Electron Transfer from Hydrophobic Porphyrin to Hydrophilic Viologen via the Photoexcited Singlet State in Water

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Viologen-linked porphyrins are a typical compound for photoinduced electron-transfer models via the photoexcited singlet state. The singlet-state electron transfer, however, does not occur in water, because solvent cage formation, which is motion of solvent molecules during electron transfer, is slow in the case of water. In order to boost the solvent cage formation of water and achieve the electron transfer via the singlet state in water, viologen-linked hydrophobic porphyrin was prepared.

Photoinduced intramolecular electron transfer in electron-acceptor-linked photosensitizers has been widely studied.[1–9] Especially, viologen-linked porphyrins are fascinating compounds for solar energy conversion, because porphyrins absorb visible light and the potential of reduced viologen moiety is high enough to facilitate electron donation to catalysts driving some reductive reactions such as proton reduction in water.[10–17]

In the electron transfer from the photoexcited porphyrin to viologen, the rate-determining step is solvent cage formation, based on Franck–Condon principle to the mechanisms of excited-state electron transfer.[4] The electron transfer includes some events; orientation of solvent molecules, nuclear motion, and then electron motion. These events have the large difference in time scale. Therefore, solvent motion is the slowest action in an intramolecular electron transfer. When electron transfer occurs, an electron donor and acceptor are surrounded by several shells of solvent molecules forming a hydrophobic sphere with the innermost cage being the solvent cage. It is believed that singlet electron transfer is likely to occur in organic solvent because solvent cage formation is faster than intersystem crossover from photoexcited singlet state to the photoexcited triplet state. Conversely, solvent cage formation in water is slow, allowing sufficient time for the singlet state to descend in the triplet state. Thus, there is intense interest in experiments which reveal how manipulate electron transfer in water. In this study, viologen-linked hydrophobic porphyrin was synthesized (Figure 1).

The porphyrin moiety is hydrophobic, the first viologen is hydrophilic and the second viologen is more hydrophilic, containing $NH_3{}^+$ at the termination of the structure. Thus, a gradually hydrophilic form is achieved in one molecule. The aim of the gradual hydrophilicity is that: (i) water molecules around hydrophobic porphyrin seem to be organized into lower hydrophilic orientation and facilitates the solvent cage formation and (ii) the two viologen moieties do not interact with each other and are aligned in a straight line so that directional electron transfer seems to occur from the first viologen to the second.

The two viologens linking porphyrin are different in redox potential, so that stepwise electron transfer occurs from porphyrin to the second viologen via the first. Redox potentials of the viologen-linked porphyrin were measured in 100 mM Tris-HCl buffer (pH 7.4) at 298 K by cyclic voltammetry. The redox potentials of the two viologens were around −440 mV (vs. SHE), being similar to methylviologen. This result shows that no electrostatic delocalization, which are dimerization in one molecule, between the two viologens occurs. If the two viologens are dimerized electrostatically, the redox potentials are around −320 mV. These results indicate that the two viologens behave independently and do not dimerize.

Figure 2 shows the energy diagram of the viologen-linked porphyrin based on the redox potentials and spectroscopic properties of porphyrin and viologen. Redox potential of two viologen is determined by cyclic voltammogram of V_A and V_B model. V_A model has 1,1′-dibutyl-4,4′-bipyridinium. V_B model is 1-ammonioethyl-1′-bromopropyl-4,4′-bipyridinium.

The energy level of the photoexcited triplet state is lower than that of the two viologens. Therefore, the photoexcited singlet state donates an electron to the first viologen as long as the solvent cage is quickly formed, and electron transfer from photoexcited triplet state to the first viologen could be blocked by uphill potential.

Triplet lifetime and fluorescence lifetime of the viologen-linked porphyrin is listed in Table 1. Triplet lifetime was measured by nanosecond laser flash photolysis, detecting time resolved T–T absorption. An excitation pulse is SHG of Nd-YAG (532 nm). Fluorescence lifetime was measured. Time-resolved fluorescence spectra were recorded by a streak scope. The excitation wavelength is 405 nm by dye laser. Triplet and fluorescence lifetime measurements were carried at 298 K.

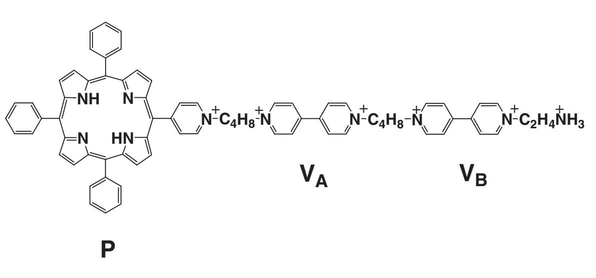

Figure 1. Structure of viologen-linked porphyrin.

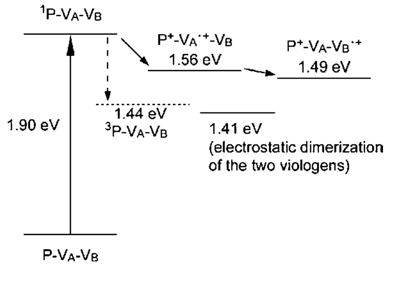

Figure 2. Energy diagram of the viologen-linked porphyrin.

Table 1. Photoexcited triplet lifetimes and fluorescence lifetimes

	Triplet lifetime /µs	Fluorescence lifetime /ns
P in DMF	90	10.2
P + V–V	37	10.2
P–V_A–V_B in DMF	92	7.2
P–V_A–V_B in water	89	3.1

Fluorescence lifetime of the porphyrin mixed with 30 µM of bisviologen (P + V–V) was measured. That viologen concentration is high enough to gain maximum reaction rate and structure of V–V is C_4H_9–V–C_4H_8–V–$C_2H_4NH_3$. The redox potential of V–V is 327 mV and the reduced V–V spectrum has peak in the shape around 500 nm, showing that the two viologens are dimerized in one molecule. Fluorescence lifetime of P + V–V is the same as that of porphyrin (P in DMF), showing that the two viologens, not linked to porphyrin, do not quench the photoexcited singlet sate of the porphyrin though V–V quench triplet state of porphyrin.

On the other hand, the singlet state is quenched by the two viologens when the viologens link to porphyrin (P–V_A–V_B), indicating that electron transfer occurs via the singlet sate. In addition, lifetime in water is shorter than that in DMF. Water does not associate with the hydrophobic porphyrin rather than repelled, while DMF is a polar molecule but associates with the porphyrin. That is the reason why solvent cage formation in water is faster than DMF. These results suggest that electron transfer is controlled by manipulating structure of porphyrin.

As expected from the energy diagram, electron transfer via singlet state mainly occurs in the viologen-linked porphyrin and electron transfer via triplet state could be blocked off. To investigate electron transfer via triple state, triplet lifetime and time dependence of reduced viologen production were measured by nanosecond pulse laser flash photolysis. Triplet lifetime of the viologen-linked porphyrin was the same as that of porphyrin free from viologen, showing that electron transfer via photoexcited triplet state does not occur as expected in energy diagrams. Figure 3 shows absorbance change at 620 nm after laser pulse flashing, with a 10-ns pulse width. Reduced viologen (cation radical form) absorb 620 nm at which neither oxidized viologen nor photoexcited state porphyrin shows absorption.

Curve (a) is for porphyrin mixed with bisviologen and curve (b) is for the viologen-linked porphyrin in DMF. At 0 ms in curve (b), absorption rises quickly, indicating that electron transfer to viologen is finished within 10 ns (pulse width); that is, electron transfer occurs via singlet state. In the case of curve (a), absorption rises slowly, showing that reduced viologen is still produced after laser pulse irradiation (10 ns pulse width). Therefore, electron transfer occurs not via singlet state but via triplet state. Decay of the curves indicates that reduced viologen is lost by back electron transfer from reduced viologen to the porphyrin ground state. Lifetime of charge-separated state is obtained by analyzing the decay. The viologen-linked porphyrin shows 40-µs lifetime, which is very long as a charge-separated state in water. Forward electron transfer occurs in a few nanoseconds while back electron transfer occurs in microseconds, so the charge-separated state remains for a notable period of time. As mentioned in the energy diagram, the viologen-linked porphyrin facilitates the solvent cage formation on forward electron transfer, because the two viologens are aligned in a straight line and redox potential does not change compared with monomer viologen.

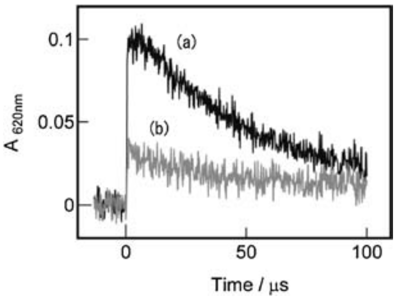

Figure 3. Transient absorption curves at 620 nm for the viologen-linked porphyrin and hydrophobic porphyrin mixed with bisviologen following laser excitation at 532 nm.

In this study, we addressed one of the better structures in porphyrin–viologen system to meet an electron transfer via photoexcited singlet state in water and a long-lived charge separation in water.

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