

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

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

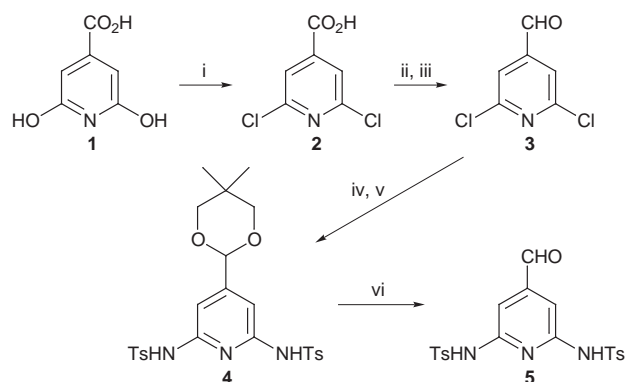
In recent years there has been a considerable upsurge in the development of hydrogen (H)-bonded assemblies that can undergo efficient electron-transfer (ET) reactions,<sup>1–6</sup> since most biological electron transfers take place in non-covalently assembled arrays of several chromophores where the 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.<sup>3,6,7</sup>

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**.<sup>8</sup> The radical anion of **10** possesses sharp and characteristic absorption bands that have proven to be particularly useful for analysis of electron-transfer kinetics.<sup>9</sup> Aldehyde **5** was prepared in six steps from citrazinic acid (Scheme 1). The cross-condensation of 3,5-di-*tert*-bu-

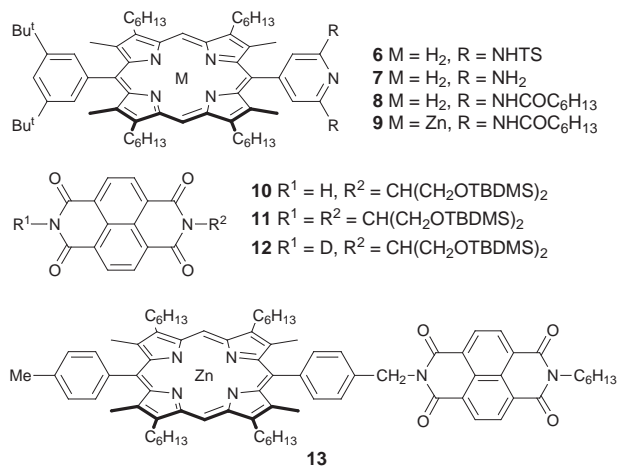
tylbenzaldehyde, aldehyde **5** and 4,4'-diethyl-3,3'-dimethyldipyrrylmethane gave porphyrin **6** in 62% yield (on the basis of **5**), which was converted to 2,6-diaminopyridyl-substituted porphyrin **7** in 67% yield by hydrolysis under acidic conditions (HBr–phenol–acetic acid). Porphyrin **9** was 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.

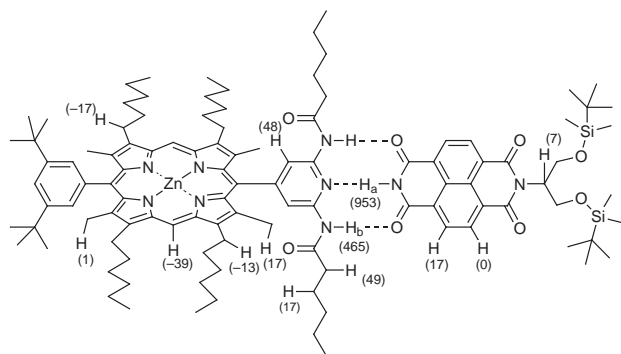
To confirm the complexation *via* H-bonding, the <sup>1</sup>H NMR spectra of **9** in the absence and presence of increasing amounts of **10** were examined in C<sub>6</sub>D<sub>6</sub>, CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub>. Typical chemical shift changes upon complexation of **9** and **10** in CDCl<sub>3</sub> are summarized in Scheme 2. Most prominently the imide H<sub>a</sub> proton and the amide H<sub>b</sub> 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<sub>6</sub>D<sub>6</sub> and CD<sub>2</sub>Cl<sub>2</sub>, while no such shifts were detected in [<sup>2</sup>H<sub>8</sub>]THF or [<sup>2</sup>H<sub>6</sub>]DMF. The observed chemical shift changes are consistent with a complexation by three-points H-bonding as depicted in Scheme 2. From the <sup>1</sup>H NMR titration, the binding constants were determined using a standard non-linear least-square curve fitting method:  $2.8 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$  in benzene,  $1.0 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$  in CDCl<sub>3</sub> and  $79 \text{ dm}^3 \text{ mol}^{-1}$  in CD<sub>2</sub>Cl<sub>2</sub>. 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** ( $1.0 \times 10^{-5} \text{ M}$ ) in the presence of **10** ( $5.0 \times 10^{-3}$

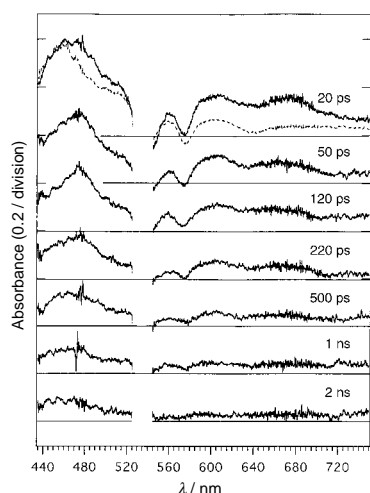


**Scheme 1** Reagents and conditions: i, POCl<sub>3</sub>, 160 °C, 78%; ii, BF<sub>3</sub>·OEt<sub>2</sub>, NaBH<sub>4</sub>, 74%; iii, activated MnO<sub>2</sub>, 66%; iv, neopentyl glycol, *p*-TsOH, 99%; v, toluene-*p*-sulfamide, Cu powder, 190 °C, 63%; vi, 10% H<sub>2</sub>SO<sub>4</sub>, TFA, 76%





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



**Fig. 1** Transient absorption spectra of a benzene solution of **9** ( $2.0 \times 10^{-4}$  M) and **10** ( $1 \times 10^{-2}$  M) at  $\lambda_{\text{ex}} = 532$  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  $\lambda_{\text{ex}} = 532$  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  $\tau = 1.6$  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  $\tau = 270$  ps. Thus, the rate of charge recombination within the complex **9–10** is  $3.7 \times 10^9$   $\text{s}^{-1}$ . 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  $4.1 \times 10^{10}$   $\text{s}^{-1}$ . 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. $\S$ ¶ The transient absorption studies revealed that the rates of charge separation and recombination in **13** are  $9.9 \times 10^{10}$  and  $6.7 \times 10^8$   $\text{s}^{-1}$ , 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  $k_{\text{CS}} = 2.9 \times 10^{10}$   $\text{s}^{-1}$  and  $k_{\text{CR}} = 2.4 \times 10^9$   $\text{s}^{-1}$ , revealing that the isotope effect  $k_{\text{H}}/k_{\text{D}}$  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 assembly 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.

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## Notes and References

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

§ The one-electron redox potentials of the donor and the acceptor moieties have been measured in  $\text{CHCl}_3$  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-dihexanoylaminoipyridine, 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.

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