Competitive photoinduced electron transfer by the complex formation of porphyrin with cyclodextrin bearing viologen†

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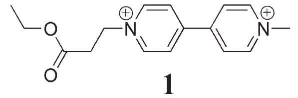
Photoinduced electron transfer between a porphyrin and a new guest cyclodextrin bearing viologen occurs by a supramolecular formation with conformational change of a guest molecule.

The core of photosynthesis is a cascade of photoinduced energy and electron transfer processes between donors and acceptors.[1] Much attention has been focused on looking for ways to study this process in a simplified model system, which is of benefit to not only the understanding of the detailed mechanism, but also the construction of artificial systems for the conversion of solar energy into chemical potential. Many dyads covalently linked to each other have been reported.[2] Non-covalent models, based on hydrogen bonding, π-stacking and metal–ligand coordination, have been addressed to fully mimic the biological electron transfer systems, which are held together by proteins without any covalent linkage.[3] The best approach to mimic the biological process is to build the non-covalent system in aqueous media, which is universal in natural systems.



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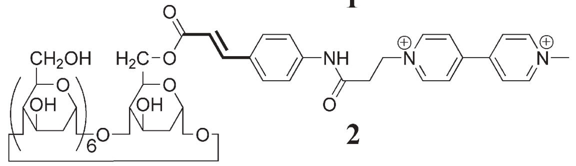

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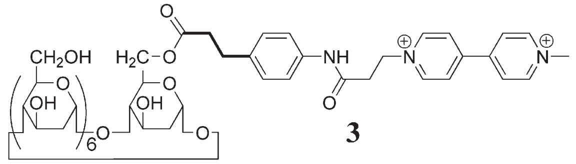

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In aqueous media, viologen derivatives and 5,10,15,20-tetrakis(4-carboxylphenyl)-21*H*,23*H*-porphyrin (TCPP) act as good electron acceptors and donor, respectively. To construct non-covalent systems in water, cyclodextrin (CD) is thought to be an important host molecules, due to its lack of interference with light, relatively rigid cavity and water-solubility. In many cases, however, the binding constants of CDs to porphyrins are less than several thousand M^{-1},[4] which is too weak to form an effective electron-transfer system. Therefore, modifying CDs seems necessary to form stable complexes with porphyrins.[5] It has been reported that tri-*O*-methylated CDs formed stable complexes with porphyrins to give supramolecular systems.[6]

Our strategy of photoinduced electron transfer involves a competitive system to build the donor–acceptor dyad in an aqueous solution. There have been many reports that electrostatic attractions and charge-transfer interactions contribute to the extraordinary stabilities of donor–acceptor complexes.[7] Thus we have considered constructing a supramolecular system by cooperation of electrostatic attraction and charge transfer. On the other hand, self-inclusion complexes with location changes can be applied as molecular machines, molecular recognizing agents and fluorescent chemosensors.[8] Therefore, novel electron acceptors **2** and **3** have been synthesized, with viologen as an acceptor and CD as the host molecule. The cinnamic group and the hydrocinnamic group were used as rigid and flexible bridges for **2** and **3**, respectively. In our previous researches, it was found that the modified CDs with flexible hydrocinnamic groups could form intra- and inter-molecular inclusion complexes while the rigid cinnamic group inhibits the formation of intramolecular complexes.[9] 2D-NMR spectroscopy indicated that acceptor **3** formed intra- to inter- molecular inclusion complexes by adding adamantane-1-carboxylic acid as a competitive guest (see ESI†). Electron acceptor **1** was synthesized, which was used as a reference compound to investigate the role of the CD.

The absorption and circular dichroism spectra showed evidence for the complex formation. Fig. 1 shows the absorbance changes of TCPP upon the addition of acceptors **2** and **3**. The Soret band of TCPP changed remarkably upon the titration of **2**, with a clear isosbestic point at 420 nm, at lower concentrations of 2.5 μM. The spectra of **3** showed an isosbestic point at 417.5 nm at the range of 10–200 μM. The red shifts of the Soret band of TCPP with **2** and **3** were much larger than that with native β-CD. This result indicated that there were ground-state interactions of TCPP with acceptors **2** and **3**. The binding constants K_a of TCPP with **2** and **3** to form 1 : 1 complexes were 8.7×10^5 and 2.5×10^4 M^{-1}, respectively. This difference of K_a should be due to the self-inclusion structure of acceptor **3** (the pseudo-stopper of viologen inhibited the formation of intermolecular inclusion complexes of **3** with TCPP[10]). The CD cavity of acceptor **2** should be vacant, because the rigid double bond prevents self-inclusion. In comparison, binding constant K_a of β-CD with TCPP was 7.4×10^3 M^{-1}, which was smaller than

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† Electronic supplementary information (ESI) available: Synthesis and characterization of compounds **1**, **2** and **3**, 2D ROESY ^1H NMR spectra of acceptor **3**, circular dichroism spectral changes of TCPP upon addition of **3**, the spectra of absorption and fluorescence and fluorescence decay of TCPP with **2** and **3**. See DOI: 10.1039/b607199f

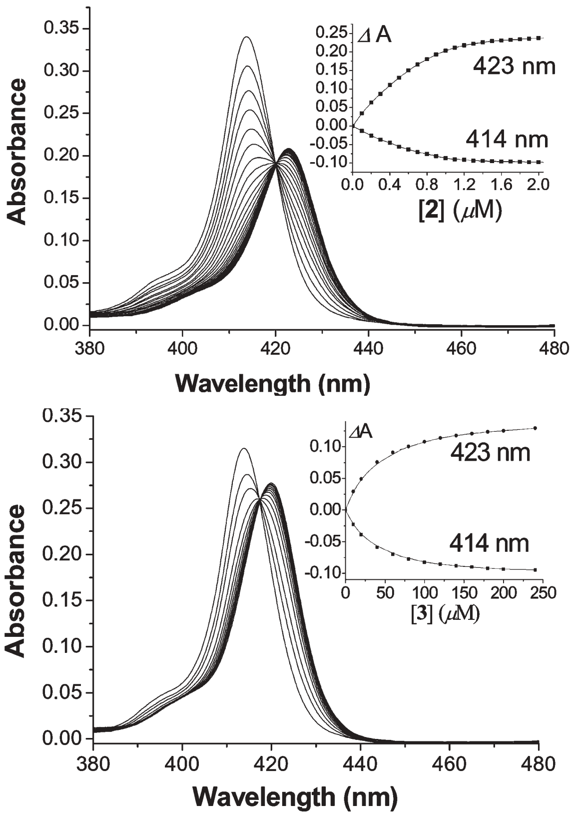

Fig. 1 Absorption spectral changes of TCPP (1.0 μM) in 0.05 M phosphate buffer at pH 7.0 upon addition of acceptors **2** (upper) and **3** (lower) at 25 °C.

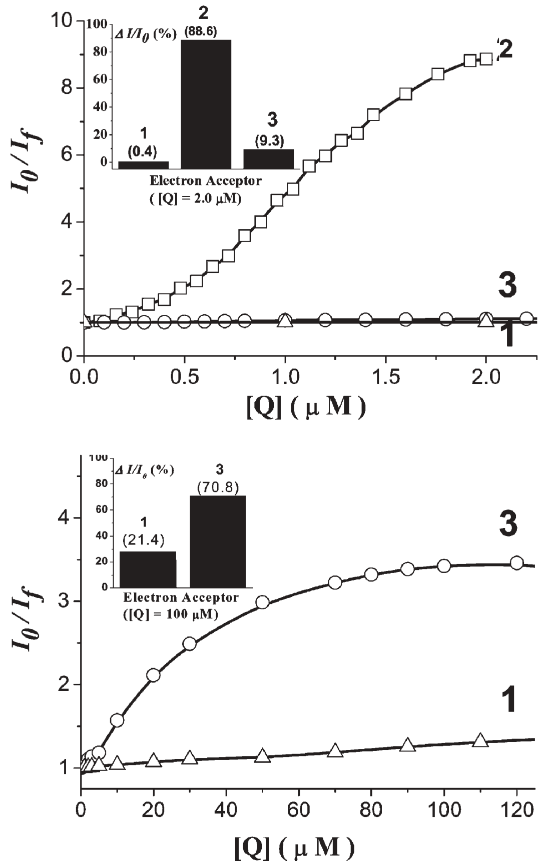

Fig. 2 Stern–Volmer plots for fluorescence quenching of TCPP (1.0 μM) in 0.05 M phosphate buffer at pH 7.0 by **1** (△), **2** (□) and **3** (○) at 25 °C. TCPP was excited at the isosbestic points. The fluorescence intensities were monitored at 647 nm. The inset indicates the percentage quenching.

that of **2** or **3**. The extraordinarily stable 1 : 1 complexes for **2** or **3** should be due to the cooperation of electrostatic attraction and charge transfer. The circular dichroism spectrum of TCPP with acceptors **2** and **3** in water showed a negative induced circular dichroism band (ICD) around 425 nm (ESI†). According to the theoretical treatment by Kodaka *et al.*,[11] the observed negative ICD band was due to the fact that the TCPP was included in the β-CD cavity parallel with the CD axis. Meanwhile, it has been confirmed that the compound **3** undergoes self-inclusion in water and the cinnamic group could be removed by the competitive guests. These results implied that the complex formation of TCPP with **3** took place by the replacement of the guest molecule from the cinnamic group to TCPP.

The interaction of TCPP with acceptors in aqueous media was investigated by steady-state fluorescence. Fig. 2 shows Stern–Volmer plots for the quenching of TCPP (1 μM) by acceptors **1**, **2** and **3**. Nonlinear Stern–Volmer plots were obtained for the acceptors **2** and **3**. With the titrations of **2** or **3**, I_0/I increased until reaching a maximum and then stayed constant. As a control experiment, the quenching processes of TCPP with acceptor **1** were examined, which has no binding site for TCPP. A linear Stern–Volmer plot was observed in the case of acceptor **1**. These results clearly indicated the difference of the quenching route of TCPP by acceptors. As the acceptors **2** and **3** include the cyclodextrin as the binding site for the porphyrin, the nonlinear fluorescence quenching could be assigned to complex formation. Fluorescence quenching within the supramolecular assembly could give rise to the nonlinear features of the Stern–Volmer plots. Meanwhile, it has been confirmed that compound **3** underwent self-inclusion in water and the cinnamic group could be displaced by competitive guests.

The inset of Fig. 2 shows the results of the control experiments. The fluorescence intensity was quenched by 0.4, 88.6 and 9.3% for **1**, **2** and **3** at 2.0 μM, respectively. Efficient fluorescence quenching occurred with **2** at low concentrations. When the concentrations of **1** and **3** was increased to 100 μM, the level of TCPP quenching was 21.4% for **1** and 70.8% for **3**, respectively. TCPP formed complexes with **2** and **3**, and the additional quenching should be due to the supramolecular electron transfer.

The photoinduced electron transfer was also studied by time-resolved fluorescence (ESI†). The fluorescence lifetimes of TCPP (1 μM) were measured in 0.05 M phosphate buffer under aerated conditions in the presence of acceptors **2** and **3** at 1 and 80 μM, respectively. TCPP was excited at 420 nm. The singlet excited state lifetime of TCPP in the absence of acceptors was 9.8 ns, while the decay in the presence of **2** was comprised of three components: 9.8 ns (19.3%), 0.7 ns (35.4%) and 50 ps (45.3%). The shorter lifetimes, 0.7 ns and 50 ps, were ascribed to the excited TCPP whose electron was transferred to the viologen. The difference in these lifetimes was ascribable to the difference of binding direction of acceptor **2** to TCPP. TCPP included in the CD cavity to form a π–π stack with the viologen moiety attached to CD which could contribute to the shortest lifetime. The longer fluorescence lifetime

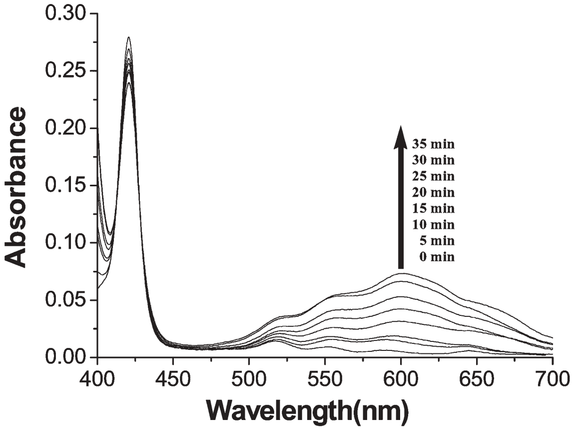

Fig. 3 Absorption spectral changes of TCPP (1.0 μM) in 0.05 M phosphate buffer at pH 7.0 with acceptor **3** (100 μM) in the presence of EDTA tetrasodium salt (10 mM) under 420 nm light irradiation.

was assigned to complex formation in the opposite direction. The TCPP–acceptor **3** system involved two components: 9.8 ns (59%) and 0.9 ns (41%), the latter being the lifetime of excited TCPP bound to acceptor **3**. These results indicated that TCPP displaced the cinnamic part to form a complex and that photoinduced electron transfer occurred between TCPP and acceptor **3**.

The UV-Vis spectra of TCPP with acceptor **3** were measured to confirm the electron transfer products. Fig. 3 shows the spectral changes of TCPP with acceptor **3** upon the irradiation of 420 nm light in the presence of an excess amount of ethylenediaminetetraacetic acid tetrasodium salt as a sacrificial donor. A dramatic increase of the absorbance was observed at 602 nm. The new peak was ascribable to the reduced viologen unit[12] with the production of cationic radical of viologen. Taking into account the appearance of the shorter excited-state lifetimes for TCPP in the presence of **2** and **3** with the increase of the amount of cationic radical products, it was indicated that photoinduced electron transfer from TCPP to acceptors occurred *via* supramolecular complex formation between TCPP and **2** or **3**.

The acceptor **3** was found to form the complex with TCPP by replacement of the guest molecule attached to the CD. A possible mechanism of the electron transfer between TCPP and **3** is shown in Fig. 4.

In conclusion, a new strategy of efficient supramolecular electron transfer has been presented. The supramolecular complex between TCPP and acceptor **2** with a very high binding constant showed an efficient fluorescence quenching. A competitive system of TCPP with acceptor **3** was investigated, in which supramolecular electron transfer occurs by conformational changes of the guest molecule modified to the CD.

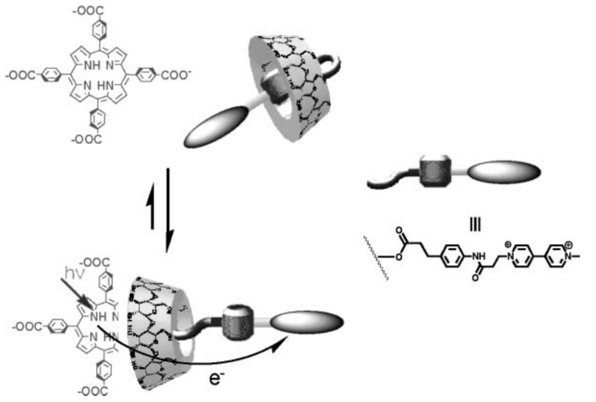

Fig. 4 A possible mechanism of electron transfer between TCPP and **3** in aqueous media.

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