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Long-lived Charge Separated States from Zinc Porphyrin-Free Base Porphyrin-Diimide-Quinone Tetrads

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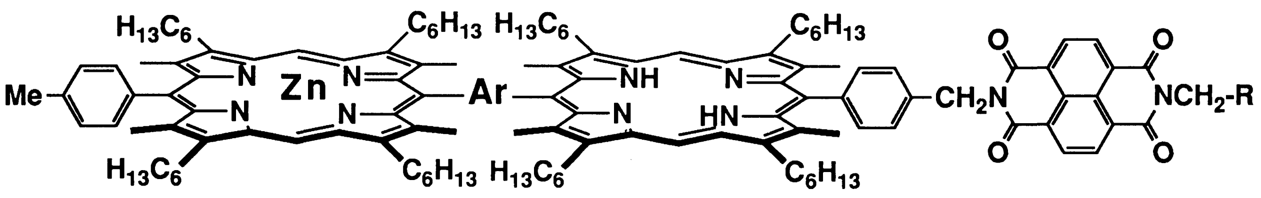
Tetrads consisting of zinc porphyrin (ZnP), free base porphyrin (H_2P), naphthalene-1,4,5,8-tetracarboxylic diimide (NIm), and quinone (Q) were synthesized. Upon photoexcitation, these tetrads provide ion pair states $(ZnP)^+$-H_2P-NIm-$(Q)^-$, whose lifetimes are much longer, reaching more than 100 μs in THF-butyronitrile, in biphenyl-bridged models but shorter in diphenylmethyl-bridged models in comparison to the corresponding Q-free triads.

Recently, considerable effort has been devoted to the synthesis and characterization of artificial photosynthetic models in order to better understand the detail mechanism of virtually quantitative charge separation (CS) in the photosynthetic reaction center.1) Among these, formation of long-lived charge separated ion pair (IP) states via initial electron-transfer reactions within the singlet manifold has been an important, long-standing issue.2,3) We report here the generation of such IP states lasting more than 100 μs at room temperature from conformationally restricted tetrads. Synthetic models employed here are covalently-linked zinc porphyrin (ZnP)-free base porphyrin (H_2P)-naphthalene-1,4,5,8-tetracarboxylic diimide (NIm)-quinone (Q) tetrads **1-4**, in which the ZnP and H_2P moieties are bridged by 4,4'-biphenylylene- or methylenebis(1,4-phenylene)-group and a methylene bridge is inserted both between the H_2P and NIm and between the NIm and Q. Recently, we reported the photo-induced formation of long-lived IP states from ZnP-H_2P-pyromellitimide (PIm) and ZnP-H_2P-NIm triads via initially formed charge separated states ZnP-$(H_2P)^+$-$(Im)^-$3) and the efficient charge shift reaction: $(ZnP)^+$-$(PIm)^-$-Q —> $(ZnP)^+$-PIm-$(Q)^-$ in ZnP-PIm-Q triads.4) The former finding indicates the hole transfer from $(H_2P)^+$ to ZnP can compete with energy-wasteful charge recombination (CR) in ZnP-$(H_2P)^+$-$(Im)^-$ and the latter finding allows an estimation of rates of charge-shift reaction from $(Im)^-$ to Q.5) It is also expected that more efficient initial CS takes place in models bearing NIm in comparison to those bearing PIm, since the NIm moiety is stronger electron acceptor than PIm.3b,6) Therefore, it is quite reasonable to envisage that in tetrads **1-4** a series of sequential ET may lead to the ultimate formation of $(ZnP)^+$-H_2P-NIm-$(Q)^-$ having much longer lifetimes in substantial quantum yields.4) This has indeed been confirmed in **1** and **2** by the measurement of transient absorption spectroscopy.

The models **1-4** were prepared by following the now conventional route often employed for our earlier conformationally restricted porphyrin models.3b,4,7) First, the formyl-substituted porphyrins **5-8** were prepared from cross-condensation reaction of aldehydes **9** and **10**, and aldehydes **11** and **12** with dipyrromethane **13** followed by acidic deprotection (trifluoroacetic acid, reflux) in 18-35% yields. Second



1; Ar = Ph-Ph, R = Q_a

2; Ar = Ph-Ph, R = Q_b

3; Ar = Ph-CH_2-Ph, R = Q_a

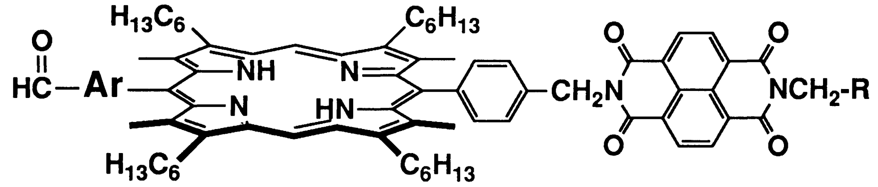
4; Ar = Ph-CH_2-Ph, R = Q_b

5; Ar = Ph-Ph, R = Q_aM

6; Ar = Ph-Ph, R = Q_bM

7; Ar = Ph-CH_2-Ph, R = Q_aM

8; Ar = Ph-CH_2-Ph, R = Q_bM

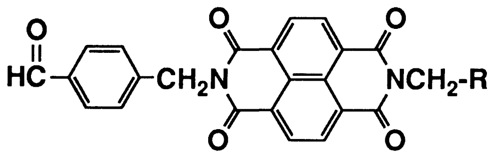


5; Ar = Ph-Ph, R = Q_aM

6; Ar = Ph-Ph, R = Q_bM

7; Ar = Ph-CH_2-Ph, R = Q_aM

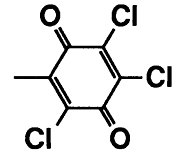
8; Ar = Ph-CH_2-Ph, R = Q_bM



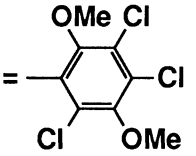
9; R = Q_aM

10; R = Q_bM

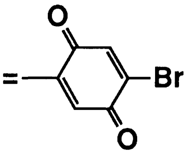
Q_a =



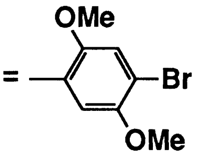
Q_aM =



Q_b =

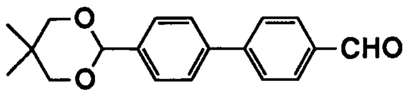


Q_bM =



condensation of **5**-**8** and *p*-tolualdehyde with **13** provided diimide-linked diporphyrins in 30-41% based on the amount of **5**-**8** used and subsequent demethylation with BBr_3 in CH_2Cl_2 gave quinone-containing tetrads in nearly quantitative yields. Finally, partial zinc ion insertion followed by repeated separation over silica gel column furnished **1**-**4**.[8] Quinone-free reference triads **1a**-**4a** were similarly prepared by the partial metalation of the corresponding diimide-linked diporphyrins.

In the fluorescence spectra of **1**-**4** and **1a**-**4a**, the fluorescence from the ZnP moiety is quenched through the intramolecular singlet-singlet energy transfer to the H_2P and that from the H_2P moiety is quenched through the intramolecular electron transfer to the NIm. On the basis of the fluorescence lifetime of the reference NIm-linked H_2P, we can conclude the quantum yield for formation of ZnP-$(H_2P)^+$-$(NIm)^-$-Q in THF is more than 0.99.3b) The fluorescence from the H_2P in **1**-**4** is more quenched in comparison to that in **1a**-**4a**, indicating that $^1(H_2P)^*$ in **1**-**4** is additionally quenched by the Q.



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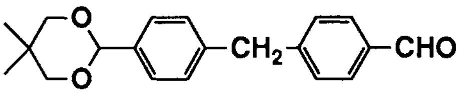
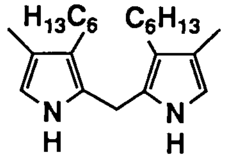


12



13

Formation of long-lived IP states ($(ZnP)^+$-H_2P-NIm-$(Q)^-$ from **1**-**4** and $(ZnP)^+$-H_2P-$(NIm)^-$-QM from **1a**-**4a**) was readily confirmed by the transient absorption spectroscopy. We determined the lifetimes (τ_{CS}) of IP states in **1**-**4** and **1a**-**4a** in THF at room temperature as follows; **1** (16 μs), **2** (12 μs), **3** (1.8 μs), **4** (1.4 μs), **1a** (0.8 μs), **2a** (1.1 μs), **3a** (6.5 μs), and **4a** (6.7 μs). Interesting kinetic features observed are following; (1) in the biphenyl-bridged series τ_{CS} in ZnP-H_2P-NIm-Q are longer than those in ZnP-H_2P-NIm-QM , (2) in the diphenylmethyl-bridged series τ_{CS} in ZnP-H_2P-NIm-Q are shorter than those in ZnP-H_2P-NIm-QM, and (3) in all the cases examined the τ_{CS} of $(ZnP)^+$-H_2P-NIm-$(Q_a)^-$ are slightly longer than those of $(ZnP)^+$-H_2P-NIm-$(Q_b)^-$. Kinetic outcomes by attaching the Q moieties are remarkably contrasting between the two series. One possible explanation may be that IP states in **3** and **4** take, owing to the presence of three flexible methylene linkages, somewhat folded conformations in which the $(ZnP)^+$ and $(Q)^-$ sites come near. Probably, such conformation is not accessible for the tetrads **1** and **2**.9) However, more systematic works involving conformational molecular dynamics as well as temperature effects on the CR process are apparently necessary for a clearer understanding. We have also found that the lifetimes of the IP states increase greatly upon increase of the solvent polarity, and thus in THF-butyronitrile (1:1) mixture the lifetimes of the IP states $(ZnP)^+$-H_2P-NIm-$(Q)^-$ generated from **1** and **2** are longer than 100 μs, and those from **3** and **4** are 13 and 9.6 μs, respectively. These solvent effects are considerably larger than those observed for the related triads.3b,7)

In conclusion, advantage of these conformationally restricted models for generation of long-lived IP states should be emphasized, since the synthesis is rather straightforward and the charged sites formed by photo-induced electron-transfer reactions are well kept at certain long distances, thereby making the IP states long-lived as demonstrated in **1** and **2**.

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4) A. Takahashi, M. Ohkouchi, N. Mataga, T. Okada, A. Osuka, H. Yamada, and K. Maruyama, *J. Am. Chem. Soc.*, in press.
5) The rate of charge shift reaction from $(ZnP)^+$-$(PIm)^-$-Q to $(ZnP)^+$-PIm-$(Q)^-$ has been determined to be 2.5 x 10^9 s^{-1} for 0.07 eV exothermicity, 3.0 x 10^{10} s^{-1} for 0.24 eV, more than 2 x 10^{11} s^{-1} for 0.68 eV, in THF at room temperature (Ref. 5).
6) One-electron reduction potentials of NIm, Q_a, and Q_b were determined by cyclic voltammetry to be -0.99, -0.55, and -0.81 V, respectively, vs. ferrocence/ferrocenium ion in DMF.
7) A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, Y. Nishimura, T. Ohno, and K. Nozaki, *J. Am. Chem. Soc.*, **115**, 4457 (1993).
8) All new compounds described in this paper gave satisfactory spectral data consistent with the assigned structures. The mass spectra were measured by a JEOL HX-100 spectrometer; the positive-FAB ionization method, accelerating voltage 10 kV, *m*-nitrobenzyl alcohol matrix. Observed mass numbers are as follows; **1**, 2286 (M^+ + 3); **2**, 2262 (M^+ +2); **3**, 2301 (M^+ + 4); **4**, 2280 (M^+ + 6); **1a**, 2315 (M^+ +2); **2a**, 2292 (M^+ 2); **3a**, 2331 (M^+ +4); **4a**, 2305 (M^+ +1).
9) The center-to-cneter distances between the ZnP and Q are estimated to be 32 - 36 Å for **1** and **2** and 23 - 32 Å for **3** and **4** on the basis of Corey-Pauling-Koltum models.

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