Electron transfer in a hydrogen-bonded assembly consisting of porphyrin–diimide

Atsuhiro Osuka,*[a] Ryusho Yoneshima,[a] Hideo Shiratori,[a] Tadashi Okada,*[b] Seiji Taniguchi[b] and Noboru Mataga[c]

[a] *Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*
[b] *Department of Chemistry, Graduate School of Engineering Science and Research Center for Materials Science at Extreme Conditions, Osaka University, Toyonaka 560-8531, Japan*
[c] *Institute for Laser Technology, Utsubo Honmachi, Nishi-ku, Osaka 550-0004, Japan*

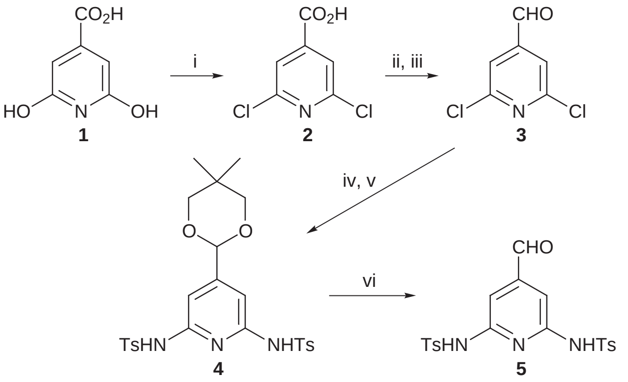
Electron-transfer reactions in an H-bonded assembly composed of a diacylaminopyridine bearing zinc porphyrin and 1,8 : 4,5-naphthalenetetracarboxylic diimide (K_a = 2.8 × 10^2 dm^3 mol^{-1}) in benzene occur with k_{CS} = 4.1 × 10^{10} s^{-1} and k_{CR} = 3.7 × 10^9 s^{-1}, while the corresponding covalently linked model with a comparable distance and energy gap undergoes electron transfer with k_{CS} = 9.9 × 10^{10} s^{-1} and k_{CR} = 6.7 × 10^8 s^{-1}.

In recent years there has been a considerable upsurge in the development of hydrogen (H)-bonded assemblies that can undergo efficient electron-transfer (ET) reactions,[1–6] since most biological electron transfers take place in non-covalently assembled arrays of several chromophores where the overall electronic coupling between the donor and acceptor seems to depend on the electronic interaction at a non-covalent H-bonded motif. Although several synthetic models have been presented to display ET within H-bonded assemblies, key aspects of ET dynamics still remain unclarified. In particular, ion-pair states have been only scarcely identified by transient absorption spectroscopy, leaving behavior of photogenerated ion pairs across H-bonds unknown except for a limited number of examples.[3,6,7]

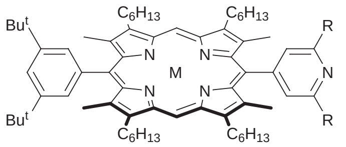
Here, we study an H-bonded assembly of a photoexcitable electron-donor zinc porphyrin **9** and electron-acceptor 1,8 : 4,5-naphthalenetetracarboxylic diimide **10** and ET dynamics within the assembly. Porphyrin **9** bears a *meso*-substituted 2,6-diacylaminopyridyl group that is expected to form a strong H bond to the diimide **10**.[8] The radical anion of **10** possesses sharp and characteristic absorption bands that have proven to be particularly useful for analysis of electron-transfer kinetics.[9] Aldehyde **5** was prepared in six steps from citrazinic acid (Scheme 1). The cross-condensation of 3,5-di-*tert*-butylbenzaldehyde, aldehyde **5** and 4,4′-diethyl-3,3′-dimethyldipyrrylmethane gave porphyrin **6** in 62% yield (on the basis of **5**), which was converted to a 2,6-diaminopyridyl-substituted porphyrin **7** in 67% yield by hydrolysis under acidic conditions (HBr–phenol–acetic acid). Porphyrin **9** was prepared by the reaction of **7** with hexanoyl chloride and subsequent insertion of Zn.‡ Diimides **10** and **11** were prepared by the cross-condensation of 1,8 : 4,5-naphthalenetetracarboxylic dianhydride with urea and 2-aminopropane-1,3-diol followed by silylation with *tert*-butyldimethylsilyl chloride in *ca.* 30 and 13% yields, respectively. The siloxyl substituents were introduced in order to increase the solubilities of these diimides in non-polar organic solvents.

To confirm the complexation *via* H-bonding, the ^{1}H NMR spectra of **9** in the absence and presence of increasing amounts of **10** were examined in C_6D_6, $CDCl_3$ and CD_2Cl_2. Typical chemical shift changes upon complexation of **9** and **10** in $CDCl_3$ are summarized in Scheme 2. Most prominently the imide H_a proton and the amide H_b protons were downfield shifted, while the other protons were essentially unperturbed. The fact that no particular upfield shift was observed for the aromatic protons of **10** precludes the coordination of **10** to the zinc centre in **9**. Similar shifts were observed in C_6D_6 and CD_2Cl_2, while no such shifts were detected in [$^2H_8$]THF or [$^2H_6$]DMF. The observed chemical shift changes are consistent with a complexation by three-points H-bonding as depicted in Scheme 2. From the ^{1}H NMR titration, the binding constants were determined using a standard non-linear least-square curve fitting method: 2.8 × 10^2 dm^3 mol^{-1} in benzene, 1.0 × 10^2 dm^3 mol^{-1} in $CDCl_3$ and 79 dm^3 mol^{-1} in CD_2Cl_2. Further, the continuous variation method (Job's plot) was used to determine the complexation stoichiometry as 1 : 1.

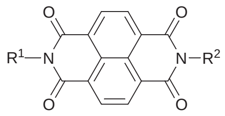
Steady-state fluorescence studies carried with a benzene solution of **9** (1.0 × 10^{-5} M)) in the presence of **10** (5.0 × 10^{-3}



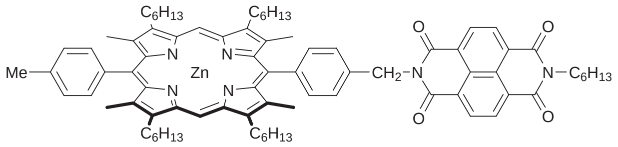
Scheme 1 *Reagents and conditions*: i, $POCl_3$, 160 °C, 78%; ii, $BF_3 \cdot OEt_2$, $NaBH_4$, 74%; iii, activated MnO_2, 66%; iv, neopentyl glycol, *p*-TsOH, 99%; v, toluene-*p*-sulfamide, Cu powder, 190 °C, 63%; vi, 10% H_2SO_4, TFA, 76%



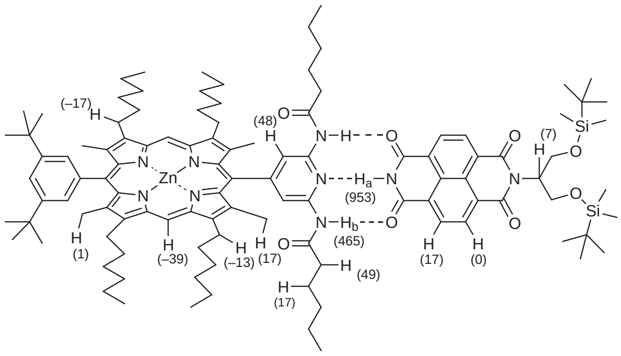
6 M = H_2, R = NHTS
7 M = H_2, R = NH_2
8 M = H_2, R = $NHCOC_6H_{13}$
9 M = Zn, R = $NHCOC_6H_{13}$



10 R^1 = H, R^2 = $CH(CH_2OTBDMS)_2$
11 R^1 = R^2 = $CH(CH_2OTBDMS)_2$
12 R^1 = D, R^2 = $CH(CH_2OTBDMS)_2$



13



Scheme 2 Complexation-induced (20%) changes in ^{1}H NMR chemical shifts (ppb) for **9**–**10** in CDCl$_3$

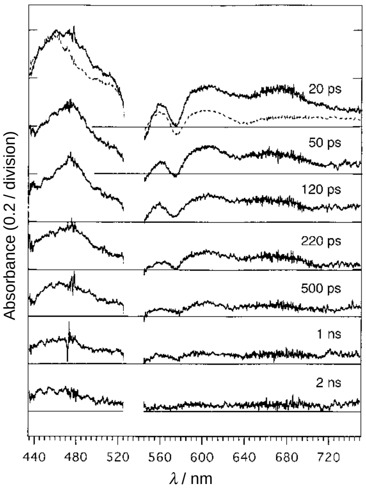


Fig. 1 Transient absorption spectra of a benzene solution of **9** (2.0×10^{-4} M) and **10** (1×10^{-2} M) at λ_{ex} = 532 nm. The dotted line shows the spectrum at a 20 ps delay time for **9** alone.

M) revealed substantial fluorescence quenching (70%) compared with the fluorescence of **9** alone. Such fluorescence quenching was not observed in THF and DMF nor for a solution of **9** and **11**, indicating that a complexation *via* H-bonding was crucial for fluorescence quenching, rather than diffusional encounters.

To provide further support for ET *via* H-bonding, time-resolved transient absorption studies were carried out. Fig. 1 shows the picosecond transient absorption spectra of **9** alone and in the presence of **10** at λ_{ex} = 532 nm in benzene. Under the conditions used, >95% of **9** was complexed with **10** and the fluorescence of **9** was completely quenched. The transient spectrum of **9** alone (shown by dotted line at a delay time of 20 ps) is a typical transient absorption spectrum of a 5,15-diaryl-octaalkyl zinc porphyrin, in which the absorption band at 458 nm is due to $S_n \leftarrow S_1$ absorption and the bleaching at 640 nm is due to stimulated emission of the S_1 state and these two bands decay with τ = 1.6 ns. The transient absorption spectra of the complex **9**–**10** provided clear evidence for the formation of a diimide anion radical (474 nm) and a zinc porphyrin cation radical (655 nm), both of which were observed early at 20 ps delay time and decayed with τ = 270 ps. Thus, the rate of charge recombination within the complex **9**–**10** is 3.7×10^{9} s^{-1}. By analyzing the time profile at 458 nm where the main absorbing species is the S_1 state of the zinc porphyrin, the rate of charge separation has been determined to be 4.1×10^{10} s^{-1}. These ET rates across an H-bond were compared with those in a related covalently linked model **13**, which has a similar energy diagram and a slightly shorter center-to-center distance, to characterize ET across an H-bond bridge.§¶ The transient absorption studies revealed that the rates of charge separation and recombination in **13** are 9.9×10^{10} and 6.7×10^{8} s^{-1}, respectively. Thus it may be concluded that (1) electronic coupling across an H-bond interface necessary for charge separation is comparable to that across two C–C single bonds, in line with recent results reported by Therien and coworkers,[5] and (2) an ion-pair across H-bonds is considerably shorter-lived in comparison to a covalently linked ion-pair. The latter aspect that can account for difficulty in detecting an ion-pair across H-bonds may be understood in terms of stabilization of the ion pair, thus the decrease in $-\Delta G$ in the inverted region, by H-bond reorganization which is accompanied by the charge separation.[7] The assembly **9**–**12** has been also studied by transient absorption spectroscopy and found to undergo ET-reaction with k_{CS} = 2.9×10^{10} s^{-1} and k_{CR} = 2.4×10^{9} s^{-1}, revealing that the isotope effect k_H/k_D is 1.4 and 1.5 for charge separation and recombination, respectively, roughly in line with results reported by Nocera and coworkers.[3a] Our next target will be the development of a H-bonded asembly of donor–acceptor triads and tetrads which can realize long-lived charge separation in spite of inherently shorter-lived ion-pairs across H-bonds. Our attempts in this direction will be reported elsewhere.

This work was supported by Grant-in-Aids for Scientific Research (No. 09440217 and 08874074) from the Ministry of Education, Science, Sports and Culture of Japan and by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST).

Notes and References

† E-mail: osuka@kuchem.kyoto-u.ac.jp

‡ All new compounds were fully characterized by 500 MHz ^{1}H NMR and FAB mass spectra.

§ The one-electron redox potentials of the donor and the acceptor moieties have been measured in CHCl$_3$ by cyclic voltammetry *vs.* ferrocene–ferrocenium ion. The oxidation potential of **9** was 0.16 V and the reduction potential of **10** was −1.05 V in the free form and −0.97 V in an H-bonded assembly with 2,6-dihexanoylaminopyridine, while the oxidation and reduction potentials of **13** were 0.11 and −1.06 V.

¶ Estimated center-to-center distances are 14.7 and 12.8 Å for **9**–**10** and **13**, respectively.

1 Y. Aoyama, M. Asakawa, Y. Matsui and H. Ogoshi, *J. Am. Chem. Soc.*, 1991, **113**, 6233; T. Hayashi, T. Miyahara, N. Hashizume and H. Ogoshi, *J. Am. Chem. Soc.*, 1993, **115**, 2049.

2 A. Harriman, Y. Kubo and J. L. Sessler, *J. Am. Chem. Soc.*, 1992, **114**, 388; T. Arimura, C. T. Brown, S. L. Springs and J. L. Sessler, *Chem. Commun.*, 1996, 2293.

3 (*a*) C. Turro, C. K. Chang, G. E. Leroi, R. I. Cukier and D. G. Nocera, *J. Am. Chem. Soc.*, 1992, **114**, 4013; (*b*) T. Hayashi, T. Miyahara, S. Kumazaki, H. Ogoshi and K. Yoshihara, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1964.

4 J. P. Kirby, N. A. van Dantzig, C. K. Chang and D. G. Nocera, *Tetrahedron Lett.*, 1995, **36**, 3477; J. A. Roberts, J. P. Kirby and D. G. Nocera, *J. Am. Chem. Soc.*, 1995, **117**, 8051; J. P. Kirby, J. A. Roberts and D. G. Nocera, *J. Am. Chem. Soc.*, 1997, **119**, 9230; Y. Deng, J. A. Roberts, S.-M., Peng, C. K. Chang and D. Nocera, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2124.

5 P. J. F. de Rege, S. A. Williams and M. J. Therien, *Science*, 1995, **269**, 1409.

6 A. Osuka, H. Shiratori, R. Yoneshima, T. Okada, S. Taniguchi and N. Mataga, *Chem. Lett.*, 1995, 913.

7 H. Miyasaka, A. Tabane, K. Kamada and N. Mataga, *J. Am. Chem. Soc.*, 1993, **115**, 7335 and references therein.

8 A. D. Hamilton, N. Pant and A. Muehldorf, *Pure Appl. Chem.*, 1988, **60**, 535; M. Kotera, J.-M. Lehn and J. P. Vigneron, *Tetrahedron*, 1995, **51**, 1953.

9 A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, Y. Nishimura, T. Ohno and K. Nozaki, *J. Am. Chem. Soc.*, 1993, **115**, 4577; G. P. Wiederrecht, M. P. Niemczyk, W. A. Svec and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1996, **118**, 81.

Received in Cambridge, UK, 12th May 1998; 8/03541E