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Specific Electron Transfer Mechanism from the Photoexcited Tetrasulfonated Zn(II)-Tetraphenylporphyrin to Methylviologen via Self-Assembled Ionic Complex

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Summary: Electron transfer from photoexcited tetrasulfonated Zn(II)-tetraphenylporphyrin (ZnTSTPP) to methyviologen (MV^{2+}) was studied. From the investigation of relative fluorescence intensity and emission lifetime against the MV^{2+} concentration, it was concluded that the electron transfer takes place by a static mechanism. Based on the analysis of the quenching behavior, it was concluded that the static reaction did not follow an ordinary Perrin model, but interaction of the donor (photoexcited Zn-TSTPP) and the acceptor (MV^{2+}) molecules, ionic interaction in the present case, is responsible. The analysis of the quenching gave the equilibrium constant for the interaction to be $K = 6.5 \times 10^4\ M^{-1}$. A two-dimensional selfassembled macromolecular ionic complex between ZnTSTPP and MV^{2+} is proposed.

Keywords: electron transfer; methylviologen; static mechanism; tetrasulfonated tetraphenylporphyrin-zinc complex

Introduction

Creation of new energy resource system is an urgent subject to resolve global environmental problems such as green house effect by CO_2. Since biological activities and our fossil fuels are almost supported by solar energy, conversion and utilization of solar energy are one of the most promising and attractive approaches to create new energy resource compatible with the nature.[1-3] Many researches have been carried out to photolyze water to H_2 and O_2 by utilizing semiconductor particles.[1-6] However, their systems use only UV light; it has been difficult to utilize visible light which is the main component of the solar irradiation. There have been only a few systems reporting visible light cleavage of water using narrow bandgap semiconductor powders,[7,8] but the efficiency remains only low. Tremendous researches have been carried out to photolyze water with sensitizer (dye) and visible light,[1-3] but without success due to the predominant and unavoidable charge recombination reactions. It is an important subject to study the mechanism of electron transfer from

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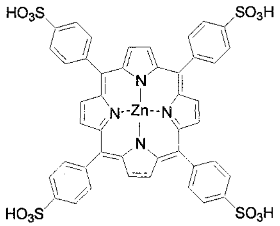
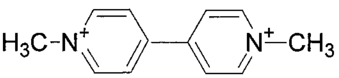
photoexcited sensitizer to an electron-accepting mediator or from an electron-donating mediator to a photoexcited sensitizer in order to control the process.

One of the present authors proposed a fundamental artificial photosynthetic system comprising water oxidation catalyst (C_2), hole mediator (M_2), photoexcitation center (sensitizer) (P), electron mediator (M_1) and proton reduction catalyst (C_1) to photolyze water by visible light.[9] After this our group has been investigating each reaction unit in detail, i.e., new and highly active water oxidation[10] and proton reduction catalysts,[11] photoexcited state electron transfer from a sensitizer to a mediator in a heterogeneous polymer phase,[12] as well as charge transport mechanism in a polymer membrane through redox compounds.[12] Since such a complicated system can be achieved only by utilizing a heterogeneous phase such as molecular or polymeric aggregates,[13] it is of importance to investigate the effect of microenvironment or molecular interaction of the components on the electron transfer event. As for the photoexcited state electron transfer, dynamic mechanism usually takes place in a homogeneous solution for which the reactants diffuse and collide leading to electron transfer.[12,13] However, in a heterogeneous phase static mechanism often takes place for which the reactants do not move at all or only slightly move to result in electron transfer.[12,13] It is now of much importance and interest what kind of mechanism takes place when the electron donor and acceptor interacts strongly. Metal-porphyrins and metal-phthalocyanines are attracting great deal attention as a sensitizer for photochemical conversion due to the similarity with the chlorophyll sensitizer in the photosynthesis, but their insolubility in water limited their investigation in an aqueous solution. In the present paper, the water-soluble anionic tetrasulfonated Zn(II)-tetraphenylporphyrin (ZnTSTPP,**1**) and the cationic acceptor, methylviologen (MV^{2+}, **2**), were used. There have been some reports[14-16] on the electron transfer from the photoexcited ZnTSTPP to MV^{2+}, but they reported only the dynamics of the process and no report appeared that verifies the mechanism; their interesting mechanism of photoinduced electron transfer in an aqueous solution will be elucidated here.



1(ZnTSTPP)



2 (MV^{2+})

Experimental

5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin-Zn(II) (ZnTSTPP) was prepared as follows: 100mg (9.79×10^{-5} mol) metal free 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (purchased from Porphyrin Systems) was dissolved in 20 ml DMF, and 108 mg (4.9×10^{-4} mol) zinc(II) acetate dihydrate was added. The solution was stirred for 12 h at 80 ℃. After cooling the solution was filtered, and then the DMF was distilled off under vacuum. The purification was carried out by dialysis (pore diameter of the tube ~2.4 nm) in deionized water. The yield was quantitative. Methylviologen was purchased from Tokyo Kasei Co.Ltd. Visible absorption spectrum was measured by a Shimadzu Multispec-1500 spectrophotometer. Quenching of the photoexcited state ZnTSTPP (5 μ M) by MV^{2+} (0 – 100 μ M) in a homogeneous aqueous solution was studied by measuring the fluorescence intensity at 606 and 659 nm by exciting the ZnTSTPP at 422 nm with a Shimadzu RF-5300PC fluorescence spectrophotometer. Emission decay was studied by a time-correlated single photon counting apparatus (Hitachi-Horiba NAES-550) equipped with a 10-atm nitrogen lamp, for which a UV-30 cutoff filter (Hoya Corporation) was used at the excitation side, and O58 cutoff filter (Toshiba Glass Co.Ltd.) at the monitoring side.

Results and Discussion

The absorption spectrum of ZnTSTPP in an aqueous solution is shown in Figure 1 with the fluorescence and excitation ones. The absorption spectrum shows a typical Soret band with an

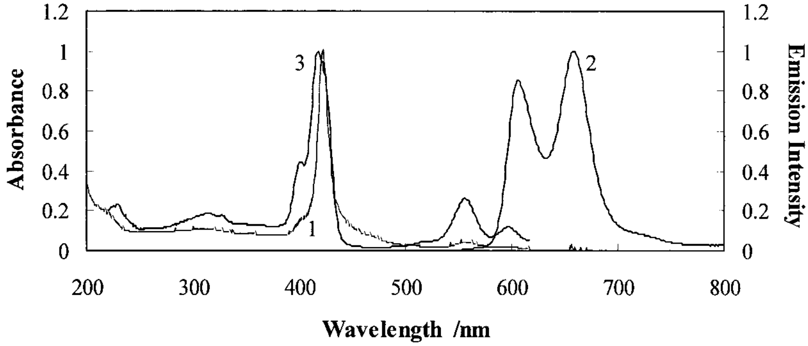


Fig. 1. Absorption(1), fluorescence(2), and excitation(3) spectra of ZnTSTPP in an aqueous solution (5 μ M).

absorption peak at 422 nm as well as Q band between 500 and 600 nm. The spectrum shows clearly the one characteristic for monomeric species. The fluorescence shows two peaks a 606 and 659 nms. The excitation spectrum shows a similar feature as the absorption one, but with higher contribution by the Q band especially by the absorptions at 560 and 590 nm.

The emission from the photoexcited ZnTSTPP was quenched by MV^{2+} as shown in Figure 2. It has been well established that electron transfer takes place from the photoexcited state of porphyrins and phthalocyanines to MV^{2+}.[1,3] so that the quenching mechanism is electron transfer (i.e., oxidative quenching). The emission intensity decreased drastically with the MV^{2+} concentration, but the emission spectrum shape does not change much. The emission decay is shown in Figure 3 showing that the decay does not change much with the MV^{2+} concentration.

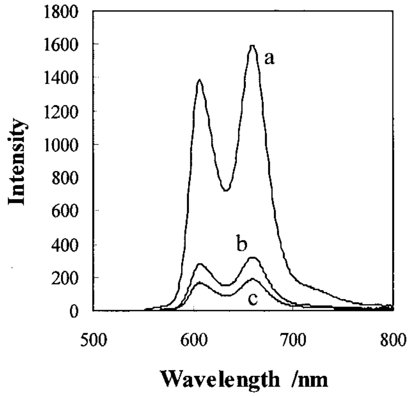


Fig. 2. Change of emission intensity with the addition of MV^{2+}. ZnTSTPP, 5 μM, [MV^{2+}] = 0(a), 0.05(b), and 0.1(c)mM.

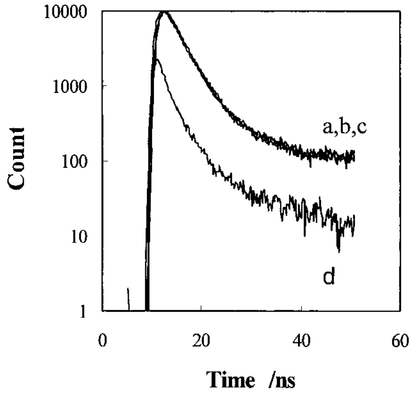


Fig. 3. Emission decay curves of ZnTSTPP (5 μM). [MV^{2+}] = 0(a), 0.05(b), and 0.1(c) mM, excitation lamp profile(d).

The relative emission intensity (I_0/I, where I_0 is the intensity in the absence of MV^{2+}) and relative lifetime (τ_0/τ) against MV^{2+} concentration are shown in Figure 4. These plots are called Stern-Volmer plots (eq.1).[17] The I_0/I plots shows a linear relationship, while the τ_0/τ plots show almost no slope,

$$I_0/I = 1 + k_{sv}[Q] \qquad (1)$$

where k_{sv} is the Stern-Volmer constant, and [Q] quencher concentration in M (mol dm^{-3}).

The rate constant for the electron transfer, k_2, can be determined by

$$k_2 = k_{sv} / \tau_0 \tag{2}$$

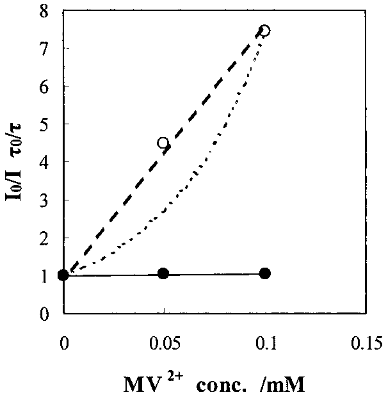


Fig. 4. Plots of I_0/I and τ_0/τ against MV^{2+} concentration. I_0/I(○), τ_0/τ (●). ······ is the best fit curve based on eq.(4), and ----- based on eq.(3).

As for the photoexcited state electron transfer mechanism, there are principally two mechanisms.[12,13] One is a dynamic mechanism for which the donor and acceptor molecules diffuse and collide to react. The other is a static mechanism for which the donor and acceptor molecules interact with each other, or they are located within a quenching distance, so that electron transfer takes place after photoexcitation without diffusion of the molecules. There are combinations of these two mechanisms, and the present authors proposed[18] various models for photoinduced electron transfer.[12,13,18] In a homogeneous solution dynamic mechanism usually takes place. However, in a solid matrix such as a polymer membrane or polymer assemblies, static mechanism is predominant. The dynamic and static cases can be discriminated by the Stern-Volmer plots based on I_0/I and τ_0/τ plots as follows:

1) Entirely dynamic mechanism: Both the Io/I and τ_0/τ plots fall on a same line, i.e., $I_0/I = \tau_0/\tau$.
2) Entirely static mechanism: τ_0/τ plots do not show a slope (the $\tau_0/\tau = 1$, independent of the quencher concentration).
3) Combination of the dynamic and static mechanisms: The τ_0/τ values are smaller than the I_0/I ones. In this case the k_2 can be determined by dividing the slope of the τ_0/τ plots by τ_0.

The Io/I and τ_0/τ plots in Figure 4 shows unambiguously that the mechanism is a static one. It is now important to discuss what kind of interaction brings about such a static mechanism in the present system. For the almost entirely static mechanism following possibilities can exist in the present system:[18]

a) The donor and acceptor molecules interact with each other, e.g., they form a complex. In this case,

$$I_0/I = 1 + K[Q] \qquad (3)$$

where K is the equilibrium constant for the interaction.[18]

b) The quencher molecule is incorporated into the quenching sphere around the photoexcitation center molecule, and the number of the quencher in the quenching sphere obeys a Poisson statistics. In this case the I_0/I is expressed by the so-called Perrin equation[19](eq.4),

$$I_0/I = \exp(VN_A[Q]) \qquad (4)$$

where V is the quenching sphere volume and N_A Avogadro's number.

Both the equations (2) and (3) were applied to the I_0/I plots in Figure 4. Eq.(4) could not be applied to the data (refer the best fit curve in Fig. 4 based on, eq. (4)), but the eq.(3) resulted in a good fitting to give $K = 6.5 \times 10^4\ M^{-1}$ (Table 1).

The rate of dynamic electron transfer was estimated from the ratio of the slopes of I_0/I and τ_0/τ plots ($6.5 \times 10^4 : 3.7 \times 10^2$) to be 99.5 % for static and 0.5 % for dynamic mechasnims. Important parameters for the electron transfer quenching are summarized in Table 1.

As for the interaction between the tetraanionic ZnTSTPP and the dicationic MV^{2+}, an ion complex could be proposed as eq.5 where they form a 1:2 (ZnTSTPP:MV^{2+}) complex.

$$ZnTSTPP^{4-} + 2\,MV^{2+} \Leftrightarrow MV^{2+}\text{---}ZnTSTPP^{4-}\text{---}MV^{2+} \qquad (5)$$

Table 1. Parameters for the electron transfer.

Mechanism		Parameters
Static	99.5 %	Equilibrium const. for complex $K = 6.5 \times 10^4\ M^{-1}$
Dynamic	0.5 %	Rate constant* $k_2 = 2.6 \times 10^7\ M^{-1}s^{-1}$

* τ_0 was 1.4 ns

When considering the rather rigid nature of the viologen molecule with two separated cations located near the end of the molecule as well as the planar ZnTSTPP structure with separated four sulfonate anions, they could form most probably a two-dimensional network structure based on ionic interactions rather than an isolated and small 1:2 complex when they are present at the 1:2 ratio. To further investigate this, quenching of photoexcited ZnTSTPP by MV^{2+} was measured in methyl alcohol with much lower dielectric constant than water (Fig. 5). In comparison with the quenching in water, the quenching in methanol proceeded very efficiently even at the molar ratio of 1:2 (ca. 86% quenching) supporting the possible aggregate formation at this ratio. The details to prove this should be investigated in future.

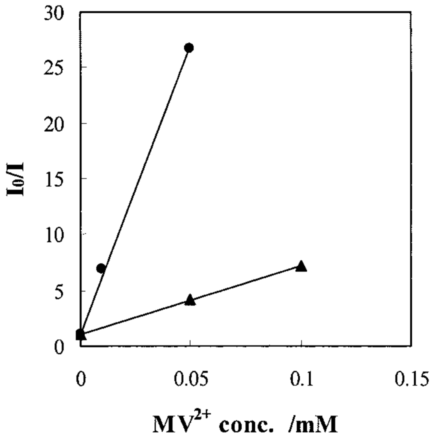


Fig. 5. Plots of I_0/I against MV^{2+} concentration in methanol (●) and water(▲).

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