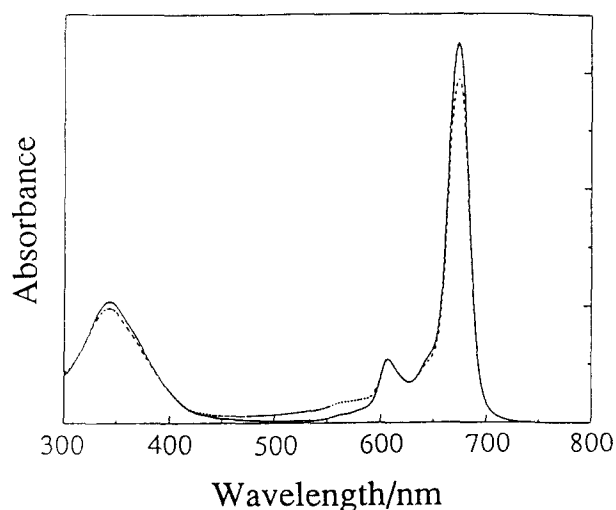
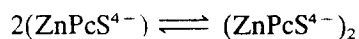


Fig. 7. Absorption spectra of ZnPcS^{4-} ($2 \times 10^{-5} \text{ mol dm}^{-3}$) in aqueous acetonitrile in the presence of 0.8 mol dm^{-3} TEOA before (—) and after (···) repeated two-colour (623 nm + 500 nm) laser excitation.

4. Discussion

4.1. The equilibrium between monomeric and dimeric species of ZnPcS^{4-}

In aqueous solutions ZnPcS^{4-} exists as monomeric ($\lambda_{\text{max}} = 667 \text{ nm}$) and dimeric ($\lambda_{\text{max}} = 635 \text{ nm}$) forms in an equilibrium [20]:



In a very dilute aqueous solution, ZnPcS^{4-} mostly exists as the monomeric form. With increase in concentration it tends to dimerize by hydrophobic interaction between the phthalocyanine nuclei. From the plots of ϵ_{635} and ϵ_{670} against $\log[\text{ZnPcS}^{4-}]$ (Fig. 2), the equilibrium constant K between the dimeric and monomeric forms can be determined according to the following equation, where ϵ_m and ϵ_D denote molar extinction coefficients of the monomeric and dimeric species respectively at the wavelength for measurement, and c means the total concentration of ZnPcS^{4-} added:

$$K = \frac{(\epsilon - \epsilon_m)(\epsilon_d - \epsilon_m)}{2c(\epsilon_d - \epsilon)^2}$$

that is,

$$\epsilon = \epsilon_d - \frac{(\epsilon_m - \epsilon_d)[1 - (1 + 8cK)^{1/2}]}{4cK}$$

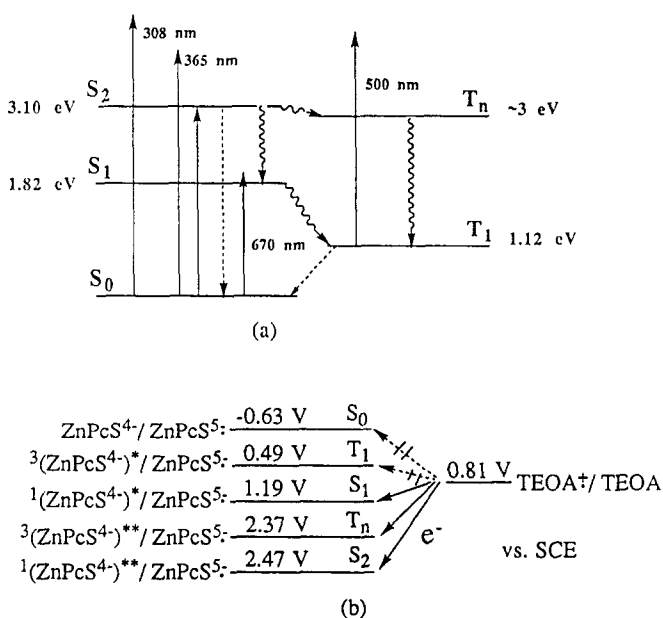
Treatment of the results in Fig. 2 by the above equation gives ϵ_m ($\text{mmol}^{-1} \text{ cm}^2$) at 635 nm and 670 nm as 6.5×10^4 and 2.8×10^4 respectively and K as $4.7 \times 10^5 \text{ mol}^{-1} \text{ dm}^3$. The above very high K value reflects a high degree of dimerization of ZnPcS^{4-} in the aqueous solution. On addition of either acetonitrile (Fig. 1) or TEOA (Fig. 4) to the aqueous solution, the absorption due to the dimeric species is reduced and finally disappears; however, the absorption and fluorescence spectra around 680 nm are essentially unaffected by either acetonitrile or TEOA. These facts mean that acetonitrile or added TEOA serve as hydrophobic species to as-

sociate with a phthalocyanine molecule in place of another phthalocyanine molecule in the aqueous solution.

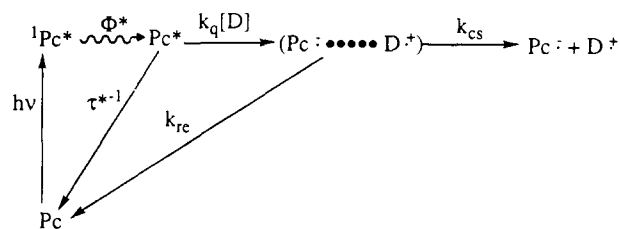
4.2. Mechanism of the photoreduction

ZnPcS⁴⁻ is not photoreduced by amines on visible light irradiation, but it is photoreduced on UV light irradiation. The T₁ state observed on excitation with either 308 or 670 nm laser is not quenched by amines. These facts suggest that a higher excited state resulting from excitation of the Soret band, that is either the second excited singlet state, S₂, or a higher triplet state, T_n, produced from S₂, may participate in the reaction with amines. The standard free energy change ΔG⁰ for the electron transfer from TEOA to T₁ is estimated to be 0.32 eV endoergonic on the basis of the triplet excitation energy of ZnPcS⁴⁻ of 1.12 eV [4] and the oxidation potential of TEOA determined as 0.81 V vs. SCE. On the contrary, the electron transfer to any higher excited state can take place as an exoergonic process as shown in Scheme 1. The ΔG⁰ values for electron transfer to the S₂ and T_n states are estimated as nearly 1.66 eV and ca. 1.6 eV exothermic respectively on the basis of the energies of S₂ and T_n as described below.

As Fig. 5 indicates, 1/Φ_r of ZnPcS⁴⁻ is almost linearly increased with increasing reciprocal concentration of electron donors. This relationship indicates that the reaction may proceed through a mechanism shown in Scheme 2, where Pc stands for MPcS⁴⁻ and Pc* for the excited reactive species, and Φ* denotes the quantum



Scheme 1. (a) An estimated energy diagram of ZnPcS⁴⁻ and (b) estimated electrochemical potentials for reduction of several states of ZnPcS⁴⁻ with TEOA.



Scheme 2. An estimated mechanism for photoreduction of metal-phthalocyanines in the higher excited states.

yield for production of the reactive excited state. Thus, an excited state Pc* resulting from the Soret band excitation is quenched by a donor D with a rate constant k_q in competition with deactivation (rate constant (τ*)⁻¹) to give a radical ion pair of Pc^{-•} and D^{+•}, which subsequently undergoes either charge separation (k_{cs}) into free radical ions or reverse electron transfer (k_{re}) with an efficiency for charge separation of f_{cs} = k_{cs} / (k_{cs} + k_{re}).

On the basis of the above mechanism, Φ_r is expressed by the following equation:

$$\Phi_r = \Phi^* f_{cs} \frac{k_q[D]}{k_q[D] + (\tau^*)^{-1}}$$

$$\Phi_r^{-1} = (\Phi^*)^{-1} f_{cs}^{-1} \left(1 + \frac{1}{k_q \tau^* [D]} \right)$$

In Fig. 5(a), the reciprocal of the intercept gives Φ* f_{cs} ≈ 1–3 × 10⁻³ and division of the intercept by the slope affords k_qτ* as 310 mol⁻¹ dm³ for TEOA. When the quenching of the reactive excited state by D is assumed to proceed with a nearly diffusion controlled rate constant, 1 × 10¹⁰ mol⁻¹ dm³ s⁻¹, τ* ≈ 3 × 10⁻⁸ s. Likewise, the results of photoreduction of ZnPcS⁴⁻ with TEA (Fig. 5(b)) afford the values of nearly the same magnitudes as above for Φ* f_{cs} and k_qτ* as 1.1 × 10⁻³ and 220 mol⁻¹ dm³ respectively.

Among the amines examined, TEOA, TEA, EDTA, DABCO, DMA and pyridine with oxidation potentials of 0.81, 0.76 [21], 0.76 [22], 0.57 [21], 0.81 [23] and 2.12 [24] V vs. SCE in that order, the former three acyclic aliphatic amines effectively act as electron donors, but the latter three do not in spite of comparable magnitudes of the oxidation potentials of DABCO and DMA to those of the reactive amines. This fact may be due to lower reactivities of the resulting radical cations from the inefficient amines, DMA^{+•}, DABCO^{+•} and pyridine^{+•}, in subsequent dehydrogenation than those of the reactive amines. The capability of the resulting radicals for further dehydrogenation will suppress the reverse electron transfer with ZnPcS⁵⁻.

The photoreduction with cystein proceeds on visible light irradiation as previously reported [5d] and is not dependent on excitation wavelength. Φ_r was essentially the same on 365 and 656 nm irradiation. This is

attributable to a very low oxidation potential of cystein (-0.46 V vs. SCE) [25], which makes the electron transfer to T_1 and a higher excited state exothermic.

The photochemical behaviour of CuPcS^{4-} is essentially similar to that of ZnPcS^{4-} ; the plot of Φ_{τ}^{-1} against $[\text{TEOA}]^{-1}$ (Fig. 5(c)) gives a nearly linear relationship with an intercept of 1.2×10^3 and a slope of $9.6 \text{ mol}^{-1} \text{ dm}^3$, affording $\Phi^* f_{cs}$ as nearly 10^{-3} and $k_q \tau^*$ as $120 \text{ mol}^{-1} \text{ dm}^3$. These results again suggest that the reactive excited state can be alive for times of the order of 10^{-8} s.

As to the wavelength-dependent photochemical reactions, Ferraudi reported that UV irradiation of CuPcS^{4-} in acidic solutions led to dissociation of its dimer into oxidized and reduced species [26]. However, this is not the case for the present reaction carried out under the conditions where the most MPcS^{4-} exists as monomeric species. The present work is in keeping with reports by Prasad and Ferraudi that UV irradiation of copper(II) tetrakis(*N*-octadecylsulphamoyl)-phthalocyanine more effectively led to hydrogen atom abstraction from chloroform than visible light irradiation by participation of a higher excited state [27].

A few candidates can be considered as the reactive excited states which have properties of $\Phi^* f_{cs} \approx 10^{-3}$ and $\tau^* \approx 10^{-8}$ s. First, the second excited singlet state, S_2 , directly resulting from the Soret band excitation will exhibit $\Phi^* \approx 1$, $f_{cs} \leq 10^{-3}$ and $\tau^* \leq 10^{-8}$ s; the singlet radical ion pair generally undergoes very poor charge separation and the situation is similar to the higher excited singlet state of some metalloporphyrins which undergo specific emission and reactions competing with non-radiative deactivation to the S_1 state [28,29].

Secondly, the T_n state produced by intersystem crossing of S_2 will exhibit $f_{cs} \approx 10^{-1}$ and a very small value of Φ^* of the order of 10^{-2} since the triplet radical ion pair undergoes efficient charge separation and the higher excited singlet state generally undergoes internal conversion to S_1 in preference to the intersystem crossing. Higher excited triplet states are generally very short lived, but could undergo bimolecular reaction with a suitable quencher [30]. Thirdly, the metallophthalocyanines in the ground state may interact with amines to give coordinated complexes which would exhibit nearly the same spectra as the uncomplexed species [31] and their higher excited states might be reactive.

Among these candidates, the higher excited singlet state seems improbable. On 360 nm excitation, ZnPcS^{4-} exhibits a very weak emission around 450 nm together with a strong emission at 680 nm similarly to several metallophthalocyanines exhibiting emission at the violet region [7,14–16]. The S_2 state generally undergoes internal conversion to S_1 facily; however, S_2 lying at a much higher energy level than S_1 emits specific fluorescence in addition to the fluorescence from S_1 as observed in azulene [32] and zinc(II) tetraphenylpor-

phyrin [29]. The energy gap between S_2 and S_1 in ZnPcS^{4-} estimated as 1.28 eV is larger than 0.71 eV in zinc(II) tetraphenylporphyrin [29], although smaller than 1.61 eV in azulene [33]; therefore, the S_2 state of ZnPcS^{4-} could participate in the reaction competing with the violet emission and internal conversion to the S_1 state. However, the violet emission arising from excitation of the Soret band is not effectively quenched by TEOA in aqueous acetonitrile.

The τ^* value estimated as 10^{-8} s may be slightly large for higher triplet states. However, the results of two-colour laser excitation support the participation of the upper excited triplet state, T_n . The repeated two-colour laser irradiation, with the first laser at 623 nm to populate the T_1 state and with the subsequent second laser at 500 nm to excite the T_1 state to a higher triplet state, resulted in reduction of ZnPcS^{4-} as for the steady irradiation of 365 nm light. This means that the S_2 state resulting from the excitation of the Soret band can undergo intersystem crossing to the T_n state, which seems to lie at nearly the same energy level as the S_2 state. The energy for S_2 is estimated as 3.10 eV over S_0 from the overlap point of the Soret band absorption and the emission in the violet region, and that of T_n is estimated as about 3 eV from the longer part of the T–T absorption. The efficiency of the intersystem crossing must be poor because of competition with very rapid internal conversion. When the T_n state participates, f_{cs} could be 10^{-1} , and then Φ^* may be around 10^{-2} .

A coordinated complex between ZnPcS^{4-} and the amines as the third candidate of the reactive state is excluded, since the intensity of the S_1 fluorescence was not quenched by amines.

In conclusion, ZnPcS^{4-} and CuPcS^{4-} are photo-reduced with amines such as TEOA, TEA and EDTA in aqueous acetonitrile with relatively small quantum yields of the order of 10^{-3} under irradiation with UV light but not with visible light. The reaction seems to take place at a higher excited state such as the T_n state derived from S_2 .

Acknowledgments

The authors thank the Ministry of Education, Science and Culture for their Grant-in-Aid for Scientific Research (63104001), the University of Tsukuba for the President's Special Grant for Education and Research (1990, K.T.) and Nippon Kayaku Co. Ltd. for their grant for the support of the present research.

References

- [1] A.B.P. Lever and C.C. Leznoff (eds.), *Phthalocyanine. Principles and Properties*, VCH, New York, 1989.

- [2] J.D. Spikes, *Photochem. Photobiol.*, **43** (1986) 691. E. Reddi, C. Zhou, R. Biolo, E. Menegaldo and G. Jori, *Br. J. Cancer*, **61** (1990) 407 and related papers.
- [3] Y. Nishimura, Y. Kaneko, T. Arai, H. Sakuragi, K. Tokumaru, M. Kiten, S. Yamamura and D. Matsunaga, *Chem. Lett.*, (1990) 1935.
- [4] J.R. Darwent, P. Douglas, A. Harriman, G. Porter and M.C. Richoux, *Coord. Chem. Rev.*, **44** (1982) 83.
- [5] (a) A.B.P. Lever, S. Licoccia, B.S. Ramaswamy, S.A. Kandil and D.V. Stynes, *Inorg. Chim. Acta*, **51** (1981) 169.
(b) T. Tanno, D. Woehrle, M. Kaneko and A. Yamada, *Ber. Bunsenges. Phys. Chem.*, **84** (1980) 1032.
(c) A. Harriman and M.C. Richoux, *J. Chem. Soc., Faraday Trans. II*, **76** (1980) 1618.
(d) J.R. Darwent, *J. Chem. Soc., Chem. Commun.*, (1980) 805.
(e) D. Woehrle and M. Kaneko, *Yuki Gosei Kagaku Kyokaiishi*, **45** (1987) 837.
- [6] T. Ohno and S. Kato, *J. Phys. Chem.*, **88** (1984) 1670.
- [7] D. Chahraoui and J. Kossanyi, *J. Chim. Phys.*, **89** (1992) 47.
- [8] T. Nyokong, Z. Gasyna and M.J. Stillman, *Inorg. Chem.*, **26** (1987) 1087.
- [9] J. Mack and M.J. Stillman, *J. Am. Chem. Soc.*, **116** (1994) 1292.
- [10] S. Niizuma and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **36** (1963) 1629.
- [11] H. Furuuchi, Y. Kuriyama, T. Arai, H. Sakuragi and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **64** (1991) 1601.
- [12] A.H.-H. Hau, O. Johansen and W.H.F. Sasse, *Photochem. Photobiol.*, **41** (1985) 503.
- [13] H. Kobayashi, Y. Torii and N. Fukada, *Nippon Kagaku Zasshi*, **81** (1960) 694.
- [14] N. Kobayashi and A.B.P. Lever, *J. Am. Chem. Soc.*, **109** (1987) 7433. N. Kobayashi, T. Ashida and T. Osa, *Chem. Lett.*, (1992) 2031.
- [15] S. Muralidharan, G. Ferraudi and L.K. Patterson, *Inorg. Chim. Acta*, **65** (1982) L235. G. Ferraudi and S. Muralidharan, *Inorg. Chem.*, **22** (1983) 1369.
- [16] D. Chahraoui, P. Valat and J. Kossanyi, *Res. Chem. Intermed.*, **17** (1992) 219.
- [17] G. Valduga, E. Reddi and G. Jori, *J. Inorg. Biochem.*, **29** (1987) 59.
- [18] T. Tsukamoto, S. Taguchi, T. Nakahira, S. Iwabuchi, K. Kojima and T. Sugiura, *Polym. Commun.*, **31** (1990) 108.
- [19] L.D. Rollmann and R.T. Iwamoto, *J. Am. Chem. Soc.*, **90** (1968) 1455.
- [20] A. Harriman and M.C. Richoux, *J. Photochem.*, **14** (1980) 253. P.C. Martin, M. Gouterman, B.V. Pepich, G.E. Renzoni and D.C. Schindele, *Inorg. Chem.*, **30** (1991) 3305.
- [21] W. Hub, S. Schneider, F. Dorr, J.D. Oxman and F.D. Lewis, *J. Am. Chem. Soc.*, **106** (1984) 701.
- [22] L. Meites, P. Zuman, W.J. Scott, B.H. Cumpbell and A.M. Kardos, *Electrochemical Data*, Wiley, New York, 1974.
- [23] D.G. Nocera and H.B. Gray, *J. Am. Chem. Soc.*, **103** (1981) 7349.
- [24] J.W. Arbogast, C.S. Foote and M. Kao, *J. Am. Chem. Soc.*, **114** (1992) 2277.
- [25] S. Okumura, N. Toshioka, S. Asakura, M. Ohya and S. Nagamori, *Yakugaku Zasshi*, **94** (1974) 655.
- [26] G. Ferraudi, *Inorg. Chem.*, **18** (1979) 1005.
- [27] D.R. Prasad and G. Ferraudi, *Inorg. Chem.*, **21** (1982) 2967; *Inorg. Chim. Acta*, **54** (1981) L231.
- [28] M. Hoshino and Y. Kashiwagi, *J. Phys. Chem.*, **94** (1990) 673.
- [29] S. Tobita and I. Tanaka, *Chem. Phys. Lett.*, **96** (1983) 517. S. Tobita, Y. Kaizu, H. Kobayashi and I. Tanaka, *J. Chem. Phys.*, **81** (1984) 2962.
- [30] G.I. Kobyshev, G.N. Lyalin and A.N. Terenin, *Opt. Spectrosc.*, **21** (1966) 74. J. Saltiel, D.E. Townsend and A. Sykes, *J. Am. Chem. Soc.*, **105** (1983) 2530. R.S.H. Liu and J.R. Edman, *J. Am. Chem. Soc.*, **91** (1969) 1492. Y. Miyashita, S. Niizuma, H. Kokubun and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **46** (1973) 3373. P. de Mayo, J.-P. Pete and M. Tchir, *J. Am. Chem. Soc.*, **89** (1967) 5712.
- [31] T. Kobayashi, T. Ashida, N. Uyeda, E. Saito and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **44** (1971) 2095.
- [32] H.C. Longuet-Higgins and M. Beer, *J. Chem. Phys.*, **23** (1955) 1390.
- [33] G. Viswanath and M. Kasha, *J. Chem. Phys.*, **24** (1956) 574.