Intracomplex Electron Transfer in a Hydrogen-Bonded Porphyrin—Diimide System

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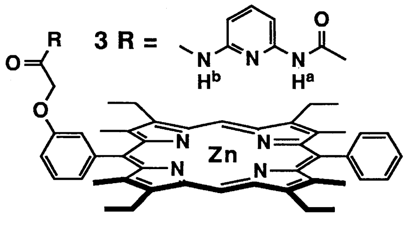
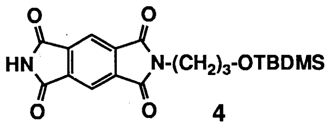
Excitation of a hydrogen-bonded complex of zinc porphyrin bearing a 2,6-diacylaminopyridine binding site and N-monosubstituted 1,8:4,5-naphthalene-tetracarboxamide in benzene results in efficient electron transfer to give a charge separated state detectable by picosecond transient absorption spectroscopy.

In recent years there has been a considerable upsurge in interest in the study of electron transfers within hydrogen-bonded donor-acceptor pairs in relation to its importance in biological energy conversion systems.[1-4] In most cases, however, the fluorescence quenching of a photo-excited donor chromophore by an electron accepting guest has been interpreted in terms of intracomplex electron transfer without firm spectroscopic evidence for formation of charge-separated ion pair states with some exceptions.[4-6]

1 R = OMe 2 R = OH





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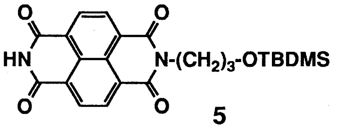

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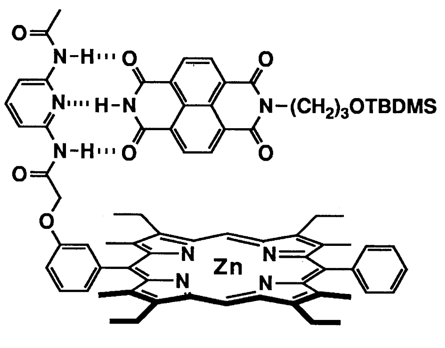

Figure 1. Expected structure of hydrogen bonded complex of 3 and 5.

Here we disclose our own results on electron transfer within a hydrogen-bonded complex consisting of photoexcitable electron-donor porphyrin **3** bearing a 2,6-diacylaminopyridine binding site and electron-accepting diimides **4** and **5**. Diimide acceptors have been proved particularly useful for analysis of electron-transfer reactions owing to the characteristic absorption bands of their anion radicals,[7] and are expected to form a strong hydrogen bond toward a 2,6-diacylaminopyridine moiety because of their cyclic imide structures.[8] Porphyrin ester **1**, that was prepared in 43% yield from the cross condensation of benzaldehyde, methyl (3-formyl)phenoxyacetate, and 4,4'-diethyl-3,3'-dimethyldipyrryl-methane, was quantitatively converted to porphyrin carboxylic acid **2** by hydrolysis under basic conditions. Treatment of **2** in CH_2Cl_2 with oxalyl chloride followed by addition of 2-acetylamino-6-aminopyridine gave a binding-site bearing porphyrin which was isolated as its zinc complex **3** in a yield of 65% from **2**. Unsymmetrically substituted diimides **4** and **5** were prepared by the cross condensation of pyromellitimide dianhydride or 1,8:4,5-naphthalenetetracarboxylic dianhydride with urea and 3-tert-butyldimethylsiloxypropylamine in ca. 8-10% yields. The siloxyl substituent (tert-butyldimethylsilyl, TBDMS) was introduced in order to increase the solubilities of these diimides in nonpolar organic solvents.

To confirm the complexation via hydrogen-bonding, the ^{1}H NMR spectra of **3** in the absence or presence of an equimolar amount of **4** or **5** were examined in $CDCl_3$ and C_6D_6. Upon addition of **4**, the H^b signal of **3** at 7.5 ppm undergoes a downfield shift by ca. 0.1 ppm, while the H^a signal at 8.6 ppm remains at nearly the original chemical shift in $CDCl_3$ and C_6D_6. On the other hand, addition of **5** induces larger downfield shifts for both the H^a and H^b protons with concomitant broadening (ca. 1.5 ppm in $CDCl_3$ and ca. 2.5 ppm in C_6D_6), indicating a much stronger binding of **5** to the 2,6-diacylaminopyridine moiety in **3**. Concurrently, the meso protons of **3** as well as the aromatic protons of **5** undergo a high-field shift, ca. 0.3 and 0.7 ppm, respectively, implying the averaged proximity of the two π-systems as shown in Figure 1. The association constants have been determined by the standard ^{1}H-NMR titrations; $(1.6 \pm 0.1) \times 10^2$ and $(2.9 \pm 0.1) \times 10^2$ M-1 for **4** in $CDCl_3$ and C_6D_6, respectively, and $(1.6 \pm 0.1) \times 10^4$ and $(1.3 \pm 0.4) \times 10^5$ M^{-1} for **5** in $CDCl_3$ and C_6D_6, respectively. Much stronger binding of **5** compared with **4** can be understood in terms of a matching three-point hydrogen bonding that is not available for **4**.

Figure 2 shows Stern-Volmer plots for the fluorescence quenching of host **3** with diimide guests. With **4**, N,N-dihexylpyromellitimide (**6**), and N,N-dihexyl-1,8:4,5-naphthalenetetracarboxamide (**7**), normal Stern-Volmer plots with slopes that reflect intermolecular collisional quenching were obtained, while addition of a small amount of **5** led to more efficient fluorescence quenching. Such efficient quenching is vanished in THF solution, where the association of **3** and **5** is suppressed as revealed by ^{1}H NMR studies.

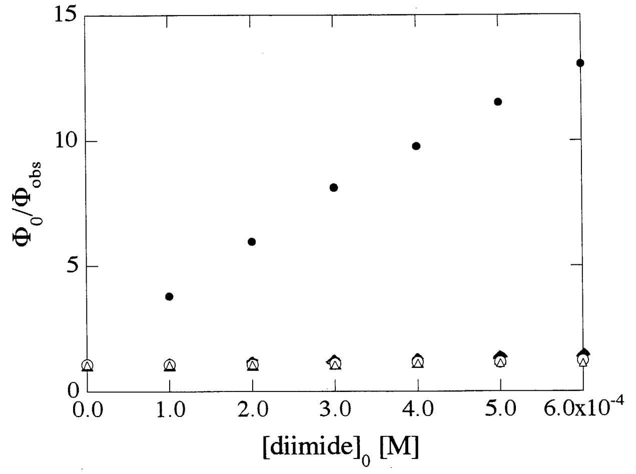

Figure 2. Stern-Volmer plots for the fluorescence quenching of host **3** with diimide guests **4** (○), **5** (●), **6** (△), and **7** (▲) in benzene at 289 K. [3] = 1.0 x 10^{-5} M. Excitation at 539 nm, and emission at 579 nm. A plot (◆) indicates the quenching of **3** with **5** in THF.

Figure 3 shows the picosecond transient absorption spectra of **3** in the absence or presence of **5** in benzene at 10-ps delay time. Under the conditions used, > 95% of **3** should form a complex with **5**. The spectrum of **3** alone is a typical transient absorption spectrum of the S_1-state of 5,15-diaryloctaalkylzinc porphyrin, in which the absorption band at 460 nm is due to $S_1 \rightarrow S_n$ absorption and the bleaching at 630 nm is due to an induced emission of the S_1 state. The transient absorption spectrum of the complex **3-5** differs significantly from that of **3** in that the absorption at 460 nm is missing and instead a sharp absorption band at 435 nm as well as a broad absorption at 580-680 nm are observed. We interpret this spectrum in terms of formation of a charge-separated ion pair by referring to the relevant spectra.[7,9] These absorption bands decay very rapidly with a time constant of less than 20 ps, leaving no appreciable amount of other transient species including the triplet excited state. We thus conclude that both the charge separation and charge recombination in the complex **3-5** are very rapid.

The fluorescence decay of **3** alone in benzene can be fit with a single exponential function and its lifetime has been determined to be 1.38 ns. In spite of the significant fluorescence quenching as evident from the steady-state measurements, we could not detect a fast decaying component in the fluorescence decay of the complex **3-5** under a variety of conditions. Even under conditions where most of **3** should be complexed with **5**, the fluorescence decay can be analyzed by a single exponential function with a time constant of ca. 1.4 ns. We interpret this fluorescence lifetime as that of uncomplexed **3**. These results strongly suggest very fast intracomplex electron transfer in the complex **3-5**, which is even faster than the time resolution of the single photon counting system used here (ca. 3-5 ps).

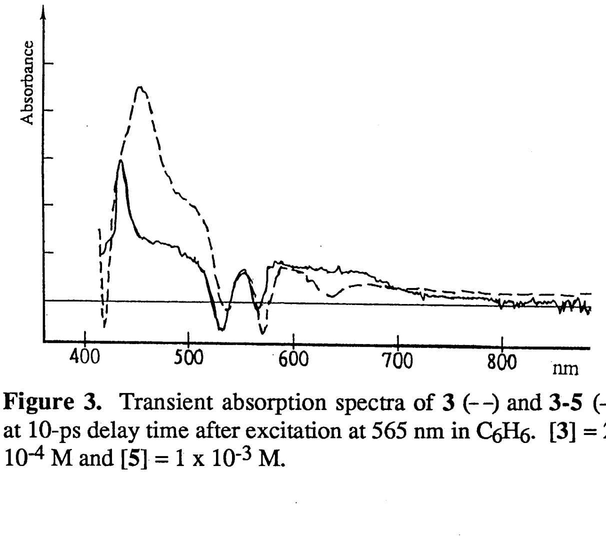

Figure 3. Transient absorption spectra of **3** (--) and **3-5** (—) at 10-ps delay time after excitation at 565 nm in C_6H_6. [3] = 2 x 10^{-4} M and [5] = 1 x 10^{-3} M.

In conclusion, excitation of the complex **3-5** in benzene leads to an efficient electron transfer to provide an ion pair which, in turn, undergoes very fast charge recombination to regenerate the ground state. The combination of a 2,6-diacylaminopyridine binding site and a 1,8:4,5-naphthalenetetracarboxamide electron acceptor guest represents a good motif for the study on electron transfer through hydrogen bonds in respects of strong binding as well as easy detection of ion pair states, and further work along this line is currently being explored in our laboratories.

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9 It is interesting to note that the spectrum obtained for the complex **3-5** is slightly different from a simple sum of (zinc porphyrin)$^+$ and (diimide)$^-$; A. Osuka, T. Okada, and N. Mataga, unpublished results. We interpret this difference being caused by protonation at the oxygen of the diimide anion radical with the host amide-hydrogens.