Excitation energy transfer and photoinduced electron transfer in organized molecular systems of porphyrins

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Several types of porphyrin molecular systems constructed by the aggregation through the charge transfer interaction or the molecular architecture by the organic synthesis are investigated on the excitation energy transfer and the photoinduced electron transfer. The photochemical properties of the porphyrin molecular systems are outlined by considering the transient absorption and emission measurements.

1. Introduction

Excitation energy transfer and photo-induced electron transfer in the porphyrin oligomers have been extensively investigated in order to elucidate the functions of the organized chromophores in the photosynthetic reaction centers (RCs) [1, 2]. However, the excited state properties of the porphyrin oligomers have been still discussed because of the great importance in the photochemical process of the RCs. On the other hand, such photochemical processes are also important for the construction of photo-functional molecular systems designed with organized reaction fields such as liquid crystals.

We have recently shown that electron-attracting gold porphyrins and electron-releasing zinc porphyrins form the hetero-aggregates with charge transfer interaction in aqueous solution [3]. The hetero-aggregates are suitable for the investigation on the fundamental features in the electron transfer of the tightly stacked donor-acceptor complex. With this in mind, we investigated the intradimer photo-induced electron transfer and the energy gap dependence of the electron transfer kinetics in the porphyrin hetero-aggregate [4]. As an alternating approach to the investigation, synthesis of large porphyrin oligomers are important, especially for the application of the functions to molecular architecture [2, 5]. In the previous paper

[6], we reported the stable axial bond formation of phosphorus porphyrin. The axial bond is useful for fixing the porphyrin rings at various distances and orientations as "wheel-and-axle". By the use of them, we constructed the molecular architecture of the porphyrins [7-9].

In this paper, the excited state properties of the porphyrin molecular systems are outlined by considering the energy transfer and the electron transfer processes.

2. Experimental Methods

A microcomputer-controlled picosecond laser photolysis system with a mode-locked Nd^{3+}:YAG laser (fwhm=24ps) was used for the measurement of the time-resolved transient absorption spectra [10]. The SHG (532 nm) pulse were used for the excitation of sample solutions. Fluorescence lifetimes were measured on a Horiba NAES-550 time-correlated single-photon counting equipment.

3. Results and Discussion

3.1 Electron transfer in the metallo-porphyrin hetero-aggregate

Since the gold porphyrins (1 - 4) and the zinc porphyrins (5 - 7) are good electron acceptors and donors, respectively, they form the hetero-aggregates with charge transfer interaction in aqueous solution. [3]
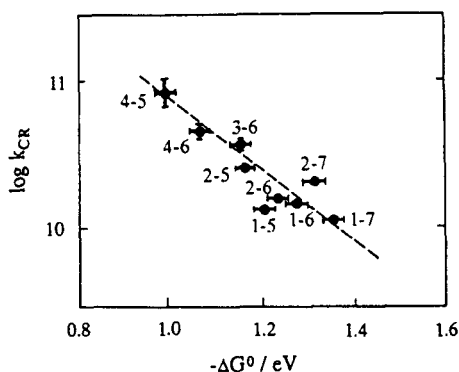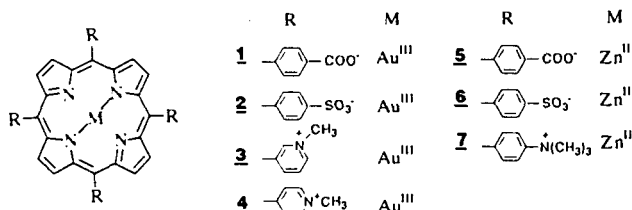
R	M	R	M
1 -⟨⟩-COO⁻	Au^{III}	**5** -⟨⟩-COO⁻	Zn^{II}
2 -⟨⟩-SO₃⁻	Au^{III}	**6** -⟨⟩-SO₃⁻	Zn^{II}
3 -⟨N⟩$^{+}$CH₃	Au^{III}	**7** -⟨⟩-N(CH₃)₃	Zn^{II}
4 -⟨⟩N⁺CH₃	Au^{III}	

$$[\,Au^{III}\,P^{\bullet-}\,]\text{-}[\,Zn^{II}\,P^{\bullet+}\,]^{+}$$

$$\xrightarrow{k_{CR}}\ [\,Au^{III}\,P\,]^{+}\text{-}[\,Zn^{II}\,P\,]$$

Figure 1. Energy gap dependence of the intradimer charge recombination rate constant (k_{CR}) of the radical ion pair formed by the photoexcitation of the porphyrin heteroaggregate in aqueous solution.

The transient absorption spectrum after the laser pulse excitation implies that the radical ion pair was directly formed by the photo-excitation of the **1-5** heterodimer through an extremely fast process within a few picosecond as follows.

$$[\,Au^{III}\,P\,]^{+}\text{-}[\,Zn^{II}\,P\,]$$

$$\xrightarrow{h\nu}\ [\,Au^{III}\,P^{\bullet-}\,]\text{-}[\,Zn^{II}\,P^{\bullet+}\,]^{+}$$
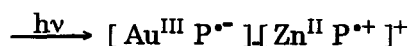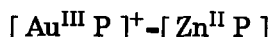
In this case, the electron transfer in the heterodimer occur on both porphyrin rings. The time profile of the transient absorption decay assigned to charge recombination process is quite simple without any shift of the absorption maxima and in accordance with single exponential component. These results suggest that the radicals form CIP and the conversion from the CIP to solvent separated species or dissociated radicals is negligible in this charge recombination process. Consequently, the charge recombination rate (k_{CR}) can be directly measured by the decay of the transient absorption.
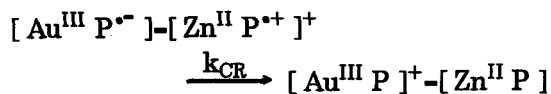
In other heterodimers (**1-6**, **1-7**, **2-5**, **2-6**, **2-7**, **3-6**, **4-5** and **4-6**), almost the same transient absorption spectra assigned to their CIPs were obtained, whereas the k_{CR} is strongly affected by the difference of the combination of the porphyrins. The difference of the k_{CR} can be correlated to charge recombination energy ($-\Delta G^0$) of the CIP of the heterodimer. Figure 1 shows energy gap dependence of the intradimer k_{CR} of the CIP of the porphyrin hetero-aggregate in aqueous solution. Interestingly, the k_{CR} decreases with increasing the exothermicity of the charge recombination as if it was in the "'inverted region'" even at the small $-\Delta G^0$. This energy gap dependence seems difficult to be given a reasonable interpretation by traditional electron transfer theories, because the considerably low solvent reorganization energy must be applied for a good fitting in spite of the reaction in highly polar water. The observed results for the CIPs of the hetero-aggregates can be represented approximately by the simple relation

$$k_{CR}\ \sim\ \alpha\ \exp[-\beta(-\Delta G^0)]$$

where α and β are constants independent of the $-\Delta G^0$ [11]. It is interesting to see that the energy gap dependence is qualitatively analogous to that of the radiationless transition probability in the so-called "weak coupling" limit [12]. These results suggest the traditional electron transfer theories may not be appropriate for the interpretation of the CT state of the porphyrin aggregate stacked tightly.

3.2 Excited properties of the "wheel-and-axle-type" porphyrin array

The "wheel-and-axle-type" phosphorus porphyrin monomers (**1a**, **1b** and **1c**) and oligomers (**2a**, **2b**, **2c**, **3a**, **3b**, **3c** and **4a**) were synthesized by the condensation of the dichlorophosphorus(V)tetraphenylporphyrin

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and corresponding diol [7]. The obtained oligomers were "wheel-and-axle-type", whose porphyrin rings were separated by various lengths of stable axial bridge(s) [7].

In CHCl₃ solution, all the derivatives show the normal porphyrin absorption spectra and the Soret absorption maxima of the oligomers are blue-shifted compared with corresponding monomers, depending on the number of porphyrin rings. The absorption properties of the porphyrin arrays are elucidated from the exciton coupling between the porphyrin rings, where the spectral shifts are described by Kasha's molecular exciton model [13]. Figure 2 shows the energy shift of the Soret absorption maxima of oligomers compared with that of the corresponding monomers. The energy shifts show a linear relationship with respect to the parameter of exciton coupling which was based on the numbers of porphyrin rings and assuming the parallel orientation of the porphyrin rings. The slopes are dependent on the bridge length of the oligomers, indicating that the one-dimensional array structures are realized in the "wheel-and-axle-type" phosphorus(V)porphyrin oligomers. It is noteworthy that the "wheel-and-axle-type" phosphorus(V)porphyrin oligomers show good solubility even in highly polar solvents because of the cationic charges on their central phosphorus atoms and the hydrophilicity of their terminal hydroxyl groups. Interestingly, the lifetime of the singlet excited state of the "wheel-and-axle-type" phosphorus(V)porphyrin derivatives was obviously dependent on the numbers of porphyrin rings in the polar solvent (**1a**: 4.4 ns, **2a**: 4.2 ns, **3a**: 3.5 ns in H₂O/CH₃CN(95:5)). These results suggest that the excited states were partially quenched through intramolecular charge transfer state [8]. This was confirmed by an investigation of a series of the "wheel-and-axle-type" dimers including symmetry-disturbed dimer [8]. For each phosphorus(V)porphyrin oligomer solution of the polar solvent, absorption shoulder was observed at low energy region of the Soret absorption, suggesting that conformational
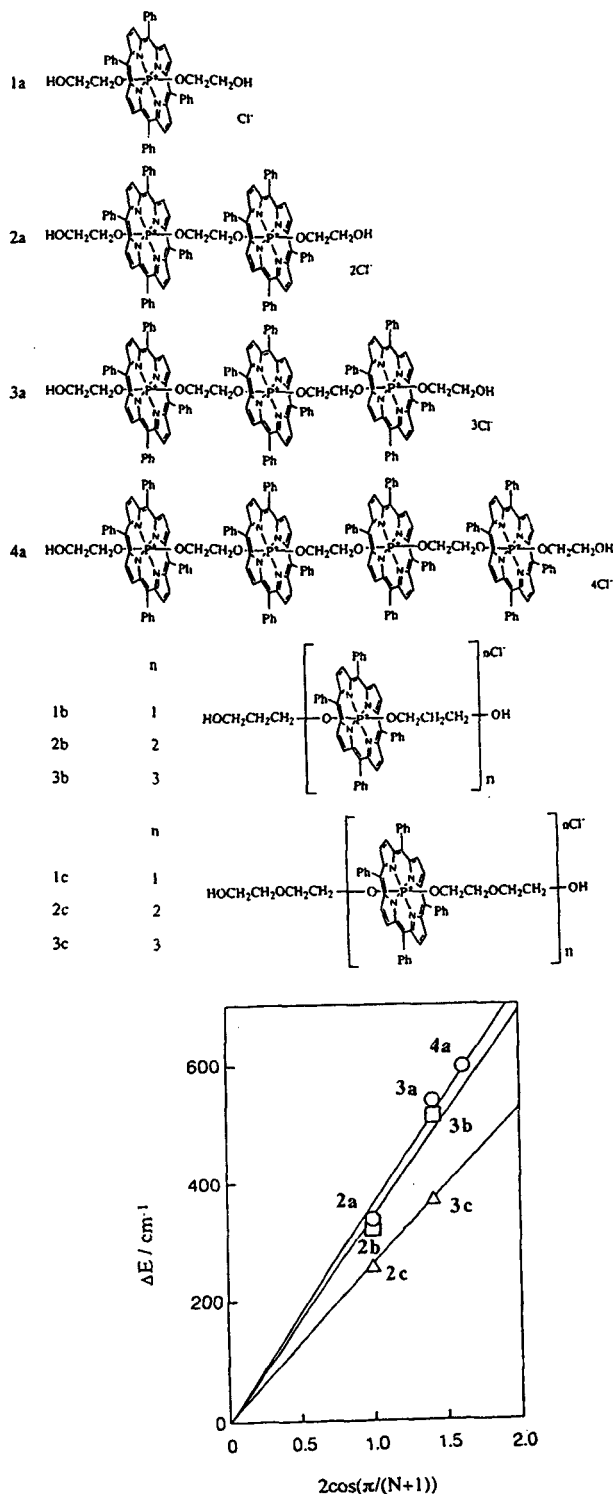

Figure 2. Plot of exciton shift energy ΔE versus $2 \cos(\pi/(N + 1))$.

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change was induced in the polar solvent. Taking into account relatively large shoulder of **2b** compared with those of **2a** and **2c**, the absorption shoulders are considered to be due to the porphyrin-porphyrin dihedral twist as a function of bridge conformation, where the oblique conformation is suitable for **2b** with an odd-numbered carbon bridge. It is noteworthy that the small conformational changes affects the excited state properties.

In the case of the "center-to-edge-type" oligomers (**PCl₂-P** and **PCl₂-P-PCl₂**), the intramolecular charge transfer quenching were enhanced. Fortunately, the "center-to-edge-type" oligomers are easily regulated in their excitation energy and redox potential, because the terminal porphyrins is controlled by the central atom incorporation and the axial coordination. Consequently, efficient energy transfer (**PCl₂-P-PCl₂**) and electron transfer (**H₂-P** and **H₂-P-PCl₂**) were accomplished as shown in Figure 3. The present synthetic method is considered to be useful for the construction of the molecular architecture for the various photo-functional systems.

Acknowledgment

Figure 3.. Energy level diagrams for excited singlet states and charge separated states of H_2-P-PCl$_2$ in CH_2Cl_2.

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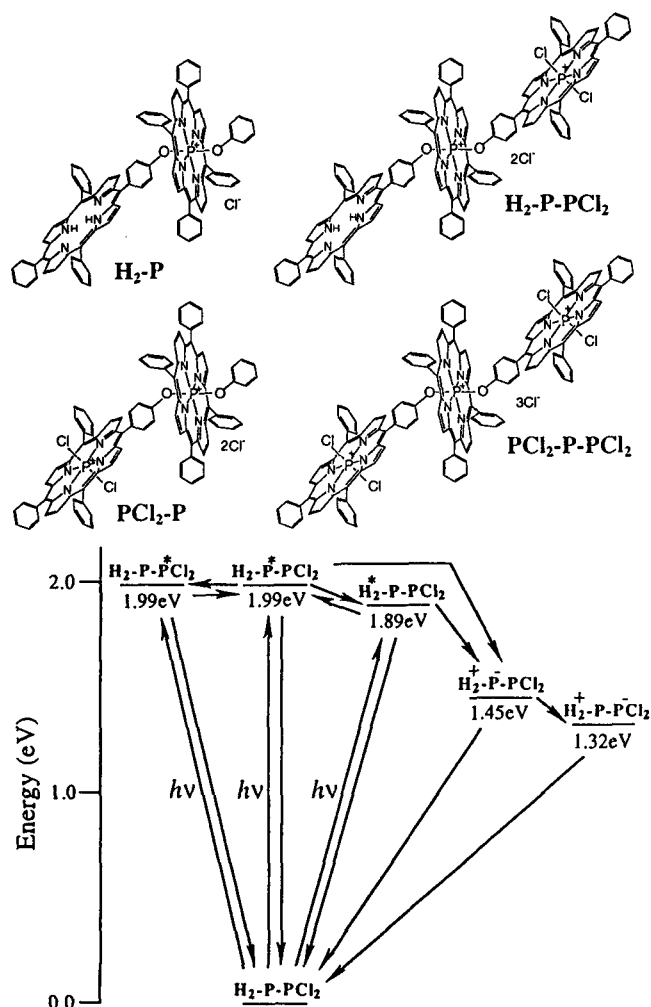6. H. Segawa, K. Kunimoto, A. Nakamoto, T. Shimidzu, J. Chem. Soc., Perkin Trans. 1 (1992) 939.

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