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

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Many of the more hotly debated issues in the biological electrontransfer (ET) area involve questions of how electron-transfer events proceed through noncovalently linked protein pathways.¹ For some time, therefore, we² and others³ 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



 $\mathsf{R} = \mathsf{CH}_2\mathsf{C}_6\mathsf{H}_4\mathsf{O}(\mathsf{CH}_2)_2\mathsf{O}(\mathsf{CH}_2)_2\mathsf{O}\mathsf{CH}_3$

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 tertbutyldimethylsilyl (TBDMS) protecting groups on the ribose

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1. HMDS, Py TBDMS-C imidazole, DMF 2. 2.3-dimethyl-1,4dimethoxybenzene. h 75.8% 3. H⁺/MeOH 25.1% 1.2.4-triazole CIPhOPOCI, P CAN CH3CN/H2O 2. NH4OH/dioxa 3. NH₃/MeOH 749 42.5% 10. R = TBDMS 2. R = TBDMS

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-Nbutylammonium perchlorate is -0.86 V vs SCE. This is considerably more negative than that found for either 2,3dimethylbenzoquinone ($E^{\circ} = -0.50$ V vs SCE) or the quinonecontaining electron-acceptor portion of aggregate I ($E^{\circ} \approx -0.40$ 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 CH₂Cl₂ indicated monoexponential decay kinetics with a lifetime of 1.8

(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.

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 \pm 0.1 ns, independent of wavelength and of porphyrin concentration ($\leq 60 \mu$ M).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 \pm 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 ¹H 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-5,15diphenylporphyrin 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 threepoint 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).

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

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 ($\Delta G^{\circ} = -0.5 \text{ eV}$), for which the rate constant is ca. $8 \times 10^8 \text{ s}^{-1,12}$ 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. Nonethe 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.

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

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

⁽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 \pm 2000 M⁻¹ in CD₂Cl₂ at 25 °C (see supplementary material); for the interaction of 2',3',5'-tripentanoylguanosine and 4-ethylcytosine in CDCl₃ 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.

⁽¹⁰⁾ Temperature dependence studies made in CH₂Cl₂ 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 $\Delta G^{\circ} = -0.5$ 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.

⁽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 $D = 4 \times 10^{-6}$ cm² 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.