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Oxidative fluorescence quenching of *meso*-diphenyltetrabenzoporphyrins with onium salts

Madoka Yasuike*, Kenichi Koseki, Tsuguo Yamaoka
Department of Image Science and Technology, Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Chiba 260 (Japan)
Kunihiro Ichimura, Masako Sakuragi
Research Institute for Polymers and Textiles, 1-1-4 Higashi, Tsukubashi, Ibaraki 305 (Japan)
and **Osamu Ohno**
Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152 (Japan)

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Abstract

The fluorescence quenching of either *meso*-diphenyltetrabenzoporphyrin zinc or magnesium complexes, ZnP_2TBP and MgP_2TBP, respectively, by onium salts has been studied in acetonitrile. The dependence of the fluorescence quenching rate constants, k_q, on the free energy change, ΔG, indicates that the photosensitization between these substances primarily takes place based on the photoinduced electron transfer from the singlet excited TBP molecule to the quencher.

Introduction

Recently, increasing attention has been paid to photosensitized polymerization with a high sensitivity in the region of visible wavelength, especially with visible lasers such as Ar ion and He–Ne lasers [1, 2]. From this point of view, it is necessary to develop an efficient photoinitiator system consisting of a dye sensitizer and a radical generator [3–8].

In this regard, we have already reported that the combinations of *meso*-phenyl substituted tetrabenzoporphyrins (PTBP) [9] as photosensitizers with onium salts such as diphenyliodonium hexafluorophosphate (DPI), triphenylsulfonium hexafluorophosphate (TPS) and triphenylselenium hexafluorophosphate (TPSe) as a coinitiator induce the radical polymerization of a polymer with (meth)acryloyl groups on He–Ne laser exposure, and the photosensitivity depends on the ability of these onium salts as radical generators in the following order; DPI, TPS and TPSe [10]. It has been presumed that the photoinduced electron transfer occurs from the excited PTBP molecules to the onium salts in these photosensitized reactions because in both singlet and triplet sensitizations the excitation energies of the TBPs are far less than the energies required to excite the onium salts to their excited state. Recently, it has been proved that the photoinduced electron transfer reaction has occurred in some cases with dyes and the onium salts using laser flash photolysis techniques [11, 12].

In the present work, the photosensitized reaction is explained on the basis of the relationship between the estimation of the free energy change, ΔG, related to the photoinduced electron transfer and the fluorescence quenching rate constant, k_q.

Experimental

Materials

The *meso*-diphenyltetrabenzoporphyrin zinc complex (ZnP_2TBP) was prepared from the reaction of 3-benzylidenephthalimidine (3-BPI) in the presence of zinc acetate at 360 °C, following repeated purification by TLC on aluminum oxide using a solvent mixture of benzene/hexane/THF (10:10:1), as previously reported [9].

The magnesium complex was obtained as follows. ZnP_2TBP was demetallated with trifluoroacetic acid in chloroform at room temperature

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*Author to whom correspondence should be addressed.

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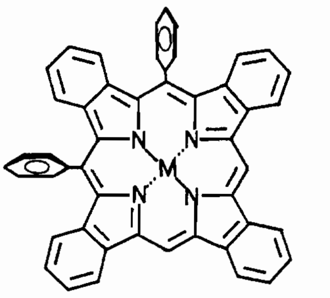


M = Zn or Mg

Structure of meso-diphenyltetrabenzoporphyrin

[13], followed by the insertion of magnesium ion in the metal-free compound, H_2P_2TBP, with magnesium perchlorate in pyridine under reflux. The reaction mixture was concentrated by evaporation *in vacuo*, and then diluted with ether. This ether solution of MgP_2TBP with pyridine was washed with 0.1 N HCl solution in order to remove the pyridine ligand from the axis of MgP_2TBP. After evaporation of the solvent, further purification was carried out in the same manner as above. FD-MS: $m/z = 684$; UV–Vis: 414(0.13), 438(1.0), 592(0.034), 637(0.20) nm in dichloromethane (Intensity ratio).

DPI, TPS and TPSe were prepared using the synthetic methods reported by Crivello and Lam [14].

Physical measurements

Fluorescence and fluorescence excitation spectra were obtained in acetonitrile solutions on a JASCO 770FP fluorospectrophotometer which was equipped with a red-sensitive photomultiplier (Hamamatsu Photonics R928).

Cyclic voltammetric measurements were made on a Hokuto Denko HB-104 function generator and HA-501 potentiostat/galvanostat with a Yokogawa 3086 X-Y recorder, utilizing a three electrode system which consisted of stationary platinum, platinum wire auxiliary, and $Ag/AgClO_4$ reference electrodes. The supporting electrolyte used was 0.1 M tetra-*n*-butylammonium perchlorate in DMF. The scanning voltage was $100\,mV\,s^{-1}$.

Fluorescence quenching experiments were carried out in acetonitrile solutions in the presence of the onium salts, prepared through purging with N_2 gas, using a conventional time-correlated single photon counting method with HORIBA NAES-1100 at 20 °C. Optically diluted solutions of TBPs (10^{-6} M) were used.

Results and discussion

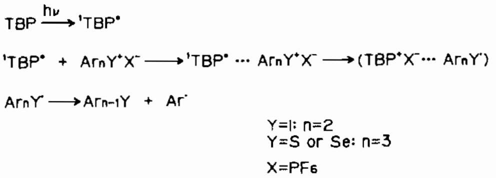
Estimation of free energy changes (ΔG)

There have been many studies on the photoinduced electron transfer reactions between various donors and acceptors [15]. In particular, the relationship between the free energy change, ΔG, associated with the electron transfer process and the quenching rate constant of the excited molecule by the quencher has been established by Rehm and Weller, using a number of systems consisting of fluorescent aromatic hydrocarbons and various quenchers [16, 17]. They have described that the ΔG value is expressed by eqn. (1).

$$\Delta G\,(\mathrm{kcal\ mol^{-1}}) = 23.06 \times [E(\mathrm{D/D^+}) - E(\mathrm{A/A^-}) - e^2/\varepsilon a] - E_{00}(\mathrm{kcal\,mol^{-1}}) \quad (1)$$

where $E(\mathrm{D/D^+})$ and $E(\mathrm{A/A^-})$ are the oxidation and reduction potentials of electron donor and acceptor, respectively, and the term of $e^2/\varepsilon a$ denotes the coulombic interaction energy between the radical ions at the encounter distance a in a solvent of dielectric constant ε.

According to the Rehm–Weller theory, it is inferred that the ΔG value related to the photoinduced electron transfer reaction is an important factor for interpretation of the efficiency of the free radical generation resulting from the photosensitized reaction between the TBP, electron donor, and the onium salt, electron acceptor, as shown in Scheme 1. In order to confirm this speculation, the oxidation potentials (E_{ox}) of the TBPs, the reduction potentials (E_{red}) of the onium salts, and the excited singlet state of TBPs were measured by cyclic voltammetry and a fluorospectrophotometer. Since the electrochemical oxidation of P_2TBPs occurred reversibly on CV measurements as shown in Fig. 1, the first E_{ox} of each TBP was correctly determined from their half-wave potentials. On the other hand, the peak potentials were employed in the case of the reduction potentials of the onium salts because of their irreversible reduction behavior. The E_{red} decreases from −0.26 V for DPI, to −1.36 V for TPS, and to −1.44 V for TPSe. This indicates that DPI is the most reducible compound among the other salts. Figure 2 shows the excitation and the fluorescence spectra of ZnP_2TBP where the lowest



Scheme 1.

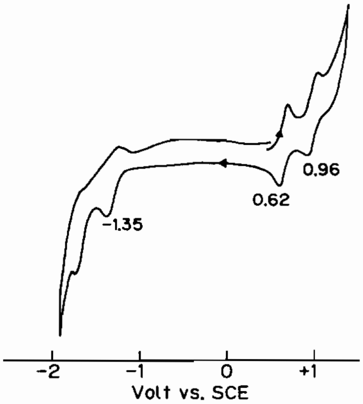


Fig. 1. Cyclic voltammogram of ZnP_2TBP in DMF. Electrode system: Pt/Pt/($Ag/AgClO_4$). Supporting electrolyte: 0.1 M $(n\text{-}Bu)_4N^+ClO_4^-$. Scanning voltage: 100 mV s^{-1}.

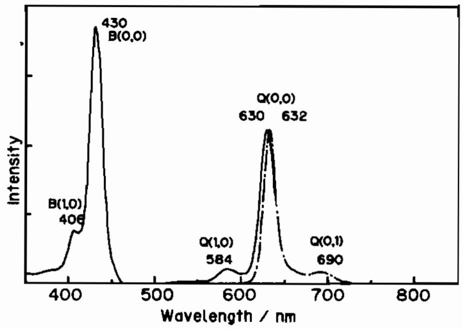


Fig. 2. Fluorescence (– · –) and fluorescence excitation (——) spectra of ZnP_2TBP in acetonitrile.

singlet excited energy level is determined from its O–O band. In addition to these data, the ΔG values derived from eqn. (1) are also summarized in Table 1, where it is shown that the ΔG values increase in the order of DPI > TPS > TPSe in both combinations with either ZnP_2TBP or MgP_2TBP. In the case of DPI, the photoinduced electron transfer from the excited singlet state of the TBPs is exothermic by 25–27 kcal mol^{-1}, but is either endothermic or slightly exothermic with respect to TPS and TPSe, respectively.

Fluorescence quenching study

At first, the fluorescence quenching was carried out by recording the fluorescence intensity changes of ZnP_2TBP in acetonitrile solutions of DPI (0.1–2 mM) under the condition that it was excited at its Soret band. The addition of DPI to the ZnP_2TBP solution does not affect the absorption spectrum of the TBP. Both the wavelength of maximum emission and the shape of the fluorescence spectra are unchanged in all solutions, as shown in Fig. 3. These results lead to the conclusion that static quenching does not occur in the fluorescence quenching of ZnP_2TBP by DPI and that exciplex formation does not occur in these acetonitrile solutions. This fluorescence quenching study gives this combination the rate constant, $3.6 \times 10^{10}\,M^{-1}\,s^{-1}$, which is derived from the slope of Stern–Volmer plots, $F_0/F = 1 + k_q\tau_0[Q]$, where F_0 and F are the intensity of fluorescence in the absence and presence of quencher, respectivley, k_q is the quenching rate constant, and τ_0 is the observed lifetime of the excited singlet of ZnP_2TBP with 1.15 ns by the single-photon counting method. However, this steady state technique led to the bleaching of TBPs in the photoreaction with DPI, resulting in a higher value of k_q compared to the diffusion-controlled limit in acetonitrile, $2.0 \times 10^{10}\,M^{-1}\,s^{-1}$.

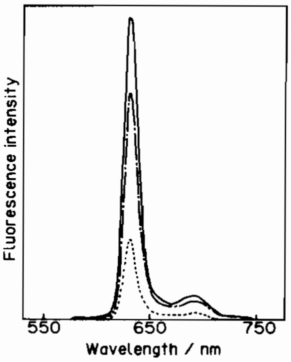


Fig. 3. Fluorescence spectra changes of ZnP_2TBP in the presence of DPI in acetonitrile solution: —, 1.6×10^{-6} M of ZnP_2TBP; – · –, in the presence of DPI (1.68×10^{-4} M); – – –, in the presence of DPI (2.18×10^{-3} M).

TABLE 1. Electrochemical properties of metallo-P_2TBP and free energy changes (ΔG) related to photoinduced electron transfer in combination with onium salts

TBP	$E(M/M^+)$ (V)	$^1E(O=O^*)$ (V)	$E(M^*/M^+)$ (V)	ΔG (kcal mol^{-1})[a]		
				DPI	TPS	TPSe
MgP_2TBP	0.50	1.94	−1.44	−27.2	−1.91	−0.06
ZnP_2TBP	0.62	1.96	−1.34	−24.9	0.56	2.40

[a] Reduction potentials of onium salts: DPI (−0.26), TPS (−1.36), TPSe (−1.44).

Fluorescence quenching was also studied by another technique: decay measurement of the fluorescence of TBPs in known concentrations of the onium salts, with a time-correlated single-photon counting. The plots of the inverse of lifetime, $1/\tau$, *versus* the concentration of quencher, [Q], give a straight line according to eqn. (2).

$$1/\tau = k_q[Q] + (k_d + k_{isc}) \qquad (2)$$

where k_q, and k_d, and k_{isc} denote the fluorescence quenching rate constant, the physical quenching rate constant, and the intersystem crossing rate constant, respectively. Figure 4 demonstrates the plots in the system of ZnP_2TBP with DPI where a straight line is shown. The k_q in this combination, $9.0 \times 10^9\ M^{-1}\ s^{-1}$, is derived from the slope of the plots. The plots also give the other systems straight lines. The k_q data are summarized in Table 2.

Figure 5 shows the quenching rate constants (k_q) as a function of the free energy change (ΔG) of electron transfer, in which the solid line represents the prediction curve for k_q according to eqn. (3) [16, 17]

$$k_q = 2.0 \times 10^{10}/[1 + 0.25 \exp(\Delta G^{\ddagger}/RT) + \exp(\Delta G/RT)] \qquad (3)$$

where ΔG and $\Delta G^{\ddagger}$ are the overall free energy change and the free energy of activation between the encounter complex and the ion pair, respectively. When DPI, with which the free energy changes are strongly negative in the combinations of both ZnP_2TBPs and MgP_2TBP, is used as a quencher, the quenching rate constants nearly reach the calculated encounter limit. In the region of slightly negative and positive ΔG values, as in the case of TPS and TPSe, the rate constants are sharply decreased as predicted by the Rehm–Weller treatment. The approximate agreement between the experimental and theoretical k_q data indicates that the photosensitized reaction of the TBPs with the onium salts primarily takes place by the photoinduced electron transfer from the excited singlet state P_2TBP to the onium salts.

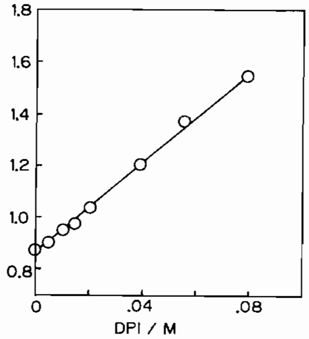


Fig. 4. Plots of inverse of fluorescence lifetimes of ZnP_2TBP in the either absence or presence of DPI vs. concentration of DPI in acetonitrile. Fluorescence quenching rate constant in this system was $9.0 \times 10^9\ M^{-1}\ s^{-1}$ from the slope.

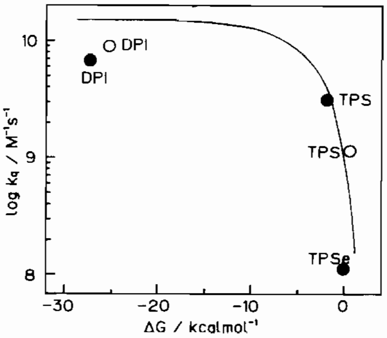


Fig. 5. Relation between free energy changes (ΔG) on photoinduced electron transfer in the system of either ZnP_2TBP or MgP_2TBP with onium salts and fluorescence quenching rate constants ($\log k_q$). The solid line stands for prediction curve for k_q according to Rehm–Weller eqn. (3) [16, 17]. ○, ZnP_2TBP; ●, MgP_2TBP.

Conclusions

The photosensitized reaction of metallo-P_2TBP with the onium salts occurs on the basis of photoinduced electron transfer reaction from the excited single state TBPs to the onium salts which is a rate-determining step in photopolymerization application, where the photosensitivity is enhanced in the following order, DPI (0.3 mJ/cm^2) > TPS (6.0 mJ/cm^2) ≫ TPSe (2000 mJ/cm^2) for He–Ne laser exposure [10].

TABLE 2. Fluorescence lifetimes of metallo-P_2TBPs and fluorescence quenching rate constants (k_q) in the combinations of TBPs and onium salts

Metallo-P_2TBP	τ_f (ns)	k_q ($10^9\ M^{-1}\ s^{-1}$)		
		DPI	TPS	TPSe
ZnP_2TBP	1.15	9.0	1.1	[a]
MgP_2TBP	5.28	6.8	2.1	0.11

[a] Not measured because a high concentration of TPSe is necessary to determine the k_q of this system.

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