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Effect of excitation wavelength on photoreduction of metal-free and copper(II) 1,4,8,11,15,18,22,25-octabutoxyphthalocyanines with triethanolamine

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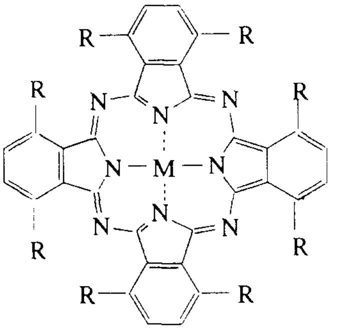
Abstract

Irradiation of 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine ($H_2Pc(OBu)_8$) and its copper derivative ($CuPc(OBu)_8$) in degassed ethanol solutions containing triethanolamine with red light at 656 nm exciting their Q band did not induce any reaction but the irradiation with UV-violet light at 313–425 nm exciting their Soret band led to their reduction. The reciprocal quantum yields for photoreduction of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ on 365 nm excitation increased with increasing reciprocal concentration of triethanolamine. Among the excitation light wavelengths, 360 nm light was the most effective for photoreduction. On the basis of these and other findings, the mechanism of the reaction is discussed and the participation of a higher excited state of the phthalocyanines is suggested.

Keywords: Octabutoxyphthalocyanine; Octabutoxy-copper(II)phthalocyanine; Wavelength-dependent photochemical reaction; Photoreduction

1. Introduction

Previously we found that tetrasodium tetrasulphonatozinc(II)phthalocyanine was photoreduced with triethanolamine (TEOA) in degassed aqueous solutions or aqueous acetonitrile (1:1 by volume) solutions on excitation of its Soret band with 365 nm light but was not at all on excitation of its Q band with 656 nm light [1]. However, this phthalocyanine tends to aggregate in aqueous solutions, particularly in higher concentrations. Therefore, one could argue the possibility that excitation of the aggregated species would result in the observed wavelength-dependent photochemical reaction. To exclude this possibility, we have investigated the behaviour of 1,4,8,11,15,18,22,25-octabutoxyphthalocyanines, which are moderately soluble in organic solvents [2]. We now report that the irradiation of metal-free 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine ($H_2Pc(OBu)_8$) and its copper(II) derivative ($CuPc(OBu)_8$) with UV light in ethanol containing TEOA led to their reduction whereas the irradiation with red light was not effective. The results clearly indicate that the wavelength-dependent photochemical reduction of phthalocyanines is not due to their aggregation.



$H_2Pc(OBu)_8$: M=H_2, R=OC_4H_9 (I)
$CuPc(OBu)_8$: M=Cu, R=OC_4H_9 (II)

2. Experimental details

2.1. Materials

Octabutoxyphthalocyanines $H_2Pc(OBu)_8$ and CuPc-$(OBu)_8$ were supplied from Kawamura Institute of Chemical Research. TEOA was purchased from Nacalai Tesque.

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2.2. Spectroscopy

Absorption spectra were recorded with a JASCO Ubest 55 spectrophotometer and fluorescence spectra with a Hitachi F-4000 and a JASCO FP-1000 spectrofluorimeter. The lifetimes of emission from $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ were determined in ethanol under argon on excitation with 379 nm laser pulses from a second harmonic generator of Ti:sapphire laser (Spectra Physics 3900 Tsunami) pumped by a continuous wave argon ion laser (Spectra Physics 2060). The emission was passed through a grating monochromator (Jobin Yvon CP200) and detected with a streak scope (Hamamatsu C4334) and transferred to a personal computer (Apple Macintosh IIfx). The system was computer controlled and the data were analysed by a personal computer.

2.3. Cyclic voltammetry

Cyclic voltammetry of the phthalocyanines (5×10^{-4} mol dm^{-3}) was carried out with nitrogen-bubbled *N,N*-dimethylformamide (DMF) solutions containing 0.1 mol dm^{-3} of Bu_4NClO_4 (Nacalai Tesque) as a supporting electrolyte by employing a platinum electrode as a working electrode against a saturated calomel electrode (SCE) with a potentiostat–galvanostat (Hokuto HA-201) combined with a function generator (Hokuto HB-104).

2.4. Quantum yields for photoreduction

Irradiation was carried out for degassed ethanol solutions of the phthalocyanines with 365 ± 25 nm light obtained through Toshiba UVD-36B and L-35 glass filters or with 656 ± 5 nm light extracted through a bandpath filter (Melles Griot 03FIR006) from a 300 W xenon arc lamp. The quantum yields for photoreduction of the phthalocyanines were determined with chemical actinometry of dimerization of acridine in methanol [3]. Spectral change of the sample solutions was monitored on irradiation at 365 or 656 nm. In determination of action spectra of the photoreduction of the phthalocyanines ($(2–3)\times10^{-5}$ mol dm^{-3}) with TEOA (0.01 mol dm^{-3}) under UV–violet light irradiation, appropriate wavelengths of light were obtained by passing the light from a xenon lamp through suitable Melles Griot bandpass filters and the quantum yields were determined with potassium tris(oxalato)ferrate(III) chemical actinometry.

2.5. Transient spectroscopy

Transient absorption spectra were measured on excitation of the sample solutions with 360 nm and 723 nm laser pulses from a dye laser (Lambda Physik Fl-3002; full width at half-maximum (FWHM), 10 ns) using DMQ and rhodamine 700 respectively as dyes, pumped by an XeCl excimer laser (Lambda Physik LPX-100; 308 nm) combined with an optical detection system [4].

2.6. Two-colour pulsed laser excitation

Two-colour pulsed laser excitation was performed with 723 and 600 nm laser pulses with an appropriate delay time. The 723 nm and 600 nm pulses were obtained from excimer-laser-pumped dye lasers (Lambda Physik LPX100–FL3002 (rhodamine 700) and Lambda Physik Lextra 100L–Scanmate 2E (rhodamine B) respectively).

2.7. Quantum yields for emission

The quantum yields Φ_F of emissions of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ with maxima around 440 nm were determined for their ethanol solutions by use of rhodamine B ($\Phi_F=0.42$) [5] as a reference on excitation with 360 nm light in a spectrofluorimeter (Hitachi F-4000).

3. Results

3.1. Absorption spectra

Fig. 1 depicts absorption spectra of octabutoxyphthalocyanines $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ in ethanol. H_2Pc-

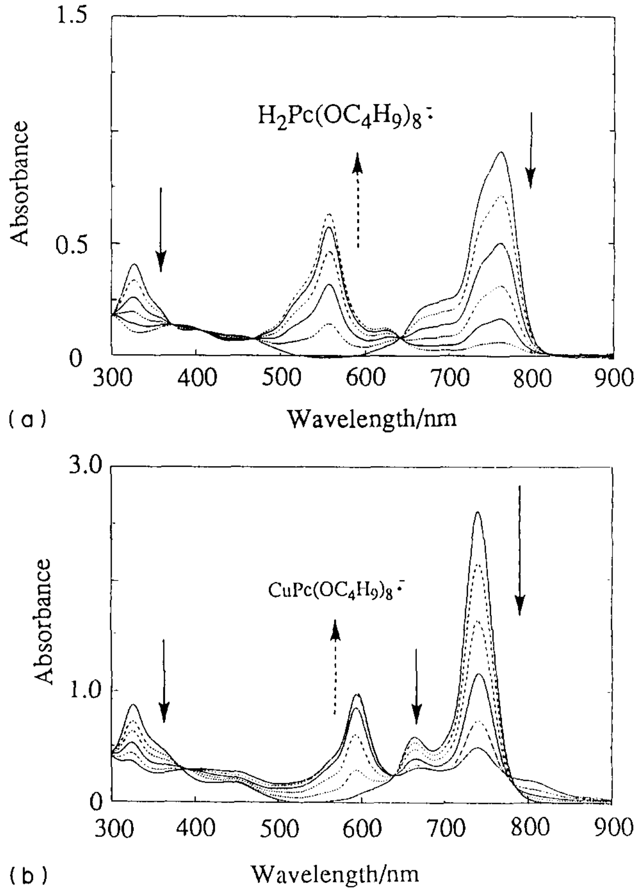


Fig. 1. Absorption spectra and spectral changes of phthalocyanines (a) $H_2Pc(OBu)_8$ and (b) $CuPc(OBu)_8$ on 365 nm excitation in degassed ethanol solutions containing TEOA.

$(OBu)_8$ exhibits absorption maxima at 327 nm in the Soret band and at 764 nm in the Q band with a shoulder at 740 nm; the spectral features are the same as those in benzene reported previously [6]. $CuPc(OBu)_8$ exhibits absorption maxima at 327 nm in the Soret band and 740 and 663 nm in the Q band. The Q band maxima of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ are shifted towards the near-IR region compared with those of unsubstituted phthalocyanines [7]. The absorption profiles are not varied with the concentrations in ethanol indicating that these phthalocyanines are not aggregated in ethanol. The absorption spectra were not affected at all with the added TEOA for both dyes.

3.2. Electrochemical potentials

In cyclic voltammetry in DMF, the reduction potentials $E_{1/2}^{red}$ were determined as −0.73 V and −0.87 V against SCE for $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ respectively; the oxidation potentials $E_{1/2}^{ox}$ were 0.54 V for both $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$.

3.3. Stationary light irradiation

Fig. 1(a) also illustrates the spectral change on irradiation of $H_2Pc(OBu)_8$ with 365 nm light in degassed ethanol in the presence of 0.01 mol TEOA dm^{-3}. On irradiation the characteristic absorptions of $H_2Pc(OBu)_8$ were decreased and concurrently a new absorption band grew up at 559 nm. After the irradiation was over, the irradiated solution was allowed to make contact with air, and then the new absorption quickly disappeared and the characteristic absorption of $H_2Pc(OBu)_8$ was recovered to nearly 50%. The above facts suggest that the absorption resulting from the irradiation is attributed to the one-electron reduced species of $H_2Pc(OBu)_8$, $H_2Pc(OBu)_8^{-\bullet}$ (the spectra of one electron reduced species of tetrasodium metal-free and copper(II) phthalocyanines are given in Ref. [8]), although the fate of the unrecovered phthalocyanine was not clear. On the contrary, the irradiation of a similar solution of $H_2Pc(OBu)_8$ with TEOA at 656 nm did not give any detectable change in the absorption spectrum.

$CuPc(OBu)_8$ behaved similarly to $H_2Pc(OBu)_8$ on irradiation. Thus, as shown in Fig. 1(b), the irradiation of $CuPc(OBu)_8$ with 365 nm light in degassed ethanol in the presence of 0.01 mol TEOA dm^{-3} led to a decrease in the absorption of $CuPc(OBu)_8$ and a concurrent increase in an absorption attributable to $CuPc(OBu)_8^{-\bullet}$ at 595 nm [8]. Introduction of air to the irradiated solution made the absorption at 595 nm disappear and recovered the absorption of $CuPc(OBu)_8$ to nearly 90% of the original value.

3.4. Quantum yields for photoreduction

Quantum yields Φ_r for photoreduction of $H_2Pc(OBu)_8$ (3×10^{-5} mol dm^{-3}) and $CuPc(OBu)_8$ (3×10^{-5} mol dm^{-3}) were determined in degassed ethanol in the presence of varying concentrations of TEOA from 4.1×10^{-4} to 1.0×10^{-2} mol dm^{-3} under irradiation with 365±25 nm light. $H_2Pc(OBu)_8$ was more efficiently reduced than $CuPc(OBu)_8$. For example, Φ_r values are 1.0×10^{-2} and 7.0×10^{-3} for $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ respectively in the presence of 1.0×10^{-2} mol TEOA dm^{-3}. Fig. 2 shows plots of the reciprocal quantum yields against the reciprocal concentrations of TEOA. This figure indicates that the reciprocal quantum yields for reduction of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ are almost linearly increased with the reciprocal concentration of TEOA when the concentration of TEOA is lower than 0.01 mol dm^{-3}. The intercepts of the plots are 113 and 114 and the slopes are 0.55 mol^{-1} dm^3 and 0.72 mol^{-1} dm^3 for $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ respectively. Inspection of Fig. 2 shows that the slopes are slightly different between the lower and higher concentration regions as discussed later, although the plots are somehow scattered.

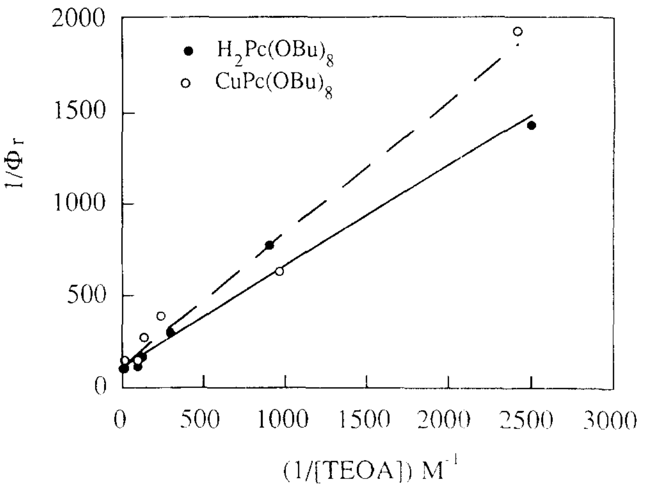


Fig. 2. Plots of the reciprocal quantum yields for photoreduction of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ against the reciprocal concentrations of TEOA on 365 nm excitation in ethanol.

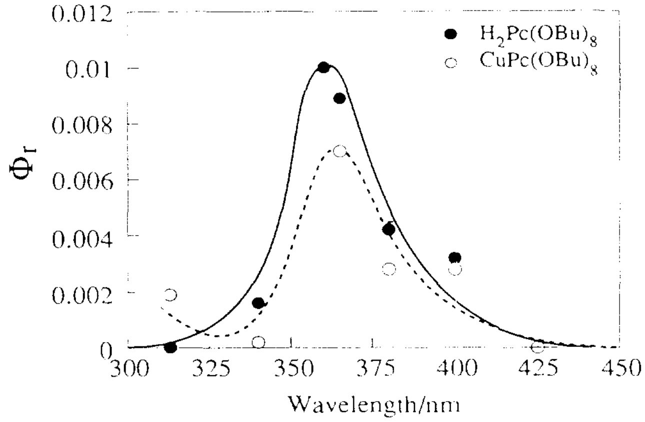


Fig. 3. Action spectra for the photoreduction of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ with TEOA (0.01 mol dm^{-3}) in ethanol.

Fig. 3 illustrates the action spectra for the photoreduction of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ ($(2–3)\times10^{-5}$ mol dm^{-3}) with TEOA (0.01 mol dm^{-3}) in ethanol on irradiation with 313, 340, 360, 365, 380, 400, and 425 nm light. The result indicates that only the light of the 325–425 nm region

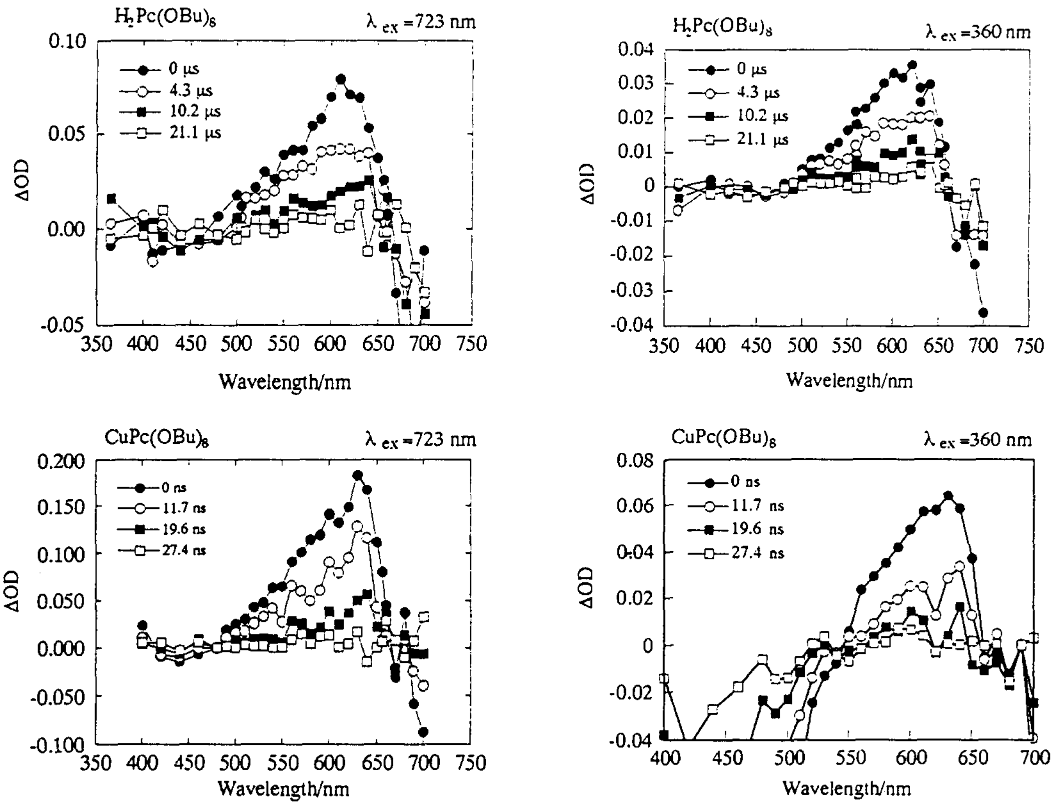


Fig. 4. Transient absorption spectra observed on 360 and 723 nm pulsed laser excitation of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ in ethanol under argon.

is effective in the photoreduction and the most efficient wavelength is around 360 nm in both cases.

3.5. Transient absorption spectra

Excitation of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ in ethanol with 723 or 360 nm laser pulses under argon atmosphere afforded broad transient absorptions in the 550–650 nm region with a maximum at 630 nm; the absorptions decayed with lifetimes of 7.6 μs for $H_2Pc(OBu)_8$ and of less than 10 ns for $CuPc(OBu)_8$, as illustrated in Fig. 4. The observed spectra are assigned to the $T_1 \rightarrow T_n$ absorption since the spectrum of $H_2Pc(OBu)_8$ is essentially the same as that reported in benzene with a maximum at 610 nm [6]. On excitation of $H_2Pc(OBu)_8$ in the presence of 0.02 mol TEOA dm^{-3}, the lifetime of the triplet state was not affected at all with the added TEOA, as monitored at the absorption maximum (630 nm).

Fig. 5 depicts the decay profiles of the absorbance monitored at 560 nm on excitation of $H_2Pc(OBu)_8$ with 360 nm laser pulses in the absence and presence of 0.02 mol TEOA dm^{-3} in ethanol. In the absence of TEOA, the absorption decays in a single-exponential way. On the contrary, in the presence of TEOA the absorbance decays with the same time constant in the initial stage as in the absence of TEOA, and therefore the decay is not affected by TEOA; however, more than 10 μs after the excitation an additional absorbance remains which is attributable to the resulting $H_2Pc(OBu)_8^{-\bullet}$.

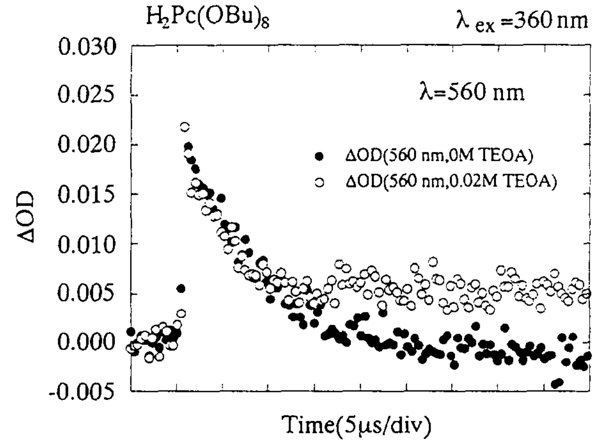


Fig. 5. Decay curves of the absorbance monitored at 560 nm on 360 nm pulsed laser excitation of $H_2Pc(OBu)_8$ in the presence and absence of TEOA in ethanol.

Excitation with 723 nm laser pulses gave no additional absorbance due to $H_2Pc(OBu)_8^{-\bullet}$.

3.6. Emission spectra

Fig. 6 shows the emission spectra observed in 360–600 nm on 360 nm light excitation of $H_2Pc(OBu)_8$ and its excitation spectrum monitored at 450 nm. The emission spectrum exhibits two bands with maxima at 788 nm and 440 nm due to fluorescence from S_1 and a higher excited state respectively, and the excitation spectrum monitored at 450 nm has a max-

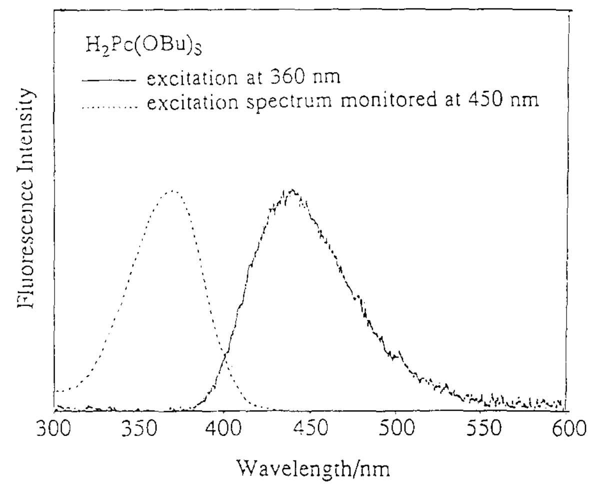


Fig. 6. An emission spectrum of $H_2Pc(OBu)_8$ in ethanol on 360 nm light excitation and its excitation spectrum monitored at 450 nm.

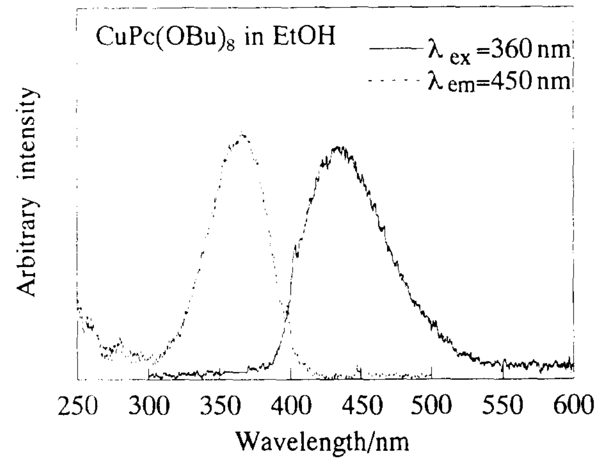


Fig. 7. An emission spectrum of $CuPc(OBu)_8$ in ethanol on 360 nm light excitation and its excitation spectrum monitored at 450 nm.

imum at 360 nm. Fig. 7 shows the emission spectrum of $CuPc(OBu)_8$ on excitation with 360 nm light and its excitation spectrum monitored at 450 nm. The quantum yields for emission in the 440 nm region were determined as 1.2×10^{-2} and 9.2×10^{-3} for $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ respectively on 360 nm excitation.

The longer-wavelength fluorescence with maximum at 788 nm of $H_2Pc(OBu)_8$ was not quenched by TEOA, but the shorter-wavelength emission was quenched by TEOA. The Stern–Volmer constant $k_q\tau$ was determined as 15 mol^{-1} dm^3, where k_q is the quenching rate constant of the emission by TEOA and τ the lifetime of the emission. According to this value the quenching ratio is about 13% in the presence of 0.01 mol TEOA dm^{-3}. The lifetime of the longer-wavelength fluorescence of $H_2Pc(OBu)_8$ was about 4.2 ns as monitored at 790 nm and those of the shorter-wavelength emission were 4.8 ns and 5.1 ns for $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ respectively as monitored at 450 nm.

3.7. Two-colour pulsed laser excitation

The results of steady state irradiation indicate that the photoreduction of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ with TEOA takes place from higher excited states. In a previous paper [9], the photoreduction of $ZnPcS^{4-}$ in the presence of TEOA was shown to take place from a higher excited triplet state (T_n) by means of a two-colour pulsed laser excitation technique. To examine the possibility of participation of T_n states in the present dyes two-colour pulsed laser excitation was carried out in degassed ethanol (10^{-5} Torr). $H_2Pc(OBu)_8$ or $CuPc(OBu)_8$ was irradiated in ethanol containing TEOA with the first laser pulse (723 nm) and then irradiated with the second laser pulse (600 nm); the first laser leads to the $S_0 \rightarrow S_1$ transition of the dye followed by intersystem crossing to populate T_1 and the second laser induces the $T_1 \rightarrow T_n$ transition. The delay time was adjusted to be 100 ns and 0 ns for $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ respectively, because the lifetimes of the triplet states of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ are 7.6 μs and less than 10 ns respectively. The two-colour pulsed laser excitation was repeated 1000 times, and the absorption spectrum was measured. The spectrum obtained was essentially identical with that before irradiation for both $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$.

4. Discussion

4.1. Emission from higher excited states of the octabutoxyphthlocyanines

The excitation spectra of the emissions of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ monitored at 450 nm appear in the 310–425 nm region with a maximum around 360 nm and are undoubtedly different from their Soret bands with λ_{max} at 327 nm. The Soret bands have a tail at the longer wavelength region of the band at 400–500 nm. However, the excitation of these absorption tails did not result in 440 nm emissions. The 440 nm emissions of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ on 360 nm excitation can be assigned to fluorescence from their higher excited states.

These emissions are similar to those of several metallophthalocyanines which were observed in the violet region and assigned to their upper excited states. Kobayashi and Lever [10] observed emissions in the range 400–600 nm on irradiation of the Soret band of phthalocyanines bearing crown ether substituents and assigned the emissions to the S_2 state. Kossanyi and coworkers [11] also reported emissions with a maximum at 430 nm from the S_2 state in magnesium, zinc, and metal-free unsubstituted phthalocyanines.

Generally, a higher excited state facilely undergoes internal conversion to a lower state. However, when an S_2 state lies in a much higher energy level than the S_1 state, the S_2 state can emit a specific fluorescence in addition to the fluorescence from S_1 as observed in azulene [12] and porphyrins [13].

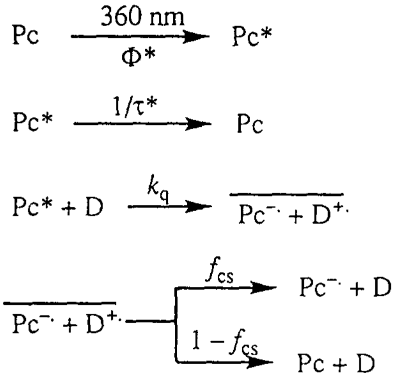
The 0–0 transition energies of the violet emissions of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ are evaluated as 3.10 eV from the wavelength of intersection of their normalized emission and emission excitation spectra (Fig. 6 and 7). The 0–0 transition energy of the S_1 fluorescence of $H_2Pc(OBu)_8$ was similarly given as 1.57 eV from its absorption and fluorescence spectra, which display an approximate mirror image relationship. The estimated energy gap (1.53 eV) between the emissive higher excited state and the S_1 state is much larger than the S_2–S_1 energy gap (0.71 eV) in zinc(II)tetraphenylporphyrin [13]. Therefore, the emissive higher excited state of $H_2Pc(OBu)_8$ might participate in the reduction, competing with the violet light emission and internal conversion to S_1.

4.2. Mechanism of the photoreduction

Octabutoxyphthalocyanines $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ are photoreduced with TEOA on excitation with light of the 360 nm region (Fig. 3) but not with 656 nm light. These facts indicate that the photoreduction does not take place from either the lowest singlet or the triplet state. Actually, the transient absorption of their lowest triplet states is not quenched with TEOA at all. $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ did not exhibit any definite phosphorescence, although, among octabutoxyphthalocyanines, ruthenium- and palladium-centred species were reported to emit phosphorescence at 910 nm (1.36 eV) and 1100 nm (1.13 eV) respectively [14].

The free energy changes for electron transfer from TEOA ($E^{ox}_{1/2}=0.81$ V vs. SCE) to the lowest triplet states of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ are estimated to be +0.53 eV and +0.30 eV respectively endergonic from the electrochemical potentials and excitation energies of the phthalocyanines by assuming that the triplet excitation energies of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ are the same as those of metal-free unsubstituted phthalocyanine, 1.24 eV [7], and its copper(II) derivative, 1.15 eV [7], respectively. The free energy changes for electron transfer from TEOA to the lowest singlet states of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ are estimated as −0.03 eV and 0 eV respectively, since the lowest singlet excitation energy for $H_2Pc(OBu)_8$ is 1.57 eV as estimated above and that of $CuPc(OBu)_8$ is estimated as 1.68 eV from the absorption maximum of 740 nm.

On the contrary, the electron transfer to the higher singlet states of the present dyes from TEOA is highly exergonic since their excitation energies are estimated to be higher than 3.10 eV for the emissive state, as described above. The photoreduction of the higher excited states will proceed with a nearly diffusion-controlled rate constant since the free energy changes are estimated as nearly −1.56 eV and −1.42 eV for $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ respectively. Therefore, their photoreduction is supposed to occur in either the higher singlet or the triplet state. Participation of a complex between $H_2Pc(OBu)_8$ or $CuPc(OBu)_8$ and TEOA may not be probable since the former having no coordinated metallic cation behaves similarly to the latter.



Scheme 1.

If the photoreduction takes place from a higher excited state resulting from the excitation of the Soret band of $H_2Pc(OBu)_8$ or $CuPc(OBu)_8$ with an efficiency Φ^*, the reaction is to proceed according to Scheme 1, where Pc and D indicate the octabutoxyphthalocyanines and TEOA respectively, τ^* and k_q denote the lifetime of the participating excited state (Pc*) and the rate constant for its quenching by TEOA, and f_{cs} denotes the efficiency for charge separation from the resulting radical ion pairs of the one electron reduced species of $H_2Pc(OBu)_8$ or $CuPc(OBu)_8$, $Pc^{-\bullet}$ and $TEOA^{+\bullet}$, $D^{+\bullet}$. Then, the reciprocal quantum yield for the reduction is expressed by the following equation:

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

The Stern–Volmer plot (Fig. 2) gave $f_{cs}\Phi^*$ (reciprocal of the intercept) as 8.9×10^{-3} and 8.8×10^{-3} and $k_q\tau^*$ (intercept divided by slope) as 205 mol^{-1} dm^3 and 158 mol^{-1} dm^3 for $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ respectively. If a singlet state is a reactive state, f_{cs} must be very small since the resulting radical ion pair, $Pc^{-\bullet}D^{+\bullet}$, facilely undergoes reverse electron transfer. On the contrary, if a triplet excited state participates, f_{cs} must be much higher than that from the singlet radical pair. If we assume that the electron transfer to higher excited states takes place with a diffusion-controlled rate constant, e.g. $k_q=1.0\times10^{10}$ dm^3 mol^{-1} s^{-1}, the lifetimes of the reactive state are to be 21 ns for $H_2Pc(OBu)_8$ and 16 ns for $CuPc(OBu)_8$ from the $k_q\tau^*$ values obtained above.

As discussed above, the higher singlet or triplet excited states are candidates for the reactive state in the photoreduction of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$. However, the result of the two-colour pulsed laser excitation which led to no detectable reduction of the phthalocyanines eliminates the possibility that a higher triplet excited state resulting from the T_1 state with a large absorption coefficient would be a candidate. Therefore, it is probable that the photoreduction takes place from a higher excited singlet state or a higher triplet state with a low transition probability from the T_1 state, for example, an n,π* type triplet state.

The $k_q\tau^*$ value obtained from the quenching of the violet emission of $H_2Pc(OBu)_8$ by TEOA is one order of magnitude lower than $k_q\tau^*$ obtained from the variation in Φ_r with TEOA concentration. This means that the emissive higher excited state, although quenched by TEOA, is not the most responsible excited state for the photoreduction.

In the cases of both $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ the action spectra of Φ_r with a maximum at 360 nm (Fig. 3) are similar to the excitation spectra of the violet emission monitored at 450 nm (Fig. 6 and 7). Furthermore, the absorption spectra of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ display a shoulder around 360 nm in their Soret bands. These facts suggest that the reactive state may lie close in energy to, and result from, the emissive higher excited state. Ferraudi and Granifo [15] reported an excitation wavelength dependence of the photochemical reactions of Mn(III)tetrasulphonatophthalocyanine, $[Mn^{(III)}Pc(SO_3)_4(OH_2)(OH)]^{4-}$, which undergoes photoinduced hydrogen abstraction from a ligand-centred n,π* excited state and elimination of an axial ligand from a ligand–metal charge transfer state.

Phthalocyanines may also have an n,π* excited state in addition to π,π* excited states. It was shown that both $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions in the phthalocyanine ring appear in the Soret band region of unsubstituted phthalocyanine and its metal derivatives on the basis of several calculations [16]. The n,π* absorption band may be hidden in the strong $\pi\rightarrow\pi^*$ band in the present phthalocyanines.

The natural radiative lifetime τ^0 of an emission can be expressed by using the FWHM $\Delta\nu_{1/2}$ of a symmetrical absorption band and the molar absorption coefficient ϵ_{max} at the absorption maximum according to the following well-known equation [17]:

$$\tau^0 = \frac{3.4\times10^8}{\nu^2\varepsilon_{max}\,\Delta\nu_{1/2}}$$

where ν denotes the wavenumber of the 0–0 transition. When we apply this equation to the 440 nm emission accompanying a nearly symmetrical excitation spectrum, we can estimate the ε_{max} values for the higher emissive state since τ^0 can be also evaluated from the following equation:

$$\tau^0 = \tau/\Phi_f$$

Since the τ values for fluorescence from the higher emissive state were determined as 4.8 ns and 5.1 ns on excitation of the Soret bands of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ respectively and Φ_f values are 1.2×10^{-2} and 9.2×10^{-3} for $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ respectively, the ε_{max} values for the higher emissive state of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ are estimated as 490 $mmol^{-1}$ cm^2 and 330 $mmol^{-1}$ cm^2 respectively. The calculated ε_{max} values are very much smaller than the apparent absorption coefficients observed around 370 nm in the Soret band. The above results suggest that the excitation spectra of $H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ monitored at 450 nm may correspond to an n,π* absorption. Therefore, it is probable that the 360 nm excitation populates the 440 nm emissive state, probably an n,π* state; the resulting state subsequently collapses to a state, either singlet or triplet, lying close to the emissive state and reactive with TEOA.

As described above, the emissive state is quenched by TEOA with $k_q\tau^* \approx 15$ mol^{-1} dm^3. In the double-reciprocal plots of Φ_r and [TEOA] (Fig. 2), the slopes seem to be different between the concentration regions of TEOA higher and lower than 0.01 mol dm^{-3}. The attempted analysis gives $k_q\tau^*$ as 235 mol^{-1} dm^3 and 114 mol^{-1} dm^3 for $H_2Pc(OBu)_8$ and 150 mol^{-1} dm^3 and 75 mol^{-1} dm^3 for $CuPc(OBu)_8$ in the lower and higher TEOA concentration ranges respectively.

If we assume that the emissive state can react with TEOA with a lower rate constant than the reactive state Pc*, the apparent $k_q\tau^*$ value may decrease in the presence of higher concentrations of TEOA owing to a contribution of the emissive state to the photoreduction; in lower TEOA concentrations, the emissive state tends to give the reactive state prior to being quenched by TEOA. Thus, for $H_2Pc(OBu)_8$ the Φ_r value increases with [TEOA] with $k_q\tau^* = 235$ mol^{-1} dm^3 when [TEOA] is lower than 0.01 mol dm^{-3}; however, in the higher TEOA concentrations such as 0.1 mol dm^{-3}, increase in Φ_r with [TEOA] becomes smaller with $k_q\tau^* = 114$ mol^{-1} dm^3 than in the lower concentration range. $CuPc(OBu)_8$ exhibits the same trend.

5. Conclusion

$H_2Pc(OBu)_8$ and $CuPc(OBu)_8$ are not aggregated in ethanol; however, they are photoreduced with TEOA in ethanol on irradiation at 313–425 nm but not on visible light irradiation. The action spectrum for the photoreduction exhibits a maximum at 360 nm. This is essentially identical with the excitation spectrum of fluorescence observed around 440 nm. It is concluded that the excitation around 360 nm populates the 440 nm emissive state, probably an n,π* state, which gives a state undergoing the reaction with TEOA. At higher TEOA concentrations both the emissive and the reactive excited state seem to react with TEOA.

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