

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

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High-optical-dense compositions for the effective light absorption in solution/membrane are required to design functional photoreactive devices. However, highly concentrated dyes in photoreaction systems often show undesirable self-quenching processes which have tendencies to decrease the total quantum yields for the expected photoinduced energy/electron transfer. These deactivation processes are thought to occur especially for the sensitizers with self-aggregative nature (aromatic hydrocarbons, porphyrins etc.). 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 and in dye-pendant polymers.

We report herein a novel strategy for controlling lifetimes of photoexcited states of self-aggregative sensitizer to improve quantum yield for photoinduced electron/energy transfer by isolation of sensitizer using cyclodextrin-inclusion. An anionic water-soluble zinc tetraphenyl porphyrin-pendant polymer (5-(4-acryloyl aminophenyl)-10,15,20-tri-*p*-tolylporphyrinate zinc(II), poly-ZnP) was used as a self-aggregative sensitizer.¹ As an isolator of zinc tetraphenyl porphyrin units, 2,3,6-tri-*O*-methyl- β -cyclodextrin (TMBCD) was used. Water-soluble γ -cyclodextrin-bicapped [60]fullerene (C₆₀/ γ -CD) was used as an electron acceptor. In aqueous homogeneously mixed solution containing poly-ZnP, quantum yields for photoinduced energy and electron transfer from photoexcited porphyrin unit in the presence/absence of TMBCD were investigated by steady-state and time-resolved spectroscopic measurements.

Time-resolved fluorescence from singlet excited states of ZnP (¹ZnP*) was observed. In the absence of TMBCD, time-course of the fluorescence showed two kinetic components. One is a very fast decay time-constant of 87.5 ps (73.5 %), which is assigned to the fluorescence component of "aggregated" zinc tetraphenyl porphyrins, and another is a 1.36 ns-decay component (26.5 %), which is assigned to a 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 critically shows that TMBCD-isolation of zinc tetraphenyl porphyrins prohibits the self-quenching derived from self-aggregation of each zinc tetraphenyl porphyrin unit.

To confirm the TMBCD-effects on quantum yield for formation of triplet excited states of ZnP (³ZnP*), a

quantitative laser flash photolysis was performed. Transient absorption spectra obtained by a 532-nm nano-second laser excitation of Ar-saturated aqueous solution of poly-ZnP. In the presence of TMBCD, an absorption intensity of the transient spectrum of ³ZnP* was increased more than that in the absence of TMBCD (Figure 2). Quantum yields for formation of ³ZnP* were estimated to be 0.27 (without TMBCD) and 0.66 (with TMBCD). It was found that the quantum yield for the triplet-excited-state generation is highly enhanced by TMBCD-inclusion and isolation of the chromophore.

In the presence of molecular oxygen, triplet-triplet energy transfer occurs to yield singlet oxygen by photo excitation of poly-ZnP. Singlet oxygen formation and its quantum yields were confirmed by direct measurements of emission from singlet oxygen at the peak of 1270 nm. The quantum yields for T-T energy transfer were calculated to be 0.11 (without TMBCD) and 0.57 (with TMBCD). In the presence of C₆₀/ γ -CD, electron transfer between photo excited-ZnP and C₆₀/ γ -CD. Quantum yields for the electron transfer were evaluated as 0.095 (without TMBCD) and 0.20 (with TMBCD) by measurements of nano-second laser flash photolysis.

In conclusion, the quantum yields for energy/electron transfer is highly enhanced in the presence of TMBCD because of the increase in quantum yield for triplet-excited-state generation. This improvement of quantum yields is similarly expectable about other self-aggregative sensitizers by the use of suitable type of cyclodextrins.

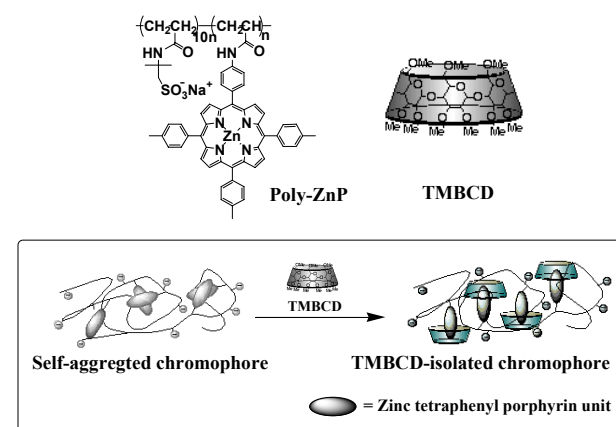


Figure 1. Schematic representation of self-aggregation of ZnP-units in solution and TMBCD-inclusion/isolation.

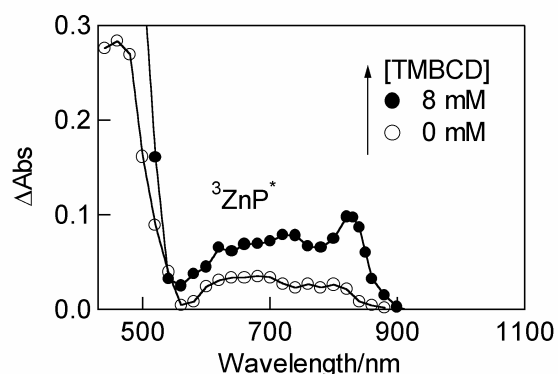


Figure 2. Transient absorption spectra obtained immediately after ns-laser exposure (250 ns) with 560-nm laser light. [zinc tetraphenyl porphyrin units] = ca. 10 μ M, [TMBCD] = 8.0 mM.

Reference

(1) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama T.; Yamada, S. *J. Am. Chem. Soc.*, **2001**, 123, 4855.