and the number of electrons involved in the transition structures are unimportant. We are extending this work to an examination of the reaction mechanisms of tetramers and of solvated monomers and dimers.

Registry No. HLi, 7580-67-8; CH$_3$Li, 917-54-4; (HLi)$_2$, 78715-95-4; (CH$_3$Li)$_2$, 74309-22-1; H$_2$C=O, 50-00-0.

High-Quantum-Yield Long-Lived Charge Separation in a Photosynthetic Reaction Center Model

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The high quantum efficiency of photosynthetic charge separation depends on favorable electron-transfer rates between electron donors and acceptors that are positioned in precise spatial relationships relative to one another and that possess redox potentials which result in movement of an electron down a stepped potential gradient. We have recently measured the dependence of photoinduced electron-transfer rates and subsequent dark charge recombination rates on the free energy of reaction in restricted distance porphyrin donor–quinone acceptor molecules.[1] Using this information we have now synthesized a molecule for which the donor–acceptor electron-transfer rates are designed to promote efficient two-step charge separation over a known long distance. In addition to a primary porphyrin–quinone donor–acceptor pair, this molecule possesses a secondary N,N-dimethylaniline donor **1**. The donor–acceptor distances and orientations in **1** are strongly

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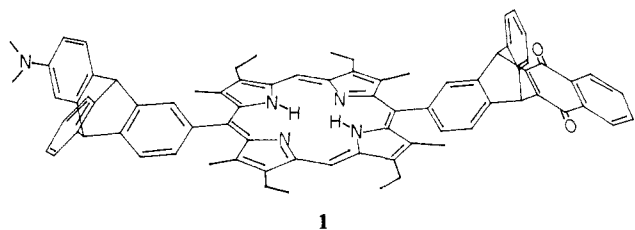
restricted by the polycyclic cage structures between them. The center-to-center distances[2] are, porphyrin–quinone, 10.5 Å, aniline–porphyrin, 10 Å, and, aniline–quinone, 25 Å.

Compound **1** was synthesized along with the analogous compound **2**, which lacks the dimethylamino group and therefore lacks the secondary electron donor. Ditriptycylporphyrin (**3**) which lacks both the dimethylamino and naphthoquinone groups was also prepared as a reference. These diphenyloctaalkylporphyrins[3] were synthesized by reaction of the appropriate benzaldehyde derivatives with 3,3′-diethyl-4,4′-dimethylpyrromethane.[4] Triptycenonaphthoquinone aldehyde (**4**) was prepared by the procedure we reported earlier.[5] 2-Nitrotriptycene[6] was monoformylated[7] in 95% yield using dichloromethyl methyl ether/AlCl$_3$ to give after

Table I. Energetics

compound	$E_{1/2}^{-\ a}$	$E_{1/2}^{+\ a}$	$\dfrac{E_{1/2}^{+}-}{E_{1/2}^{-}}$
1	−0.61, −1.42	0.78, 0.92	1.39, 1.53
2	−0.61, −1.42	0.92	1.53, 2.34
3	−1.41	0.92	2.33
2-(dimethylamino)triptycene		0.78	
triptycenonaphthoquinone	−0.61		

^{a} Redox potentials (V vs. SCE) were measured by cyclic voltammetry at a Pt disk electrode. The measurements were performed in butyronitrile containing 0.1 M tetra-n-butylammonium perchlorate at 21 °C.

chromatography 2-formyl-6-nitrotriptycene (**5**). Equimolar amounts of **4** and **5** along with 2 equiv of the pyrromethane were dissolved in CH$_3$OH/THF 4:1 v/v. Addition of an equivalent of p-toluenesulfonic acid resulted in precipitation of the *meso*-tetrahydroporphyrin (**6**) within 5 min. Oxidation of **6** with DDQ in CH$_2$Cl$_2$ gave the mixed porphyrins in 80% yield. The mixed porphyrins were treated with SnCl$_2$ in THF/concentrated HCl 1:1 v/v for 18 h to reduce the nitro group. At this stage the porphyrin isomers containing one aminotriptycene and one triptycenonaphthoquinone were easily separated by chromatography in 63% yield.[8] The amino group was dimethylated with CH$_2$O/NaBH$_3$CN[9] to yield **1**: 85%; mass spectrum (^{252}Cf fission fragment), m/z calcd 1081.5, found 1081.3. Compound **2** was prepared in a completely analogous fashion using **4**, 2-formyltriptycene (**7**), and the pyrromethane: 23%; mass spectrum (^{252}Cf fission fragment), m/z calcd 1038.5, found 1038.8. Compound **3** was also prepared by the analogous route using only **7** and the pyrromethane: 15%; mass spectrum (^{252}Cf fission fragment), m/z calcd 982.5, found 982.5.[10]

One-electron redox potentials for these molecules are listed in Table I. The redox potentials of each donor and acceptor are not altered by their incorporation into **1** and **2**. In high dielectric constant solvents the sum of the redox potentials for oxidation of the donor and reduction of the acceptor is a good estimate of the radical pair energy level.[11] Thus, in compounds **1** and **2** the energy of P$^+$Q$^-$ is 1.53 eV above the ground state, while in compound **1** the energy of D$^+$PQ$^-$ is 1.39 eV above the ground state, where P = porphyrin, Q = quinone, and D = N,N-dimethylaniline. Since the lowest excited singlet state of these molecules is the 1.95-eV singlet state of the porphyrin, the exothermicity of the reaction ^{1}*PQ → P$^+$Q$^-$ is 0.42 eV and that of the reaction DP$^+$Q$^-$ → D$^+$PQ$^-$ is 0.14 eV. Using our measured rate vs. free energy data for porphyrin–quinone molecules possessing very similar molecular structure and virtually the same donor–acceptor distances,[1] we predict the following reaction rate constants: ^{1}*PQ → P$^+$Q$^-$, 10^{11} s^{-1}; P$^+$Q$^-$ → PQ, 8 × 10^9 s^{-1}; DP$^+$Q$^-$ → D$^+$PQ$^-$, 2.5 × 10^{10} s^{-1}. Thus, the secondary electron transfer reaction DP$^+$Q$^-$ → D$^+$PQ$^-$ should be able to compete very effectively with the DP$^+$Q$^-$ → DPQ charge recombination reaction in **1**.

The ground-state optical absorption spectra of **1** and **2** are simply the sum of contributions from the individual chromophores, while the emission spectra are that of the unperturbed porphyrin alone. The fluorescence quantum yields of **1** and **2** are both 0.0002 and are highly quenched relative to the 0.06 fluorescence quantum yield of **3**. The fluorescence lifetimes of both **1** and **2** are <30 ps as determined by time-correlated photon counting. These data indicate that a better than 99% efficient nonradiative pathway for decay of the singlet excitation energy in **1** and **2** exists.

The nature of this pathway was determined by transient absorbance measurements. Compounds **1** and **2** were excited with

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(10) Spectroscopic data for compounds **1–3** are provided in the supplemental material.
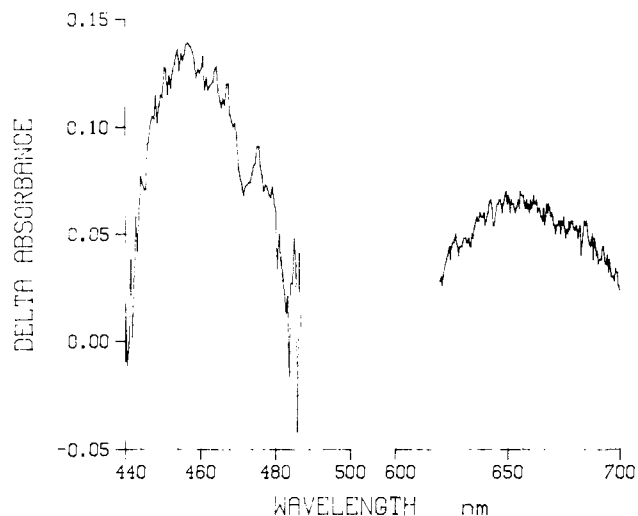(11) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *133*, 93.

Figure 1. Changes in absorbance of a 2×10^{-4} M solution of **1** in butyronitrile at 20 ps following a 0.5-mJ, 1-ps, 600-nm laser flash. Cell path length, 2 mm. Filters that reject stray light cut out the 490–620-nm wavelength region, while the sharp cutoff at 440 nm is due to the intense absorption of the porphyrin Soret band at 421 nm.

Figure 2. Transient absorbance decays measured at 460 nm of 2×10^{-4} M solutions of (A) **2** and (B) **1** in butyronitrile following a 0.5-mJ, 1-ps, 600-nm laser pulse. The superimposed smooth curves are the exponential fits to the data.

a 1-ps laser flash at 600 nm.[12] The formation and decay of the porphyrin cation were monitored at 460 and 650 nm,[13] while the formation of the naphthoquinone anion and the *N*,*N*-dimethylanilinium cation were monitored at 480[14] and 470 nm,[15] respectively. All measurements were performed in butyronitrile at 21 °C. Each transient could be described by a single exponential rise or decay.[16] Quantum yields of charge separation were determined as described previously.[5]

Excitation of either **1** or **2** results in formation of a transient spectrum due to P^+Q^- with a rate constant of 1.1×10^{11} s^{-1} (Figure 1). In compound **2** the P^+Q^- state decays cleanly back to the ground state with a rate constant of 5.6×10^9 s^{-1} (Figure 2A). For compound **1** the transient due to P^+Q^- decays more rapidly with a rate constant of 1.4×10^{10} s^{-1} to a state that possesses absorbance in the blue region of the spectrum characteristic of D^+ and Q^- with no persistent changes in the red which would indicate the presence of the porphyrin cation (Figure 2B). *The resultant D^+PQ^- state decays to the ground state of **1** with a lifetime of 2.45 μs.* A comparison between the rate constants for the competitive reactions $DP^+Q^- \rightarrow DPQ$ and $DP^+Q^- \rightarrow D^+PQ^-$ indicates that D^+PQ^- is formed from DP^+Q^- in about 71% yield. This yield is consistent with the measured transient absorbance spectra using the known extinction coefficients for D^+, P^+, and Q^-.[5,13–15]

The measured electron-transfer rate constants for **1** and **2** all agree within a factor of 2 with the values predicted by our rate vs. free energy of reaction data. Thus, our results show that it is possible to design molecules that produce high-quantum-yield long-lived charge separation provided that three requirements are met. First, the distances between the various donors and acceptors must be highly restricted. Second, for a given donor–acceptor distance the dependence of the electron transfer rates on the free energy of reaction must be known. Third, more than a single optimized electron-transfer step is necessary to achieve long-lived
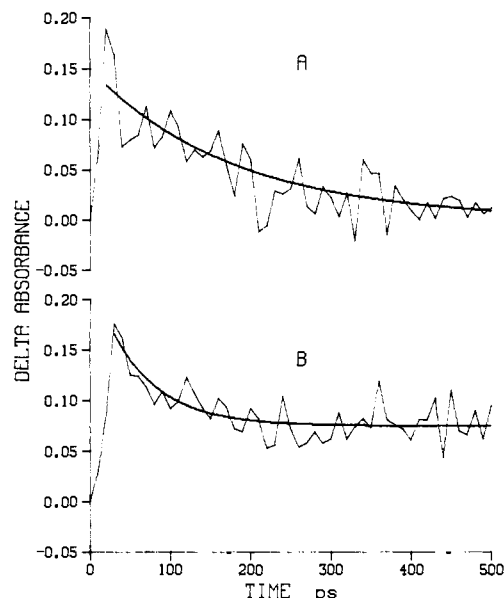
radical ion pair states in a manner analogous to photosynthesis.[17]

Supplementary Material Available: NMR and visible spectral data for **1–3** and numbering scheme for compounds (3 pages). Ordering information is given on any current masthead page.

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Protons on a Cluster Surface. Reversible Generation of Agostic (C–H–M) Hydrogens from Iron Hydrides (Fe–H–Fe) on a Saturated Triiron Cluster

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Bridging hydrogens are familiar structural features in borane, metallaborane, and metal cluster chemistry.[1] Although not as familiar, metal carbon bridging hydrogens, agostic hydrogens, have been identified in a significant number of hydrocarbyl–metal complexes.[2] We have recently reported the ferraboranes H-Fe$_3$(CO)$_9$BH$_4$ (I)[3] and HFe$_3$(CO)$_{10}$BH$_2$ (II) as well as the anions formed by respective cluster deprotonation.[4] The structures of I and II can be contrasted with those of the isoelectronic hydrocarbyl complexes IIIa and IVa.[5] The mobility of the hydrogens

(12) The 600-nm, 1-ps, 0.5-nJ output of a mode-locked Ar$^+$ synchronously pumped dye laser was amplified to 2.5 mJ by using a four-stage dye amplifier pumped by a frequency-doubled Nd-YAG laser operating at 10 Hz. A 2.0-mJ pulse was used to generate a picosecond continuum probe pulse, while a 0.5-mJ pulse was used for sample excitation. Absorbance measurements were made with a double-beam spectrometer which employed optical multichannel detection. Time delays between pump and probe pulses were accomplished with an optical delay line.
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