

# Improvement of Quantum Yields for Photoinduced Energy/Electron Transfer by Isolation of Self-Aggregative Zinc Tetraphenyl Porphyrin-Pendant Polymer Using Cyclodextrin Inclusion in Aqueous Solution

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Cyclodextrin inclusion for self-aggregative sensitizers was found to improve quantum yields for photoinduced energy/electron transfer by the isolation of sensitizers in an aqueous solution. In water, cyclodextrin derivatives can prevent self-aggregation of sensitizers, which decreases the total quantum yields for photoinduced energy/electron transfer by fast self-quenching of singlet excited states, and anionic water-soluble zinc tetraphenyl porphyrin-*pendant* polymers (poly-ZnP) show self-aggregation and self-quenching of the singlet excited state of the zinc tetraphenyl porphyrin moiety. With the addition of 2,3,6-tri-*O*-methyl- $\beta$ -cyclodextrin (TMBCD) to an aqueous solution of poly-ZnP, cyclodextrin inclusion induces isolation of the zinc tetraphenyl porphyrin moiety, which extends extensively the lifetime of the singlet excited state. In the presence of TMBCD, the quantum yield for photoinduced triplet–triplet (T–T) energy transfer ( $\Phi_{\text{en}}$ ) from photoexcited poly-ZnP to O<sub>2</sub> was enhanced remarkably from 0.11 (without TMBCD) to 0.57 (with TMBCD) in air-saturated water. Also, the quantum yield for electron transfer ( $\Phi_{\text{et}}$ ) from photoexcited poly-ZnP to water-soluble  $\gamma$ -cyclodextrin-bicapped [60]fullerene (C<sub>60</sub>/γ-CD) increased from 0.095 (without TMBCD) to 0.20 (with TMBCD) in Ar-saturated water. Through quantitative photolysis, it has been revealed that the quantum yield for the formation of triplet excited poly-ZnP ( $\Phi_{\text{T}}$ ) is increased greatly to produce large  $\Phi_{\text{en}}$  and  $\Phi_{\text{et}}$  values with the addition of TMBCD to the solution. Demonstrated is a new strategy to improve quantum yields for photoinduced reactions using cyclodextrin derivatives as an isolator/stabilizer of photoexcited self-aggregative dyes.

## Introduction

Intensive studies for the creation of efficient photoinduced electron transfer systems in homo- or heterogeneous media (solutions, polymer films, and membranes) have been conducted over the past few decades. Photogenerated ion radicals can be utilized for solar energy conversions such as photocurrent generation<sup>1,2</sup> or the photocatalytic decomposition of water.<sup>3</sup>

High-optical-density compositions for effective light absorption in solutions/membranes are necessary in order to design functional photoreactive devices. However, highly concentrated dyes in photoreaction systems often show undesirable self-quenching processes such as the coupling of excitons,<sup>4</sup> excimer formation,<sup>5</sup> triplet–triplet (T–T) annihilation,<sup>6</sup> and dye–dye electron transfer.<sup>7</sup> All these processes have the tendency to decrease the total quantum yields for the expected photoinduced energy/electron transfer. These deactivation processes are especially thought to occur for the sensitizers of self-aggregative

nature, such as aromatic hydrocarbons and porphyrins. To establish effective photochemical systems without deactivation of the excited self-aggregative sensitizers, it is necessary to consider the photoreaction systems in which self-aggregation and self-quenching do not occur even in high-dye-concentration or dye-*pendant* polymers. It is therefore thought that studies on the control of excited states under such high-dye-concentration conditions are needed.

Various inclusion compounds such as calixarenes or crown ethers have been synthesized; thus, it is possible to design photoinduced reaction systems with a supramolecular assembly using the ideas of host–guest chemistry. For example, some sensitizing molecules connected with functional combination units such as calixarenes or crown ethers by covalent/noncovalent bonding have been reported.<sup>8,9</sup> These studies have succeeded in increasing the quantum yields for photoinduced electron transfer or in the application of an effective fluorescent chemosensor by strengthening the interaction between sensitizer and quencher/substrate using their combination units. Controlling the photoinduced reaction processes with the techniques of supramolecular chemistry is expected to provide new strategies that will provide exciting new topics in photochemistry. For the current purpose, self-quenching between the self-aggregative dyes under high-dye-concentration conditions can be controlled by the isolation of the sensitizer through cyclo-

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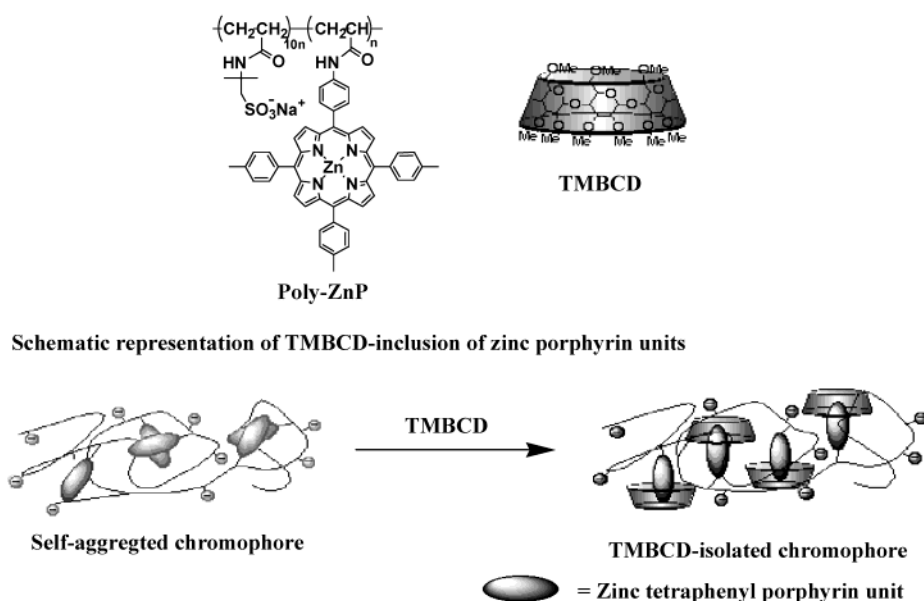
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## SCHEME 1



dextrin inclusion. Facile improvement in quantum yields for electron transfer systems can be expected with the inclusion of sensitizers.

In the present study, we have constructed a novel strategy for controlling lifetimes of photoexcited states of the self-aggregative sensitizer to improve the quantum yield for photoinduced electron/energy transfer. An anionic water-soluble zinc tetraphenyl porphyrin-pendant polymer (5-(4-acryloylamino-phenyl)-10,15,20-tri-*p*-tolylporphyrinate zinc(II), poly-ZnP) was used as a self-aggregative sensitizer (Scheme 1). In our previous study, poly-ZnP was found to be a useful compound in the construction of a donor–acceptor multilayer photocurrent generator with a cationic homooxa[3]calixarene-included [60]-fullerene ( $C_{60}$ /calixarene) layer on an indium–tin oxide (ITO) electrode by the alternate adsorption method utilizing Coulombic interaction.<sup>10</sup> However, it is regarded that the self-aggregation of zinc tetraphenyl porphyrin units causes a certain decrease of efficiency for photocurrent generation derived from photoinduced electron transfer between the excited porphyrin moiety and the  $C_{60}$  moiety.<sup>11</sup> 2,3,6-Tri-*O*-methyl- $\beta$ -cyclodextrin (TMBCD) was used as an isolator of zinc tetraphenyl porphyrin units, as it was reported as an effective host molecule for the possessing of high inclusion constants for tetraphenyl porphyrin derivatives.<sup>12</sup> This inclusion behavior originates from the pore size and molecular configuration of TMBCD, which can be changed flexibly due to the lack of intramolecular hydrogen bonding. Water-soluble  $\gamma$ -cyclodextrin-bicapped [60]fullerene ( $C_{60}/\gamma$ -CD) was used as an electron acceptor, which showed high electron-accepting ability and relatively well-resolved absorption bands of the excited states and the ion radicals in visible/near-IR regions.<sup>13</sup> In aqueous homogeneously mixed solution containing poly-ZnP, quantum yields for photoinduced energy and electron transfer from photoexcited porphyrin units in the presence/absence of TMBCD were investigated with steady-state and time-resolved spectroscopic measurements.

## Experimental Section

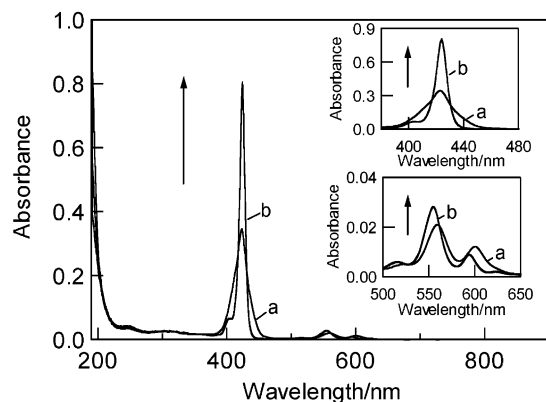
**Materials.** An anionic water-soluble zinc tetraphenyl porphyrin-pendant polymer (5-(4-acryloylamino-phenyl)-10,15,20-tri-*p*-tolylporphyrinate zinc(II), poly-ZnP) was prepared by the method described in our previous paper.<sup>10</sup> Water-soluble  $\gamma$ -cy-

clodextrin-bicapped [60]fullerene ( $C_{60}/\gamma$ -CD) was prepared with the ball milling method.<sup>13b,c,14</sup> 2,3,6-Tri-*O*-methyl- $\beta$ -cyclodextrin (TMBCD) was purchased from Wako Pure Chemical Industries Co. Ltd. Spectroscopic grade distilled water was purchased from Kanto Chemical Co. Ltd. and used as received.

**Instrumentation.** Steady-state absorption and emission spectra in the vis/near-IR region were measured with a JASCO V-570DS spectrophotometer and a Shimadzu RF-5300PC spectrophotometer, respectively. Luminescence spectra in the near-IR region were measured by using an argon-ion laser (Spectra-Physics, BeamLok 2060-10-SA, 488 nm, ca. 200 mW) as an excitation source. The emission from the sample was focused onto a monochromator (Koken Kogyo, SG-100) equipped with an InGaAs-PIN photodiode (New Focus, 2153). The output signal was recorded using a lock-in amplifier (NF Electronic Instruments, LI 5640). Time-resolved fluorescence spectra were measured with a single photon counting method using SHG (410 nm) of a Ti:sapphire laser (Spectra Physics, Tsunami 3950-L2s, 1.5 ps fwhm) and a streak scope (Hamamatsu Photonics, C4334-01) equipped with a polychromator. Transient absorption spectra and the absorption–time profiles of transient species were measured by the selective excitation of the zinc tetraphenyl porphyrin moiety with 560 nm laser light from an OPO laser (HOYA continuum Surelite OPO, 6 ns fwhm, and 10 mJ/pulse) or SHG (532 nm) of a Nd:YAG laser (Spectra Physics, Quanta-Ray GCR-130, 6 ns fwhm, and 10 mJ/pulse). For the transient absorption spectra in the near-IR region, an InGaAs-PIN photodiode module (Hamamatsu Photonics G5125-10) was employed as a detector for the probe light from a steady 150 W Xe-lamp equipped with cutoff filters to avoid further photolysis. A sample solution in a rectangular quartz reaction cell (optical path = 1 cm) was deaerated with Ar gas bubbling for 20 min before measurements.

## Results and Discussion

**Aggregation of Zinc Tetraphenyl Porphyrin Units in the Ground and Singlet Excited States.** The UV/vis absorption spectra of an aqueous solution of poly-ZnP showed the characteristic band corresponding to zinc tetraphenyl porphyrin units (spectrum a in Figure 1). The shape of the absorption is evidently more broadened than that of other zinc tetraphenyl

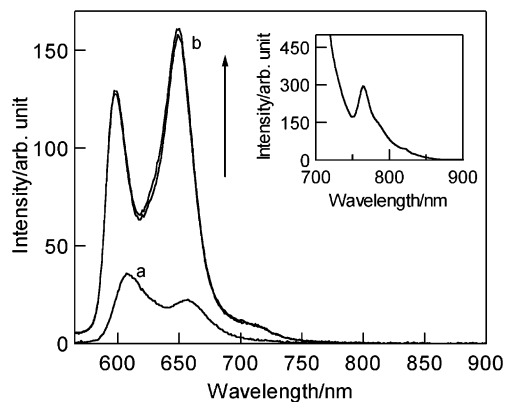


**Figure 1.** Absorption spectra of aqueous solutions: (a) poly-ZnP; (b) poly-ZnP in the presence of 1.0 mM TMBCD. Spectrum (b) overlapped completely with the spectrum observed in the presence of 8.0 mM TMBCD. [zinc tetraphenyl porphyrin units] =  $10\ \mu\text{M}$ , and optical path = 2 mm.

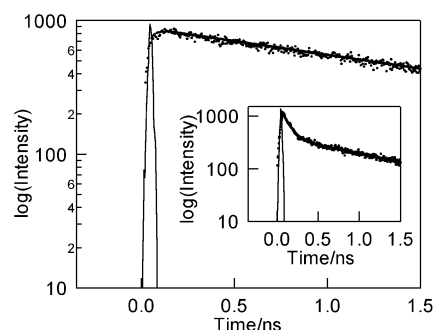
porphyrin derivatives in organic solvents. This result indicates that each porphyrin unit of poly-ZnP self-aggregates with  $\pi$ - $\pi$  interactions even at relatively low concentrations in water. Upon addition of excess TMBCD (1.0 mM) to the poly-ZnP aqueous solution, the absorption spectra show a significant change from broadened band to sharpened band especially in the 400–440 nm region. This absorption in the 400–440 nm region can be attributed to the Soret band of zinc tetraphenyl porphyrin units (spectrum b in Figure 1). This observation suggests that the aggregated zinc tetraphenyl porphyrin units can be isolated to units independent of each other through TMBCD inclusion in the ground states. Further addition of TMBCD (8.0 mM) gave the same spectrum as spectrum b in Figure 1. In the presence of  $\gamma$ -cyclodextrin, the absorption spectra showed almost the same spectral form as the poly-ZnP solution in the absence of TMBCD, which indicates that  $\gamma$ -cyclodextrin has a relatively small isolation ability toward zinc tetraphenyl porphyrin units of poly-ZnP. This tendency resulted from the cavity size and flexibility of molecular conformations of cyclodextrins. To isolate self-aggregative sensitizers, it is necessary to use cyclodextrins that have a suitable size compared to the chromophore.

The discretely insulated zinc tetraphenyl porphyrin units in the ground states are expected to play a role as an effective “free” sensitizer through photoirradiation, but not as a less effective “aggregated” sensitizer. To evaluate the TMBCD isolation effects on photoexcited zinc tetraphenyl porphyrin units, steady-state fluorescence measurements were carried out in both the presence and absence of TMBCD. By adding TMBCD under completely optically matched conditions on each sample solution and apparatus, the fluorescence derived from singlet excited states of zinc tetraphenyl porphyrin units ( $^1\text{ZnP}^*$ ) was enhanced by ca. 4 times larger than that of the solution without TMBCD, as shown in Figure 2. At liquid- $\text{N}_2$  temperature (77 K), a new emission band appeared in the 750–800 nm region only in the presence of TMBCD. This new emission can be attributed to a phosphorescence band derived from triplet excited states of zinc tetraphenyl porphyrin units ( $^3\text{ZnP}^*$ ).<sup>15,16</sup> From these findings, it can be presumed that the lifetimes of singlet excited states of zinc tetraphenyl porphyrin units are extended with TMBCD isolation in aggregative states.

Time-resolved fluorescence was observed by a single photon counting method to obtain kinetic evidence for extended lifetimes of  $^1\text{ZnP}^*$  by the TMBCD-inclusion mechanism. As shown in Figure 3, the obtained fluorescence intensity–time



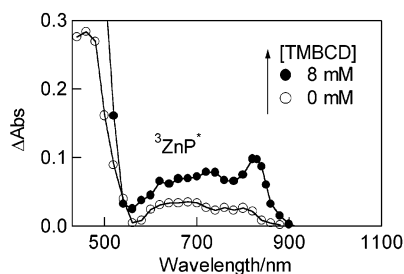
**Figure 2.** Fluorescence spectra of aqueous solutions: (a) poly-ZnP; (b) poly-ZnP in the presence of 1.0 mM TMBCD. Spectrum (b) almost overlapped with the spectrum observed in the presence of 8.0 mM TMBCD. [zinc tetraphenyl porphyrin units] =  $10\ \mu\text{M}$ . Inset: Emission spectrum of poly-ZnP in the presence of 8.0 mM TMBCD observed at 77 K. Excitation wavelength = 560 nm.



**Figure 3.** Time-resolved fluorescence measurements of poly-ZnP in water solution in the presence of TMBCD; monitored wavelength = 600–650 nm. Inset: Time–intensity profile of poly-ZnP solution in the absence of TMBCD. [zinc tetraphenyl porphyrin units] =  $10\ \mu\text{M}$ ; [TMBCD] = 8.0 mM. Excitation wavelength = 410 nm.

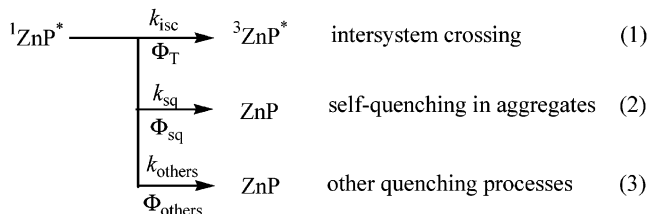
profiles were changed significantly with the addition of TMBCD. In the absence of TMBCD, the time course of fluorescence from  $^1\text{ZnP}^*$  showed a very fast decay and had two kinetic components. One was a very fast decay time constant of 87.5 ps (73.5%), which is attributed to the fluorescence component of “aggregated” zinc tetraphenyl porphyrins, and the other was a 1.36 ns decay component (26.5%), which is attributed to the fluorescence decay of “free” zinc tetraphenyl porphyrins. In the presence of TMBCD, the decay–time profile of fluorescence can be analyzed as one component decay of 2.11 ns (100%), which shows that TMBCD isolation of zinc tetraphenyl porphyrins hinders the self-quenching caused by self-aggregation of each zinc tetraphenyl porphyrin unit. These findings show that TMBCD inclusion is useful in improving the quantum yields for photoinduced reactions via singlet excited states through the suppression of the competitive fast decay process of singlet excited states. The coupling of excitons and the excimer formation along the polymer chain can be considered a cause for the fast decay component in the aggregate state.

**Study of Triplet Excited States of Zinc Tetraphenyl Porphyrin Units.** As described above, it was found that the lifetime of  $^1\text{ZnP}^*$  is extended greatly by the isolation of the chromophore with TMBCD. This finding reasonably predicts that the quantum yield for formation of  $^3\text{ZnP}^*$  is also increased by the addition of TMBCD, because intersystem crossing (ISC) to form  $^3\text{ZnP}^*$  is an important quenching process of singlet excited states, which is a process in competition with self-



**Figure 4.** Transient absorption spectra obtained immediately after ns-laser exposure (250 ns) with 560 nm laser light: (open circles) poly-ZnP solution; (solid circles) poly-ZnP/TMBCD system. [zinc tetraphenyl porphyrin units] = ca. 10  $\mu$ M, [TMBCD] = 8.0 mM.

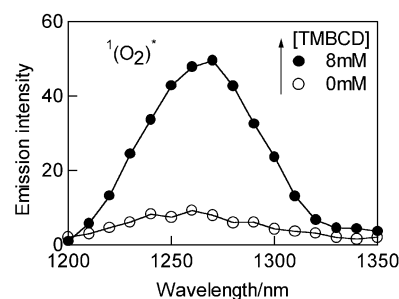
## SCHEME 2



quenching processes of singlet excited states shown in Scheme 2.

A quantitative laser flash photolysis was performed to confirm the TMBCD effects on quantum yields for  ${}^3\text{ZnP}^*$  generation. Figure 4 shows the transient absorption spectra obtained by 532 nm nanosecond laser excitation of an Ar-saturated aqueous solution of poly-ZnP. An observed transient absorption band in the 450–900 nm region was found to be an absorption that corresponds to  ${}^3\text{ZnP}^*$ . The addition of TMBCD to the poly-ZnP solution brings forth a small change in the transient spectral shape, with the exception of a sharp peak appearing at 840 nm in the presence of TMBCD. Transient spectra with a sharp peak at 840 nm were observed from other derivatives of zinc porphyrins.<sup>15</sup> Therefore, it is deduced that the broadened 840 nm peak of  ${}^3\text{ZnP}^*$  in the absence of TMBCD was observed because of self-aggregation of ZnP units. These transient spectra from laser flash photolysis were obtained under critically optically matched conditions on each sample solution and apparatus, leading to the conclusion that quantitative transient absorption intensities reflect quantum yields for  ${}^3\text{ZnP}^*$  formation. In the presence of TMBCD, the absorption intensity of the transient spectrum of  ${}^3\text{ZnP}^*$  increased more than in the absence of TMBCD, as shown in Figure 4. To calculate quantum yields for the  ${}^3\text{ZnP}^*$  generation from absorption intensities shown in Figure 4, molar absorption coefficients of  ${}^3\text{ZnP}^*$  were needed. The molar absorption coefficients of  ${}^3\text{ZnP}^*$  were obtained kinetically from the T–T energy transfer from triplet excited eosin-Y to the zinc tetraphenyl porphyrin unit of poly-ZnP in water.<sup>17</sup> The molar absorption coefficients of  ${}^3\text{ZnP}^*$  were estimated as  $3600 \pm 150 \text{ cm}^{-1} \text{ M}^{-1}$  (at 750 nm, without TMBCD) and  $4000 \pm 200 \text{ cm}^{-1} \text{ M}^{-1}$  (at 750 nm, with excess TMBCD), respectively. These values are in agreement with those of other zinc tetraphenyl porphyrin derivatives in organic solvents.<sup>15</sup>

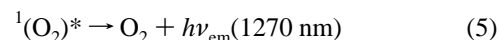
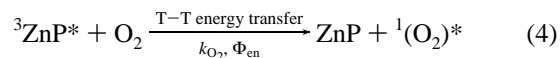
By considering the obtained molar absorption coefficients of  ${}^3\text{ZnP}^*$  and the transient absorption intensity of triplet excited states of  $\text{C}_{60}$  in benzene as an actinometer of excitation source,<sup>18a–c</sup> quantum yields for formation of  ${}^3\text{ZnP}^*$  ( $\Phi_T$ ) were estimated to be 0.27 (without TMBCD) and 0.66 (with TMBCD), as shown in Figure 4. It was found that the quantum yield for the triplet-excited-state generation is greatly enhanced



**Figure 5.** Emission spectra in near-IR region: (open circles) poly-ZnP solution, (solid circles) poly-ZnP/TMBCD system. [zinc tetraphenyl porphyrin units] = ca. 10  $\mu$ M, [TMBCD] = 8.0 mM.

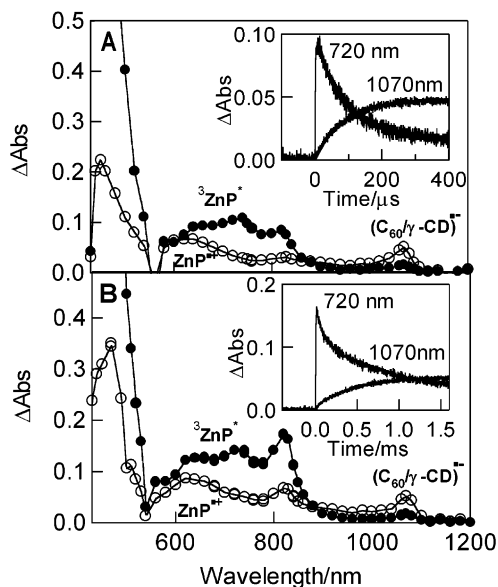
by TMBCD inclusion and the isolation of the chromophore. Decay rates of  ${}^3\text{ZnP}^*$  obeyed first-order kinetics, and the rate constants ( $k_d$ ) were calculated to be  $2.8 \times 10^2 \text{ s}^{-1}$  (without TMBCD) and  $1.0 \times 10^2 \text{ s}^{-1}$  (with TMBCD), which correspond to the lifetimes of  ${}^3\text{ZnP}^*$ , 3.6 and 10 ms, respectively; this proves the prolonged lifetime of isolated  ${}^3\text{ZnP}^*$ .

**Quantum Yields for Singlet Oxygen Generation via T–T Energy Transfer.** From these findings regarding the increase of quantum yield for  ${}^3\text{ZnP}^*$  generation with the addition of TMBCD, it can be expected that quantum yields for photoinduced energy transfer via  ${}^3\text{ZnP}^*$  by the addition of TMBCD will improve. Quantitative experiments of the T–T energy transfer from  ${}^3\text{ZnP}^*$  to molecular oxygen were conducted to prove this expectation.



T–T energy transfer occurs to yield singlet oxygen during the quenching process of  ${}^3\text{ZnP}^*$  by  $\text{O}_2$ . Singlet oxygen formation and its quantum yields were confirmed by direct measurements of emission from singlet oxygen at the peak of 1270 nm in the near-IR region, as shown in Figure 5.<sup>19</sup> These emission spectra were obtained by photolysis of a poly-ZnP air-saturated aqueous solution under the critically same optical conditions for each sample solution and apparatus. With the addition of TMBCD, a larger emission intensity was observed to be ca. 5 times in intensity compared with the original solution, indicating that the quantum yield for singlet oxygen was enhanced by ca. 5 times compared with the value in the absence of TMBCD. On the basis of the quantum yield of the singlet oxygen formation from photoexcited eosin-Y in water ( $\Phi_{\text{en}} = 0.57$ ),<sup>17,18d</sup> the  $\Phi_{\text{en}}$  values of poly-ZnP systems were calculated to be 0.11 (without TMBCD) and 0.57 (with TMBCD).<sup>19</sup> Rate constants for the quenching process of  ${}^3\text{ZnP}^*$  by  $\text{O}_2$  ( $k_{\text{O}_2}$ ) were estimated as  $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (without TMBCD) and  $4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (with 8.0 mM TMBCD) by nanosecond laser flash photolysis. It was found that the rate constants for T–T energy transfer decreased in the presence of TMBCD, while the quantum yield for singlet oxygen generation increased. The observed small  $k_{\text{O}_2}$  value in the presence of TMBCD may be attributed to the shielding effect of TMBCD. However, this shielding effect is less effective for the quantum yields for this system, and the change in quantum yield for the  ${}^3\text{ZnP}^*$  formation may contribute predominantly to the change in the quantum yield for T–T energy transfer. The reason is related to the fact that other significant quenching processes competing with T–T energy transfer were not found in this system. From these findings, it is deduced that the improvement of quantum yields is similarly expected for other energy acceptors with the addition of TMBCD.

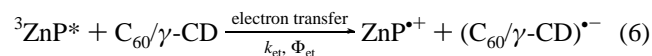




**Figure 6.** Transient absorption spectra obtained by ns-laser light (560 nm): (A) poly-ZnP solution, (solid circles) 25  $\mu$ s, (open circles) 250  $\mu$ s; (B) poly-ZnP/TMBCD system, (solid circles) 100  $\mu$ s, (open circles) 1 ms. [zinc tetraphenyl porphyrin units] = 10  $\mu$ M, [ $C_{60}/\gamma$ -CD] = 0.05 mM, [TMBCD] = 8.0 mM.

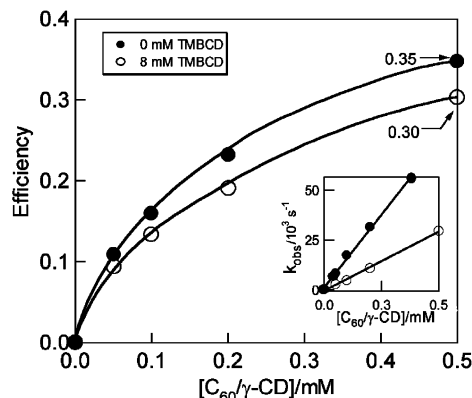
**Quantum Yield for Electron Transfer to  $C_{60}/\gamma$ -CD from  $^3ZnP^*$ .** From the increase in quantum yield for  $^3ZnP^*$  generation with the addition of TMBCD, it is also expected to improve quantum yields for photoinduced electron transfer via  $^3ZnP^*$ . To confirm the TMBCD effects on quantum yields for electron transfer, an electron transfer system between photoexcited zinc tetraphenyl porphyrin units and  $C_{60}/\gamma$ -CD was designed.

Figure 6A shows the transient absorption spectra obtained by 560 nm selective nanosecond-pulse laser excitation of zinc tetraphenyl porphyrin units in Ar-saturated aqueous solution consisting of poly-ZnP and  $C_{60}/\gamma$ -CD, without TMBCD. The transient absorption band with a characteristic spectral form which appeared in the 400–900 nm region immediately after the laser exposure can be attributed to  $^3ZnP^*$ .<sup>15,20</sup> With the decay of  $^3ZnP^*$ , new absorption bands appeared at 620 and 1040 nm, which can be attributed to  $ZnP^{*+}$  and  $(C_{60}/\gamma-CD)^{\bullet-}$ , respectively.<sup>15,20</sup> Similarly, in the presence of TMBCD, laser flash photolysis of the solution gives a similar transient spectral change from  $^3ZnP^*$  to  $ZnP^{*+}$  and  $(C_{60}/\gamma-CD)^{\bullet-}$ , as shown in Figure 6B.



To evaluate the kinetic parameters and the possible reaction mechanisms for electron transfer, the dependence of the pseudo-first-order decay rate constants for  $^3ZnP^*$  ( $k_{obs}$ ) on the  $C_{60}/\gamma$ -CD concentration was analyzed. In each system, the decay profile of  $^3ZnP^*$  obeys first-order kinetics, and a straight line is given in the pseudo-first-order plots (inset of Figure 7). The second-order quenching rate constants for  $^3ZnP^*$  by  $C_{60}/\gamma$ -CD ( $k_q$ ) were estimated from a slope of the fitted calculation line to be  $1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (without TMBCD) and  $5.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (with TMBCD). Inclusion of  $^3ZnP^*$  in TMBCD retards the collision with  $C_{60}/\gamma$ -CD through shielding effects.

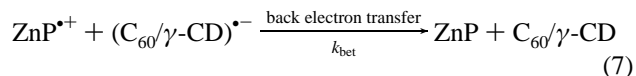
Efficiency for electron transfer via  $^3ZnP^*$  can be evaluated from the saturated ratio of  $[(C_{60}/\gamma-CD)^{\bullet-}]_{\max}$  to  $[^3ZnP^*]_{\text{initial}}$ ; these concentrations are calculated by using the molar absorption coefficients of the transient species. Figure 7 shows the efficiency curve for electron transfer from  $^3ZnP^*$  to  $C_{60}/\gamma$ -CD



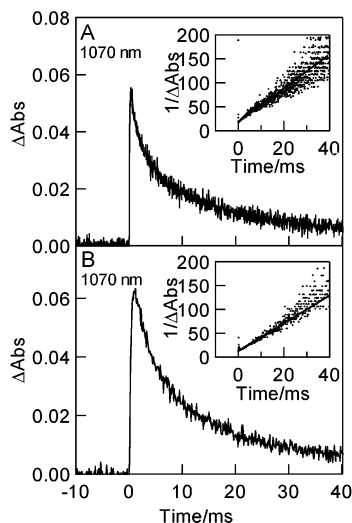
**Figure 7.** Efficiency plot for photoinduced electron transfer via  $^3ZnP^*$  obtained by laser flash photolysis: (open circles) poly-ZnP/ $(C_{60}/\gamma-CD)$  system; (closed circles) poly-ZnP/ $(C_{60}/\gamma-CD)$ /TMBCD system. Efficiency =  $[(C_{60}/\gamma-CD)^{\bullet-}]_{\max}/[^3ZnP^*]_{\text{initial}}$ . Inset: Pseudo-first-order plots of  $^3ZnP^*$  quenching by  $C_{60}/\gamma$ -CD.

with the electron transfer mechanism. The curve shows a tendency to saturate at higher concentrations of  $C_{60}/\gamma$ -CD. From the maximal ratio ( $[(C_{60}/\gamma-CD)^{\bullet-}]_{\max}/[^3ZnP^*]_{\text{initial}}$ ), the efficiencies ( $\phi_{et}$ ) for electron transfer via  $^3ZnP^*$  can be evaluated to be 0.35 (without TMBCD) and 0.30 (with TMBCD). The  $\phi_{et}$  value for the TMBCD-included system is slightly lower than the  $\phi_{et}$  value for the system without TMBCD, which reflects the difference of the  $k_q$  values for the  $^3ZnP^*$  quenching by  $C_{60}/\gamma$ -CD. The quantum yield ( $\Phi_{et}$ ) for electron transfer from  $^1ZnP^*$  to  $(C_{60}/\gamma-CD)^{\bullet-}$  (= photon to radicals) can be evaluated by the following relation:  $\Phi_{et} = \Phi_T \times \phi_{et}$ . The  $\Phi_{et}$  value for the ZnP/ $(C_{60}/\gamma-CD)$  system can thus be evaluated as 0.095 (without TMBCD) and 0.20 (with TMBCD). As in the case of the T–T energy transfer system, the quantum yield for electron transfer to  $C_{60}/\gamma$ -CD increased remarkably in the presence of TMBCD, although the rate constants decreased. This result also reflects an increase in the quantum yield for  $^3ZnP^*$  generation and the long lifetime of triplet excited states. The improvement of quantum yields is similarly expected for other electron acceptors with the addition of TMBCD.

**Lifetime of Radical Ions.** After the photoinduced electron transfer, radical ions  $(C_{60}/\gamma-CD)^{\bullet-}$  and  $ZnP^{*+}$  persisted up to 100 ms (half-life = ca. 10 ms), as shown in Figure 8 for the decay of  $(C_{60}/\gamma-CD)^{\bullet-}$ . The absorption intensity of  $ZnP^{*+}$  also began to decay with the same rate as that of  $(C_{60}/\gamma-CD)^{\bullet-}$ . These decays can be attributed to the back electron transfer process between  $(C_{60}/\gamma-CD)^{\bullet-}$  and  $ZnP^{*+}$ .



These decays obey second-order kinetics, as shown in the inset of Figure 8. The ratio of the rate constant to the molar extinction coefficient ( $k_{bet}/\epsilon(C_{60}/\gamma-CD)^{\bullet-}$ ) can be obtained from the slopes of the second-order plots. The  $k_{bet}$  values were evaluated to be  $3.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (without TMBCD) and  $3.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (with TMBCD). Both  $k_{bet}$  values are far smaller than the diffusion-controlled limit ( $5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in water). It appears that the radical cation center (holes) in the polymer escapes over the whole polymer chain apart from  $(C_{60}/\gamma-CD)^{\bullet-}$ , which retards the encounter of  $(C_{60}/\gamma-CD)^{\bullet-}$  with the hole again.<sup>21,22</sup> These  $k_{bet}$  values indicate that TMBCD-included zinc tetraphenyl porphyrin units have not lost the characteristic of hole transfer in the polymer chain. These findings are important in relation to the formation of long-lived charge-separated states,



**Figure 8.** Time-absorption profiles of  $(C_{60}/\gamma\text{-CD})^{\bullet-}$  observed on the long time scale: (A) poly-ZnP/ $(C_{60}/\gamma\text{-CD})$  system; (B) poly-ZnP/ $(C_{60}/\gamma\text{-CD})$ /TMBCD system. Inset: Second-order kinetic analysis for back electron transfer.

which are applicable to photoconductivity or photoenergy conversion systems. The lifetimes of radical ions in our present system are long enough for use as an effective electron pool, which can be applied to the second electron transfer in some photoenergy storage/conversion systems. Improvement of quantum yields by utilizing TMBCD inclusion and construction of an efficient electron transfer system generating long-lived charge-separated states have been investigated.

### Concluding Remarks

A new strategy for the facile construction of highly effective photoinduced energy/electron transfer systems utilizing the inclusion of self-aggregative sensitizers with TMBCD has been established by applying the concept of host-guest chemistry. By applying the TMBCD as an isolator/stabilizer for zinc tetraphenyl porphyrin units, the lifetimes of singlet excited states and quantum yields for triplet-excited-state generation increased remarkably. Quantum yields for energy/electron transfer were also enhanced in the presence of TMBCD because of the increase in quantum yield for triplet-excited-state generation. In the electron transfer system, the back electron transfer between  $(C_{60}/\gamma\text{-CD})^{\bullet-}$  and  $\text{ZnP}^{*+}$  is very slow; the ion radicals persisted for about 100 ms in both the presence and absence of TMBCD. From these results, we have concluded that the introduction of host-guest inclusion properties between cyclodextrin and self-aggregative zinc tetraphenyl porphyrin units as sensitizer is meaningful in improving the quantum yield (total yield) for photoinduced energy/electron transfer. It is deduced that the improvement of quantum yields is similarly expected for other self-aggregative sensitizers through the use of suitable types of cyclodextrins. We expect that the present concept obtained from the host-guest effect on the improvement of quantum yields will be developed for membrane and thin film systems on electrodes.

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### References and Notes

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