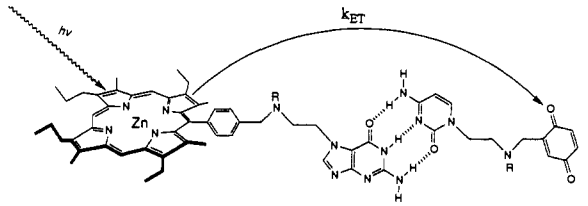
Long-Range Photoinduced Electron Transfer in an Associated but Noncovalently Linked Photosynthetic Model System

Jonathan L. Sessler,*,† Bing Wang,§ and Anthony Harriman*,‡

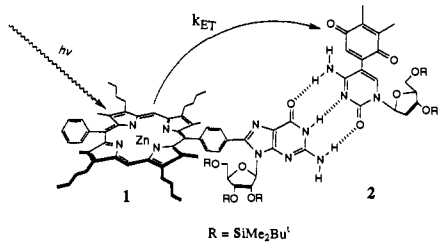
Department of Chemistry and Biochemisty and Center for Fast Kinetics Research The University of Texas at Austin Austin, Texas 78712

Received May 4, 1993

Many of the more hotly debated issues in the biological electron-transfer (ET) area involve questions of how electron-transfer events proceed through noncovalently linked protein pathways.[1] For some time, therefore, we[2] and others[3] have sought to prepare noncovalently linked photosynthetic model systems that might allow for the study of ET processes in formally unlinked but still well-associated donor–acceptor aggregates. Previously, we reported the synthesis of system **I**, in which the zinc porphyrin

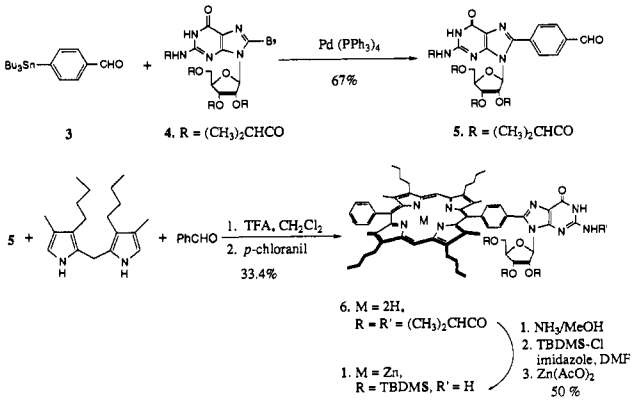


photodonor is "attached" to the benzoquinone acceptor *via* Watson–Crick base-pairing interactions.[2c] This system, however, allows for considerable conformational flexibility which serves to complicate interpretation of its excited-state dynamics. With this communication, we report the synthesis of a more rigid system (ensemble **II**) in which such concerns are removed.

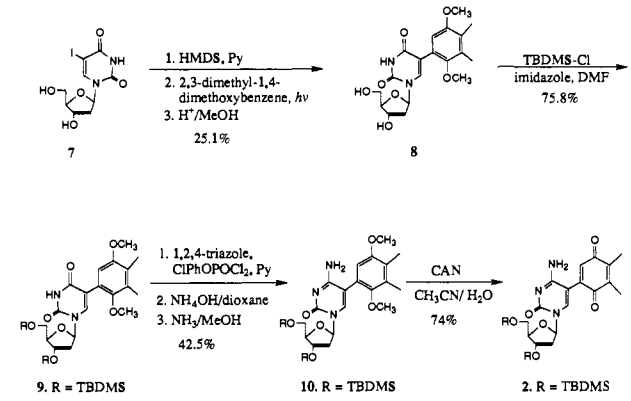


The syntheses of the guanosine-substituted porphyrin photodonor and cytidine-substituted quinone acceptor components of system **II** (compounds **1** and **2**) are shown in Schemes **I** and **II**, respectively.[4] For **1**, the key step involved the preparation of an *O*- and *N*-protected guanosine bearing a masked benzaldehyde substituent (**5**) and subsequently elaborating this latter group into a porphyrin subunit. For **2**, it involved the preparation of the protected hydroquinone-to-functionalized cytidine bond.[5] Then, once **8** was in hand, further elaboration to the desired product **2** proved straightforward. Both **1** and **2** incorporate *tert*-butyldimethylsilyl (TBDMS) protecting groups on the ribose

Scheme I



Scheme II



hydroxyls which increase the solubility in organic solvents and greatly facilitate product purification.

The one-electron reduction potential of the cytosine-substituted quinone **2** in dichloromethane containing 0.2 M tetra-*N*-butylammonium perchlorate is –0.86 V vs SCE. This is considerably more negative than that found for either 2,3-dimethylbenzoquinone ($E°$ = –0.50 V vs SCE) or the quinone-containing electron-acceptor portion of aggregate **I** ($E° \approx$ –0.40 V vs SCE), no doubt due to the electron-donating nature of the directly appended cytosine. The redox potential for one-electron oxidation of the porphyrin subunit **1** is 0.72 V vs SCE, while its excitation energy, taken from the intersection between absorption and fluorescence spectra, was found to be 2.08 eV. Therefore, photoinduced electron transfer from the zinc porphyrin excited singlet state of **1** to the quinone **2** is thermodynamically favored by ca. 0.50 eV, compared to a thermodynamic driving force of ca. 1.0 eV for aggregate **I**.[2c]

Time-resolved fluorescence studies made with **1** in dry CH_2Cl_2 indicated monoexponential decay kinetics with a lifetime of 1.8

† Department of Chemistry and Biochemistry.
‡ Center for Fast Kinetics Research.

(1) See, for instance: (a) Moser, C. C.; Keske, J. M.; Warncke, K.; Farid, R. S.; Dutton, P. L. *Nature* **1992**, *355*, 796–802. (b) Pelletier, H.; Kraut, J. *Science* **1992**, *258*, 1748–1755. (c) Beratan, D. N.; Onuchic, J. N.; Winkler, J. R.; Gray, H. B. *Science* **1992**, *258*, 1740–1741.

(2) (a) Harriman, A.; Magda, D.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 345–348. (b) Harriman, A.; Magda, D. J.; Sessler, J. L. *J. Phys. Chem.* **1991**, *95*, 1530–1532. (c) Harriman, A.; Kubo, Y.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 388–390.

(3) (a) Tecilla, P.; Dixon, R. P.; Slobodkin, G.; Alavi, D. S.; Waldeck, D. H.; Hamilton, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 9408–9410. (b) Aoyama, Y.; Asakawa, M.; Matsui, Y.; Ogoshi, H. *Ibid.* **1991**, *113*, 6233–6240. (c) Hayashi, T.; Miyahara, T.; Hashizume, N.; Ogoshi, H. *J. Am. Chem. Soc.* **1993**, *115*, 2049–2051. (d) Turro, C.; Chang, C. K.; Leroi, G. E.; Cukier, R. I.; Nocera, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 4013–4015. (e) Drain, C. M.; Fischer, R.; Nolen, E. G.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 243–245. (f) Ojadi, E.; Selzer, R.; Linschitz, H. *J. Am. Chem. Soc.* **1985**, *107*, 7783–7784. (g) Hofstra, U.; Koehorst, R. B. M.; Schaafsma, T. J. *Chem. Phys. Lett.* **1986**, *130*, 555–559. (h) Hugerat, M.; Levanon, H.; Ojadi, E.; Biczok, L.; Linschitz, H. *Chem. Phys. Lett.* **1991**, *181*, 400–406. (i) Maiya, G. B.; Krishnan, V. *Inorg. Chem.* **1985**, *24*, 3253–3257. (j) Anderson, H. L.; Hunter, C. A.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1989**, 226–227. (k) Therien, M. J., private communication to J.L.S. on March 23, 1993.

(4) Characterization data for all new compounds is included in the supplementary material.

(5) Compound **8** was prepared with use of a modification of the known procedure: Bigge, C. F.; Mertes, M. P. *J. Org. Chem.* **1981**, *46*, 1994–1997.

0002-7863/93/1515-10418$04.00/0

± 0.1 ns, independent of wavelength and of porphyrin concentration (≤60 μM).[6] Addition of **2** (0–2 mM) caused the fluorescence decay profile to become biphasic. Throughout the entire titration, the decay profiles could be analyzed in terms of two exponential components of lifetimes, 1.8 ± 0.2 ns and 740 ± 90 ps. The fractional contribution of the shorter-lived component increased from 0 in the absence of quinone to 95% at 2 mM quinone. The longer-lived component is assigned to uncomplexed porphyrin, while the shorter-lived component is attributed to a porphyrin subunit quenched by a quinone moiety within the confines of a complex. Since the magnitude of the shorter lifetime remains independent of quinone concentration, we can eliminate diffusional contact as an important mode of fluorescence quenching. Furthermore, absorption and fluorescence spectral profiles were unperturbed by the presence of quinone, such that π-stacking between porphyrin and quinone (or cytosine) is unimportant under these conditions.

Diluting the solution but retaining the ratio of porphyrin to quinone resulted in a decrease in the fractional contribution of the shorter-lived component but did not affect the lifetime. Analysis of the fractional components in terms of a 1:1 complex between **1** and **2** gave an association constant of 8990 ± 600 M^{-1}.[6] This value is significantly higher than that observed for the more flexible aggregate **I**[2c,7] but is consistent with values obtained using standard ^{1}H NMR titrations.[8] Addition of ethanol (15% v/v) or DMSO (25% v/v) to the mixture of **1** and **2** caused the fluorescence decay profiles to become monoexponential, with a lifetime of 1.8 ns. Further, a range of control experiments, involving mixtures of (a) **1** and 2,3-dimethylbenzo-1,4-quinone, (b) zinc(II) 3,7,13,17-tetramethyl-2,8,12,18-tetrabutyl-5,15-diphenylporphyrin and **2**, and (c) this same control zinc(II) porphyrin and 2,3-dimethylbenzo-1,4-quinone, failed to provide evidence for anything other than simple bimolecular (i.e., diffusional contact) quenching.[9] The present experimental observations are thus consistent with the formation of a three-point hydrogen-bonding bridge between the guanine porphyrin **1** and the cytosine quinone **2**, as depicted in structure **II**.[10] Such a complex would position the porphyrin and quinone within an edge-to-edge separation distance of ca. 14 Å (as judged by CPK models).

Following from the considerable literature precedent,[11] the most probable mechanism for the observed quenching of porphyrin fluorescence involves photoinduced electron transfer from porphyrin to quinone (ΔG° = –0.5 eV), for which the rate constant is ca. 8×10^8 s^{-1}.[12] Picosecond laser flash photolysis studies showed that the porphyrin excited singlet state, present immediately after the excitation pulse, relaxed to the triplet state without indication of intermediate formation of the porphyrin π-radical cation. Presumably, reverse electron transfer to regenerate the ground state occurs faster than charge separation, as has often been observed in covalently linked porphyrin–quinone conjugates.[11] Neither cytosine nor cytosine-bearing 1,4-dimethoxybenzene served to quench porphyrin fluorescence when added to solutions of **1**.

The hydrogen-bonded aggregate **II** can be considered as a major improvement over its prototype **I** in view of the decreased flexibility. In fact, because of its considerable conformational freedom, it is likely that electron transfer in **I** occurs by way of diffusional encounter between partners within a hydrogen-bonded complex.[13] Here, the hydrogen bonds simply act as an anchor and tether the reactants together within close proximity. In marked contrast, electron transfer in **II** most probably occurs *via* a through-bond process involving the hydrogen-bonded network. Such superexchange processes may be facilitated by the relatively low-energy phenyl and guanine residues before reaching the hydrogen bond "bottleneck". Because of the very different nature of the spacer functions, it is inappropriate to compare quantitatively rates of electron transfer in aggregate **II** and similarly spaced covalently linked porphyrin–quinone conjugates. Nonetheless, the fact that ET is observed in the present instance stands as proof *inter alia* that charge separation processes may be effected in appropriately designed noncovalently linked synthetic donor acceptor systems.

Acknowledgment. This work was supported by the R. A. Welch Foundation (F-1018), the National Institutes of Health (GM41657 to J.L.S.), and the National Science Foundation (CHE 9102657 to A.H.). The Center for Fast Kinetics Research is supported jointly by the Biotechnology Research Resources Division of the National Institutes of Health (RR00886) and by the University of Texas at Austin.

Supplementary Material Available: Details of synthesis, photophysics, and binding constant evaluations (18 pages). Ordering information is given on any current masthead page.

(6) See supplementary material for experimental and calculational details.

(7) The low value observed for aggregate **I** is considered to be a reflection of its "floppiness" and the strong entropic dependence inherent in the overall equilibrium process.

(8) For the interaction of **1** with **10**, we obtain an association constant of 13 000 ± 2000 M^{-1} in CD_2Cl_2 at 25 °C (see supplementary material); for the interaction of 2′,3′,5′-tripentanoylguanosine and 4-ethylcytosine in $CDCl_3$ at 25 °C, a value of 10 000 M^{-1} has been obtained: Murray, T. J.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1992**, *114*, 4010–4011.

(9) See supplementary material for a full description of these control experiments.

(10) Temperature dependence studies made in CH_2Cl_2 showed that the association constant increased markedly upon cooling. Fitting the data to the van't Hoff equation gave entropy and enthalpy changes of –10.4 cal mol^{-1} K^{-1} and –8.4 kcal mol^{-1}, respectively. The rate of electron transfer decreased slightly with decreasing temperature and, fitting the data to the Marcus expression, gave an activation enthalpy change of 3.3 kcal mol^{-1}. With ΔG° = –0.5 eV, this latter value corresponds to a reorganization energy of ca. 1.4 eV and a ν of 33 cm^{-1}.

(11) For reviews of intermolecular and covalently linked porphyrin–quinone systems, see: (a) Connolly, J. S.; Bolton, J. R. In *Photoinduced Electron Transfer, Part D*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; pp 303–393. (b) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435–461. (c) Bixon, M.; Fajer, J.; Feher, G.; Freed, J. H.; Gamliel, D.; Hoff, A. J.; Levanon, H.; Möbius, K.; Norris, J. R.; Nechushtai, R.; Scherz, A.; Sessler, J.; Stehlik, D. H. A. *Isr. J. Chem.* **1992**, *32*, 369–518.

(12) The rate constant was derived as: $k = [(1/\tau_2) - (1/\tau_1)]$; see supplementary material.

(13) According to the Einstein expression for translational motion, the distance (d) that an object can move in a certain time (t) depends on its diffusion coefficient (D) according to: $d = (2Dt)^{1/2}$. Assuming $D = 4 \times 10^{-6}$ cm^2 s^{-1} and taking t as the average time for electron transfer ($t = 1/k \approx 1$ ns), the translational distance for the subunits in aggregate **I** is ca. 9 Å.