Fluorescence Resonance Energy Transfer in Host–Guest Inclusion Complexes of Cyclodextrin–Porphyrin Composite in Aqueous Solution

Kiyotada Hosokawa, Yutaka Miura, Takayuki Kiba, Toyoji Kakuchi, and Shin-ichiro Sato*
Division of Biotechnology and Macromolecular Chemistry, Graduate School of Engineering,
Hokkaido University, Sapporo 060-8628

(Received August 13, 2007; CL-070864; E-mail: s-sato@eng.hokudai.ac.jp)

A composite of zinc tetraphenylporphyrin linked with β-cyclodextrin was prepared as a convenient scaffold for a self-assembled energy-transfer complex. The energy-transfer properties of the host–guest complexes were investigated for several guest molecules (naphthalene, anthracene, 2-methylanthracene, and 9,10-dimethylanthracene) by means of fluorescence and fluorescence-excitation spectroscopies.

Fluorescence resonance energy transfer (FRET) of a linked donor–acceptor (DA) composite has been widely investigated because of its relevance to biomimetic photosynthesis.[1] The porphyrin-based DA composites, in which porphyrins are covalently linked to either an energy donor or acceptor, are one of the most important categories in the linked FRET system.[2,3] On the other hand, self-assembled supramolecular systems have been receiving great attention in many fields of material science.[4] Composites that include cyclodextrins (CDs) are a very useful scaffold for these supramolecular systems. The photoreaction properties and relaxation dynamics of excited guest molecules encapsulated in CDs have been investigated by several workers.[5] Recently, Kano et al. demonstrated the usefulness of the porphyrin–CD composite as a scaffold for heteroporphyrin arrays.[6]

In the present study, we synthesized a zinc tetraphenylporphyrin linked with β-CD (ZnP–β-CD), which was designed as a scaffold for the self-assembled energy-transfer complex. The energy-transfer properties of the host–guest complexes, in which the relative donor–acceptor geometry would be almost the same, were investigated for several guest molecules (naphthalene (NA), anthracene (AN), 2-methylanthracene (MA), and 9,10-dimethylanthracene (DMA)) by means of fluorescence and fluorescence excitation spectroscopies. The FRET efficiency of the self-assembled DA complexes is discussed herein on the basis of the Förster mechanism.

The freebase composite (H_2P–β-CD) was prepared by a condensation reaction of H_2PCOOH with 6-amino-β-CD in dry DMF/THF (1:1) mixed solvent containing a small amount of 1,3-dicyclohexylcarbodiimide, 1-hydroxybenzotriazole hydrate, and triethylamine. H_2PCOOH was obtained by dealkylation of 5-(4-methoxycarbonylphenyl)-10,15,20-triphenyl-21*H*, 23*H*-porphine (Tokyo Chemical).

H_2P–β-CD was allowed to react with zinc acetate to yield the ZnP–β-CD by stirring in a chloroform/methanol (5:1) mixed solvent for 4 days.[7] The formation of the ZnP–β-CD was confirmed by the fast atom bombardment (FAB) mass spectrometry ($m/z = 1837.7$) and ^{1}H NMR spectroscopy (δ, DMSO, 400 MHz; 3.34–5.53 (CD), 7.78 (phenyl), 8.16 (phenyl), 8.76 (β-pyrrole)).

Self-assembled DA inclusion complexes were prepared as follows. The ZnP–β-CD was dissolved in water at a saturated concentration. Guest molecules, AN (Sigma-Aldrich), MA (Nacalai tesque), DMA (Tokyo kasei), or naphthalene (NA; Sigma-Aldrich), were dissolved in ethanol. Four hundred microliters of the guest ethanol solution (ca. $10^{-4}\,\mathrm{mol\,L^{-1}}$) was added to the aqueous ZnP–β-CD solution. The solution was stirred for 12 h, and insoluble matter was removed by filtration. The host/guest stoichiometry was determined to be ca. 0.8 from their absorption spectra. The binding constant K was determined from the fluorescence titration measurements. The titration curves fitted well with the formation of a 1:1 complex and yielded binding constants: $K = 2.95 \times 10^7\,\mathrm{M^{-1}}$ for ZnP–β-CD/AN, $K = 4.86 \times 10^6\,\mathrm{M^{-1}}$ for ZnP–β-CD/MA, $K = 1.04 \times 10^6\,\mathrm{M^{-1}}$ for ZnP–β-CD/DMA.

Steady-state absorption, fluorescence, and excitation spectra at room temperature were measured with a U-3010 spectrophotometer (Hitachi) and an F-4500 fluorescence spectrometer (Hitachi), respectively.

Figure 1 shows absorption and emission spectra of ZnP–β-CD in ethanol/water (4:96) mixed solvent. The Soret, Q(0,1), and Q(0,0) absorption bands located at 433, 558, and 602 nm, respectively. The Soret band was broadened owing to aggregation. The rise of background in the UV region is the Rayleigh scattering from aggregates. The broadening of the Soret band was not observed for ZnP–β-CD in ethanol.

Figure 2 displays emission spectra of ZnP–β-CD in the presence and in the absence of the donor in ethanol/water (4:96) mixed solvent at room temperature. Each emission spectrum of AN, MA, DMA, and NA complexes was measured with the excitation of each donor absorption wavelength, at which the ZnP absorption was negligibly small; the reference spectra (thin line) were obtained for solution containing only ZnP–β-CD in order to show that no ZnP emission was observed in the absence of donor. The excitation of AN, MA, and DMA complexes gave ZnP emissions at 610 and 650 nm, whereas no ZnP emission was observed for ZnP–β-CD/NA complexes.

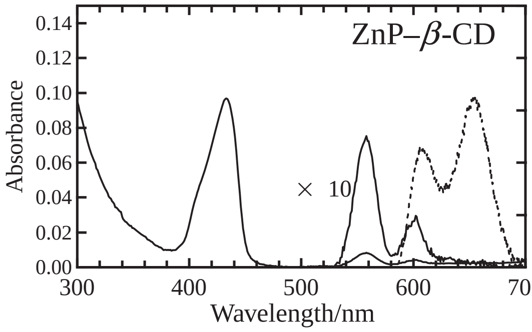

Figure 1. Absorption (solid line) and emission (dotted line) spectra of ZnP–β-CD in ethanol/water (4:96) mixed solvent.

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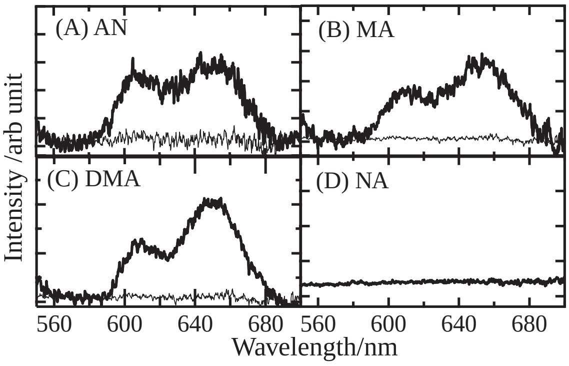

Figure 2. Emission spectra of ZnP–β-CD in the presence (thick line) and the absence (thin line) of donors: (A) AN, (B) MA, (C) DMA, and (D) NA. Each excitation wavelength was 355, 375, 375, and 276 nm, respectively.

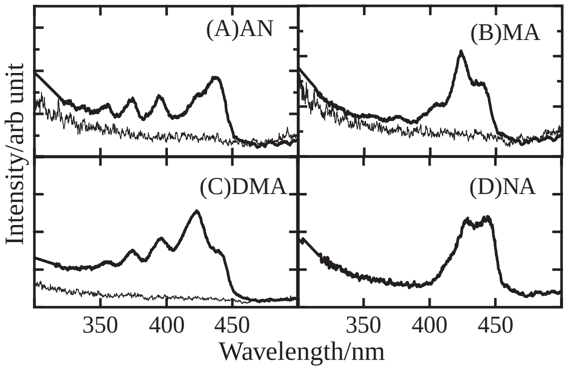

Figure 3. Excitation spectra (thick line) for the host/guest complexes monitored at 610 nm: (A) AN, (B) MA, (C) DMA, and (D) NA. For comparison, guest-only excitation spectra (thin line) are also shown.

In order to ensure the occurrence of FRET, we measured the excitation spectra by monitoring the emission of ZnP moiety at 610 nm (Figure 3). Absorption due to the donor moiety was clearly observed for the ZnP–β-CD/AN, ZnP–β-CD/MA, and ZnP–β-CD/DMA complexes, whereas no donor absorption around 276 nm was recognized for the ZnP–β-CD/NA complex, as expected from the emission spectra. The results of emission and excitation spectra strongly suggest the occurrence of FRET in the self-assembled inclusion complexes possessing anthracene derivatives as a donor.

These observations suggest that energy transfer is very likely to occur from anthracene derivatives to the ZnP moiety by the Förster mechanism, because the Soret absorption band (433 nm) of ZnP–β-CD overlapped with the emission bands of guest anthracene derivatives. In the Förster mechanism, the energy-transfer rate constant k is given by the relation, $k \propto G(\Phi_f \cdot S/\tau)$,[8] where Φ_f is the fluorescence quantum yield of the guest molecule, S is the normalized spectral overlap between the absorption of acceptor and the emission of donor, τ is the fluorescence lifetime of the donor, and G is a constant determined by the relative distance and conformation of the donor and acceptor molecules.

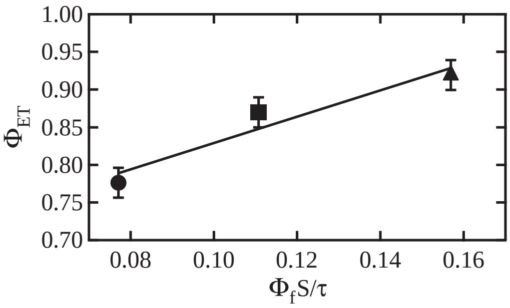

Figure 4. Efficiency of energy transfer versus $\Phi \cdot S/\tau$ of ZnP–β-CD/AN (●), ZnP–β-CD/MA (■), and ZnP–β-CD/DMA (▲).

The efficiencies of energy transfer are plotted against $\Phi_f \cdot S/\tau$ in Figure 4. The efficiency of energy transfer was determined by the absorbance and fluorescence intensity of the inclusion complex of ZnP–β-CD with donors and the Q-band fluorescence quantum yield of ZnP–β-CD when it was excited to the Soret band. The Q-band fluorescence quantum yield of ZnP–β-CD [Φ_f(ZnP–β-CD) $= 3.24 \times 10^{-5}$] was determined by using a literature value of fluorescence quantum yield for zinc tetraphenylporphyrin[9] as a standard. The values of Φ_f and τ of donors were obtained from time-resolved fluorescence experiments. The efficiency of energy transfer was proportional to the factor as shown in Figure 4, indicating that the geometrical factor G is independent of guest molecules. This result is satisfactory for our purpose to build a scaffold for the energy-transfer complex including a porphyrin unit. Detailed study including time-resolved fluorescence measurements as well as model calculations of the geometrical factor G is in progress now.

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