alternate layers of Au and Cu atoms parallel to a cube face. The symmetry is slightly distorted to tetragonal with $c/a = 0.93$. This structure transforms to orthorhombic with $b/a = 10.03$ at about 380 °C.[30] The particles produced by reduction of stoichiometric mixtures of $AuCl_3$ and $CuCl_2$ at −50 °C have an SAD pattern that corresponds to a simple cubic pattern with each Au atom at the center of a cube of Cu atoms and vice versa.

The method may be used to prepare highly dispersed metals on oxide surfaces as previously done by other methods.[5] To verify this, $AuCl_3$ adsorbed on neutral activated $Al_2O_3$ (155 $m^2/g$) was reduced with $K^+(15\text{-crown-}5)_2K^-$ in $Me_2O$. Au particles (~6-nm average diameter) were randomly dispersed on the surface. One might be able to prepare a large surface area metal oxide catalyst by coreduction of a noble metal and an active metal, followed by oxidation of the latter. It should also be possible to prepare organometallic compounds by reaction of suitable precursors with freshly prepared active metals.[5,8,31]

The objective of this study was to test the generality of homogeneous reductions of soluble metal salts by solvated electrons and/or alkali-metal anions in aprotic solvents. Although many of the metals studied can be prepared as small particles by other methods, the procedure described here has the advantage of being rapid and quantitative and of requiring only low temperatures for all steps. The initial reduction products must consist of very small, reactive particles as binary alloy formation is observed rather than mixtures of metals when two metal salts are simultaneously reduced.

The XRD patterns of the unwashed products and the absence of significant carbon signals in the XPS data of washed samples show that most of the crown ether complexant is not destroyed in the process and could be recovered if desired. This would be important in the utilization of the method because of the relatively high costs of the complexants.

Studies of reductions of other salts, binary mixtures, and mixtures of salts of active and inactive metals are continuing. Also, the factors that determine the distribution of particle sizes and the stabilities of colloidal solutions are being investigated.

**Acknowledgment.** This research was supported by the National Science Foundation Solid State Chemistry Grant No. DMR-87-14751 and by the MSU Center for Fundamental Materials Research. We acknowledge use of instrumentation in the Center for Electron Optics and the Composite Materials and Structure Center at Michigan State University.

---

(31) Kundig, E. P.; Moskovitis, M.; Ozin, G. A. *J. Mol. Struct.* **1972**, *14*, 137-144.

---

# Picosecond Studies of Quinone-Substituted Monometalated Porphyrin Dimers: Evidence for Superexchange-Mediated Electron Transfer in a Photosynthetic Model System

**Juan Rodriguez,[†,∥] Christine Kirmaier,[†] Martin R. Johnson,[‡] Richard A. Friesner,[§] Dewey Holten,*[,†] and Jonathan L. Sessler*[,‡]**

*Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, and Department of Chemistry, Columbia University, New York, New York 10027.*

*Received August 3, 1990*

**Abstract:** Time-resolved studies are reported for a series of quinone-substituted porphyrin monomers and monometalated phenyl-linked dimers. Irradiation of the simple porphyrin monomer systems Ph–Zn–Q, Ph–$H_2$–Q, and $H_2$–Q in toluene at 295 K elicits charge separation to produce the oxidized free-base ($H_2$) or zinc (Zn) porphyrin and the reduced quinone (Q) within the 350-fs excitation flash. (Ph is the phenyl spacer utilized in the porphyrin dimers.) Charge recombination occurs with a time constant of 3–6 ps, returning the system to the electronic ground state but in an excited nuclear configuration that takes ~10 ps to relax. Somewhat more complex behavior is observed for the two regioisomeric monometalated porphyrin dimers $Zn\frown H_2$–Q (gable) and Zn–$H_2$–Q (flat), although complete recovery is again observed within ~15 ps of excitation and ascribed to charge separation/recombination between the quinone and the adjacent $H_2$ subunit. In contrast, very different photodynamic behavior is found for the regioisomeric monometalated dimers $H_2\frown Zn$–Q and $H_2$–Zn–Q, in which the central Zn porphyrin forms a built-in energy barrier between the $H_2$ subunit and the quinone acceptor. In particular, a slow step having a time constant of 55–75 ps is observed at 295 K, in addition to the fast (<15 ps) charge separation/recombination process involving the quinone and adjacent Zn subunit. From the absorption changes accompanying the 55–75-ps process in the $H_2\frown Zn$–Q and $H_2$–Zn–Q systems, and their absence in the other complexes, it is concluded that the slower process involves a quinone-induced deactivation of the lowest $^1(\pi,\pi^*)$ state of the free-base subunit to the ground state. The time constant for this slower process is only weakly dependent on temperature (and solvent), increasing for $H_2\frown Zn$–Q in 2-MTHF from 55 ps at 295 K to 106 ps at 77 K. This observation, coupled with an energetic analysis, indicates that net $H_2^*$ to Q electron transfer does not involve a thermally activated step. Rather, the results suggest that it takes place by a direct Zn porphyrin mediated superexchange mechanism. Additionally, the results suggest that in all complexes charge separation/recombination between the porphyrin and adjacent quinone involve vibrationally excited states.

The three-dimensional structure of the bacterial reaction center has provided an important structural basis for understanding the primary charge separation process in photosynthesis.[1] One of the more intriguing unresolved issues is the role of the bacteriochlorophyll (BChl) monomer in mediating the rapid (~3 ps) electron transfer (ET) from the excited primary electron donor (P*), a dimer of BChls, to a bacteriopheophytin (BPh). Recent subpicosecond transient absorption and other studies have generally

---

[†] Washington University.

[‡] University of Texas.

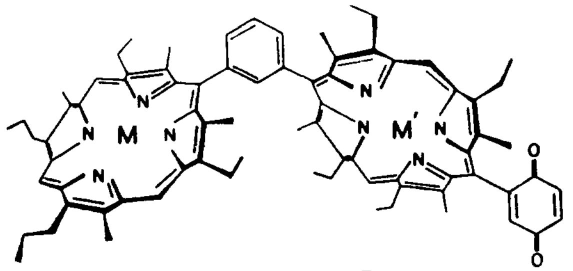
[§] Columbia University.

[∥] Present address: Department of Physics, Centenary College, Shreveport, LA 71134.

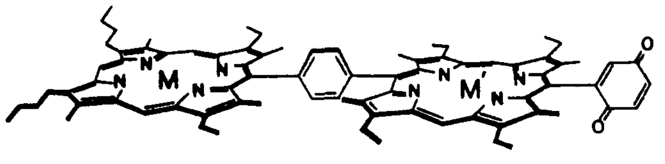
(1) (a) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385-398. (b) Allen, J. P.; Feher, G.; Yeates, T. O.; Rees, D. C.; Deisenhofer, J.; Michel, H.; Huber, R. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 8589-8593. (c) Chang, C. H.; Tiede, D.; Tang, J.; Smith, U.; Norris, J.; Schiffer, M. *FEBS Lett.* **1986**, *205*, 82-86.

0002-7863/91/1513-1652$02.50/0

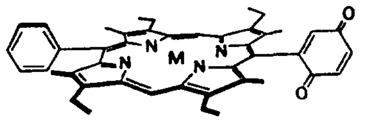
**Chart I**



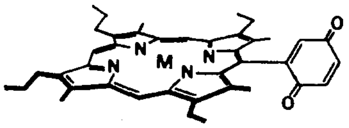
$H_2$^Zn-Q: M = 2H, M' = Zn
Zn^$H_2$-Q: M = Zn, M' = 2H



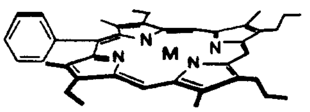
$H_2$-Zn-Q: M = 2H, M' = Zn
Zn-$H_2$-Q: M = Zn, M' = 2H



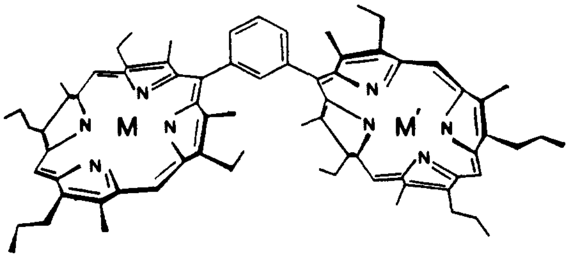
Ph-$H_2$-Q: M = 2H
Ph-Zn-Q: M = Zn



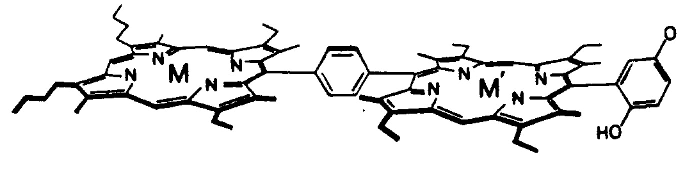
$H_2$-Q: M = 2H
Zn-Q: M = Zn



Ph-$H_2$: M = 2H
Ph-Zn: M = Zn



Zn^$H_2$: M = Zn, M' = 2H
$H_2$^$H_2$: M = M' = 2H
Zn^Zn: M = M' = Zn



Zn-$H_2$-HQ: M = Zn, M' = 2H

failed to find evidence for the formation of $P^+BChl^-$ as a chemical intermediate,[2] although recently it has been suggested that $P^+$-$BChl^-$ forms in ~3 ps and decays in ~1 ps.[3] The ultrafast rate of $P^+BPh^-$ formation, together with the spatial arragnement of the cofactors (BChl is situated somewhat between P and BPh[1]), suggests that the BChl could facilitate ET from P* to BPh via a superexchange mechanism involving quantum mechanical mixing of a $P^+BChl^-$ virtual state with P* and $P^+BPh^-$.[4] Whether the BChl is an intermediate electron carrier or serves in a superexchange role is one of the most controversial issues concerning the primary photochemistry in bacterial photosynthesis.

We report the results of subpicosecond transient absorption studies on a series of porphyrin monomer and dimer systems that have allowed us to explore fundamental aspects of photosynthetic charge separation and ET processes in general.[5-11] The synthesis and characterization[12] and fluorescence emission[13] have been described for this series of complexes, including the selectively

---

(2) (a) Woodbury, N. W.; Becker, M.; Middendorf, D.; Parson, W. W. *Biochemistry* **1985**, *24*, 7516-7521. (b) Breton, J.; Martin, J.-L.; Fleming, G. R.; Lambry, J.-C. *Biochemistry* **1988**, *27*, 8276-8284. (c) Wasielewski, M. R.; Tiede, D. M. *FEBS Lett.* **1986**, *204*, 368-372. (d) Lockhart, D. J.; Goldstein, R. F.; Boxer, S. G. *J. Chem. Phys.* **1988**, *89*, 1408-1415. (e) Kirmaier, C.; Holten, D. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 3552-3556. (f) Lockhart, D. J.; Kirmaier, C.; Holten, D.; Boxer, S. G. *J. Phys. Chem.* **1990**, *94*, 6987-6995. (g) Kirmaier, D.; Holten, D. *Biochemistry* **1991**, *30*, 609-613.

(3) Holzapfel, W.; Finkele, U.; Kaiser, W.; Oesterhelt, D.; Scheer, H.; Stilz, H. U.; Zinth, W. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 5168-5172.

(4) (a) Plato, M. Möbius, K.; Michel-Beyerle, M. E.; Bixon, M.; Jortner, J. *J. Am. Chem. Soc.* **1988**, *110*, 7279-7285. (b) Warshel, A.; Creighton, S.; Parson, W. W. *J. Phys. Chem.* **1988**, *92*, 2692-2701. (c) Won, Y.; Freisner, R. A. *Biochim. Biophys. Acta* **1988**, *977*, 99-122. (d) Scherer, P. O. J.; Fischer, S. F. *Chem. Phys.* **1989**, *131*, 115-127. (e) Marcus, R. A. *Chem. Phys. Lett.* **1988**, *339*, 111-116. (f) Hu, Y.; Mukamel, S. *Chem. Phys. Lett.* **160**, 410-416.

(5) For examples of electron transfer in porphyrin-quinone systems, see the following reviews and refs 6-11. (a) Boxer, S. G. *Biochim. Biophys. Acta* **1983**, *726*, 265-292. (b) Connolly, J. S.; Bolton, J. R. In *Photoinduced Electron Transfers*, Part D; Fox, M. A., Channon, M., Eds.; Elsevier: Amsterdam, 1988; Chapter 6.2; pp 303-393. (c) Gust, D.; Moore, T. A. *Science* **1989**, *244*, 35-41.

(6) (a) Rempel, U.; von Maltzan, B.; von Borczykowski, C. *Chem. Phys. Lett.* **1990**, *169*, 347-354. (b) Gust, D.; Moore, T. A.; Moore, A. L.; Lee, S.-J.; Bittersmann, E.; Luttrull, D. K.; Rehms, A. A.; DeGraziano, J. M.; Ma, X. C.; Gau, F.; Belford, R. E.; Trier, T. T. *Science* **1990**, *248*, 199-201. (c) Osuka, A.; Maruyama, K.; Hirayama, S. *Tetrahedron* **1989**, *45*, 4815-4830. (d) Sakata, Y.; Nakashima, S.; Goto, Y.; Tatemitsu, H.; Misumi, S.; Asahi, T.; Hagihara, M.; Nishikawa, S.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1989**, *111*, 8979-8981. (e) Cormier, R. A.; Posey, M. R.; Bell, W. L.; Fonda, H. N.; Connolly, J. S. *Tetrahedron* **1989**, *45*, 4831-4843. (f) Schmidt, J. A.; Liu, J.-Y.; Bolton, J. R.; Archer, M. D.; Gadzepo, V. P. Y. *J. Chem. Soc., Faraday Trans 1* **1989**, *85*, 1027-1041. (g) Schmidt, J. A.; McIntosh, A. R.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S.; Hurley, J. K.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1988**, *110*, 1733-1740. (h) Harrison, R. J.; Pearce, B.; Beddard, G. S.; Cowan, J. A.; Sanders, J. K. M. *Chem. Phys.* **1987**, *116*, 429-448. (i) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090-6092. (j) Knapp, S.; Murali Dhar, T. G.; Albenze, J.; Gentemann, S.; Potenza, J. A.; Holten, D.; Schugar, H. J. *J. Am. Chem. Soc.*, submitted.

(7) (a) Wasielewski, M. R.; Niemczyk, M. P.; Johnson, D. G.; Svec, W. A.; Minsek, D. W. *Tetrahedron* **1989**, *45*, 4785-4806. (b) Liddell, P. A.; Barrett, D.; Makings, L. R.; Pessiki, P. J.; Gust, D.; Moore, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 5350-5352.

(8) (a) Delaney, J. K.; Mauzerall, D. C.; Lindsey, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 957-963. (b) Wasielewski, M. R.; Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1990**, *112*, 4559-4560. (c) Wasielewski, M. R.; Johnson, D. G.; Svec, W. A.; Kersey, K. M.; Minsek, D. W. *J. Am. Chem. Soc.* **1988**, *110*, 7219-7221. (d) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571-5573.

monometalated, quinone-substituted "gable" and "flat" dimers $H_2\frown Zn$–Q and $H_2$–Zn–Q, in which the central Zn subunit is situated both physically and energetically to serve as a superexchange mediator for ET from the free-base ($H_2$) subunit to the quinone (Q). In addition to unraveling the spectral dynamics associated with charge separation/recombination in this series of molecules, including the involvement of vibrationally excited states, we have obtained clear evidence for porphyrin-mediated superexchange in a photosynthetic model system.

## Experimental Section

All compounds were prepared as described elsewhere[12] and their purity confirmed before and after the time-resolved experiments by UV-vis absorption spectroscopy and/or thin-layer chromatography with no evidence of photodecomposition being obtained. Spectroscopic grade toluene and benzonitrile were utilized. Gold label grade (Aldrich) 2-methyltetrahydrofuran (2-MTHF) was distilled from NaK alloy under argon or nitrogen. Subpicosecond transient absorption studies[14] utilized a 350-fs, ~100-μJ excitation flash at 582 nm and a white-light probe pulse. (A few measurements utilized 150-fs flashes.) Samples in 2 mm pathlength cells were ~10 μM. The 582-nm flashes were focused to 1–2 mm and typically excited ~25% of the sample.

## Results

**Structure and Energetics.** An important feature of the dimeric models studied here (in contrast to many of the earlier photosynthetic models) is that they are conformationally rigid and structurally well-defined. The complexes are constrained to two basic geometries (see Chart I). In the "gable" and "flat" series the two porphyrin subunits are bridged by a 1,3-substituted or a 1,4-substituted phenyl spacer, respectively. In the crystallographically characterized bis(copper porphyrin) bis(trimethoxyphenyl)- and bis(dimethoxyphenyl)-substituted dimers, the bridging 1,4-phenyl moiety is essentially perpendicular to the two nearly coplanar porphyrin rings in the flat dimer, whereas in the gable dimer the dihedral angles are 55.4° and 125.0° (supplement 55.0°), respectively.[12c] The edge-to-edge porphyrin separation is 5.01 and 5.86 Å in the gable and flat dimers, respectively.[12c] In the dimers and the structurally characterized $H_2$–Q monomer, the dihedral angle between the porphyrin and the quinone (or quinone-like) substituent is near the expected 90°. In all complexes, the edge-to-edge distance between the quinone and the adjacent porphyrin is ~1.5 Å. The distant (distal) porphyrin to quinone edge-to-edge distance is estimated to be 12.4 and 14.0 Å in the gable and flat systems, respectively. Supporting NMR data establish that relative subunit rotations are slow at 295 K on the millisecond time scale.[12] Thus, these are rigid conformationally locked systems.

Another key feature of the selectively monometalated compounds $Zn\frown H_2$–Q, $H_2\frown Zn$–Q, Zn–$H_2$–Q, and $H_2$–Zn–Q is that they contain three redox-active components. The lowest $^1(\pi,\pi^*)$ state of the $H_2$ porphyrin lies ~0.17 eV lower than that of the Zn subunit, judging from Q(0,0) absorption/emission band positions.[13] This together with the redox potentials defines two energetic arrangements.[12b] An energy gradient exists in $Zn\frown H_2$–Q (and Zn–$H_2$–Q) for ET from the photoexcited distal Zn porphyrin via the central $H_2$ subunit to the quinone (Figure 1A). In contrast, the central Zn porphyrin in $H_2\frown Zn$–Q (and $H_2$–Zn–Q) defines an energy barrier for ET from the excited distal $H_2$ subunit to the quinone (Figure 1B). Thus, $H_2\frown Zn$–Q and $H_2$–Zn–Q are well-defined models for examining superexchange-mediated ET via a porphyrin bridge, mimicking the apparent energetic arrangement of the P-BChl-BPh cofactors in the reaction center.

**Steady-State Absorption and Emission.** The static absorption and emission spectra of the complexes have been reported.[13] The strong near-UV Soret transitions of the two components of the porphyrin dimers (e.g., $Zn\frown H_2$) are strongly coupled and split. The much less intense Q bands, however, show little evidence for exciton splitting and can be considered weakly coupled, essentially localized, monomer states in the mixed dimers such as $Zn\frown H_2$–Q. This conclusion is in keeping with calculations on these compounds[15] and work on a variety of porphyrin dimers.[16] The spectrum of an excited or charge-separated (i.e., porphyrin cation/quinone anion) state involving a free-base subunit will thus contain bleaching of the $H_2$-like Q bands near 505, 535, 570, and 625 nm. The $^1(\pi,\pi^*)$ state will also contain stimulated (by the white-light probe pulse[14]) emission features at the positions of the Q(0,0) and Q(0,1) spontaneous fluorescence bands near 635 and 700 nm. Similarly, a Zn–porphyrin-based excited or charge-separated state will show bleaching in the Zn-like Q bands at 535 and 570 nm, and the $^1(\pi,\pi^*)$ state by Q(0,0) and Q(0,1) stimulated emission features near 580 and 635 nm.

**Time-Resolved Absorption: Assignment of the Transient States and Kinetic Pathways for Ph–Zn–Q and Ph–$H_2$–Q Monomers.** The 1-ps spectrum of Ph–Zn–Q (Figure 2, solid line) shows bleaching of the Q(1,0) band at 535 nm and a broad but distinct transient absorption band centered at 655 nm, both of which form within the 350-fs excitation flash. The spectrum is not due to the Zn–porphyrin lowest $^1(\pi,\pi^*)$ state: There is no trace of the characteristic Q(0,1) stimulated emission feature, which would appear as a trough near 635 nm having about one-third the amplitude of the Q(1,0) bleaching[14] (or $\Delta A \sim 0.06$) and would have been easily resolved. The ultrafast formation of the spectrum suggests that it is not due to the porphyrin $^3(\pi,\pi^*)$ state. Furthermore, $^3(\pi,\pi^*)$ would give a prominant band near 450 nm at least 3 times the amplitude of the Q(1,0) bleaching and a relatively weak absorption extending from 600 nm to past 900 nm with a small feature between 800 and 850 nm,[14] features that are not observed. The 655-nm band is remarkably similar to the band at this wavelength in the spectrum of the ZnOEP cation radical.[17] The 1-ps spectrum to the blue of 500 nm also compares well with the $ZnOEP^+$ spectrum. Our results demonstrate that ET from the $^1(\pi,\pi^*)$ state of the Zn porphyrin to the quinone, forming the charge-separated state Ph–$Zn^+$–$Q^-$, is complete by 1 ps. (Preliminary studies show that Ph–$Zn^+$–$Q^-$ forms during a 150-fs flash.) The 655-nm band decays exponentially with $\tau = 3.2 \pm 0.3$ ps, which we assign to charge recombination (CR) returning Ph–$Zn^+$–$Q^-$ to the electronic ground state Ph–Zn–Q.

Very similar behavior is found for the free-base monomers Ph–$H_2$–Q (Figure 3) and $H_2$–Q (data not shown).[18] A broad absorption feature centered near 710 nm emerges within the 350-fs flash [no $^1(\pi,\pi^*)$ stimulated emission is observed], which we assign

---

[9] (a) Lindsey, J. S.; Delaney, J. K.; Mauzerall, D. C.; Linschitz, H. *J. Am. Chem. Soc.* **1988**, *110*, 3610–3621. (b) Joran, A. D.; Leland, B. A.; Felker, P. M.; Zewail, A. H.; Hopfield, J. J.; Dervan, P. B. *Nature (London)* **1987**, *327*, 508–511.

[10] (a) Netzel, T. L.; Bergkamp, M. A.; Chang, C.-K.; Dalton, J. *J. Photochem.* **1981**, *17*, 451–460. (b) Bergkamp, M. A.; Dalton, J.; Netzel, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 253–259.

[11] For examples of electron transfer in non-porphyrin-based covalently linked donor–acceptor systems, see the following: (a) Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1990**, *112*, 5353–5354. (b) Johnson, M. D.; Miller, J. R.; Green, N. S.; Closs, G. L. *J. Phys. Chem.* **1989**, *93*, 1173–1176. (c) Lawson, J. M.; Craig, D. C.; Padden-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1989**, *164*, 120–125. (d) Heitele, H.; Michel-Beyerle, M. E. *J. Am. Chem. Soc.* **1985**, *107*, 8286–8288.

[12] The synthesis and spectroscopic and electrochemical properties of our complexes have been reported earlier: (a) Sessler, J. L.; Johnson, M. R. *Angew. Chem.* **1987**, *99*, 679–680; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 678–680. (b) Sessler, J. L.; Johnson, M. R.; Lin, T.-Y.; Creager, S. E. *J. Am. Chem. Soc.* **1988**, *110*, 3659–3661. (c) Sessler, J. L.; Johnson, M. R.; Creager, S. E.; Fettinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9310–9329.

[13] The ambient and 77 K fluorescence properties of the complexes have been reported: Sessler, J. L.; Johnson, M. R.; Lin, T.-Y. *Tetrahedron* **1989**, *45*, 4767–4784.

[14] Rodriguez, J.; Kirmaier, C.; Holten, D. *J. Am. Chem. Soc.* **1989**, *111*, 6500–6506.

[15] Won, Y.; Friesner, R. A.; Johnson, M. R.; Sessler, J. L. *Photosynth. Res.* **1989**, *22*, 201–210.

[16] (a) Gouterman, M.; Holten, D.; Lieberman, E. *Chem. Phys.* **1977**, *25*, 139–153. (b) Hunter, C. A.; Sanders, J. K. M.; Stone, A. J. *Chem. Phys.* **1989**, *133*, 395–404. (c) Nagata, T.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1990**, *112*, 3054–3059. (d) Greiner, S. P.; Winzenburg, J.; von Maltzan, B.; Winscom, C. J.; Möbius, K. *Chem. Phys. Lett.* **1989**, *155*, 93–98. See also ref 6a.

[17] Furhop, J.-H.; Mauzerall, D. *J. Am. Chem. Soc.* **1969**, *91*, 4174–4181.

[18] The porphyrin monomer Zn–Q and the monometalated flat dimer Zn–$H_2$ (structure not shown) were not studied due to their low solubility in toluene.

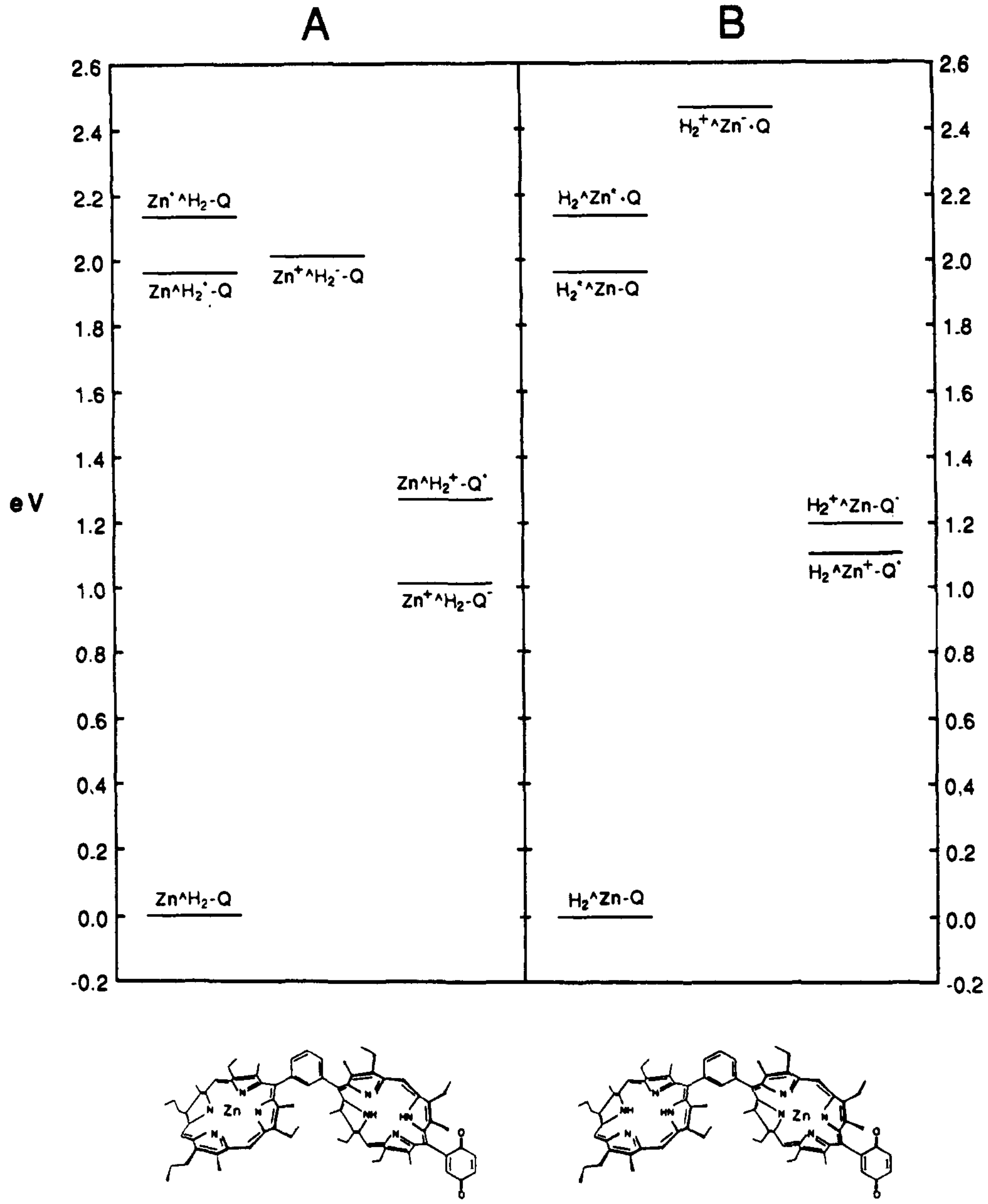


Figure 1. Free energies ($\Delta G$) of the transient states of the isomeric gable systems Zn⌒$H_2$–Q (frame A, left) and $H_2$⌒Zn–Q (frame B, right). Energies of the lowest excited singlet states were taken as the average Q(0,0) absorption and emission peak positions. Energies of the radical-pair states were calculated by using the ground-state redox potentials measured in $CH_2Cl_2$[12b,c] and are uncorrected for solvation and/or Coulombic effects (see ref 8d).

to the $H_2^+$ component in the charge-separated state Ph–$H_2^+$–$Q^-$.[19] CR in Ph–$H_2^+$–$Q^-$, measured via decay of the 710-nm band, is a bit slower ($\tau$ = 5.9 ± 0.5 ps) than in Ph–Zn–Q.

In both Ph–Zn–Q and Ph–$H_2$–Q the 3–6-ps CR process evidently does not yield precisely the same ground state (in terms of its nuclear configuration) that existed prior to excitation, as revealed by the transient spectrum at ~10 ps (Figures 2 and 3, dotted lines). The assignment of this transient is facilitated by observation that the spectrum shows absorption *only* immediately to the red of the residual bleachings (i.e., it has a spectrum similar to that of the original ground state but red shifted). Note that all known porphyrin *electronic excited and ionic states*, except d,d states (which cannot form in our complexes), absorb to the red of the Q-band bleachings and to beyond 800 nm.[14] The transient decays with a time constant of roughly 10 ps and is accompanied by a blue shift of the absorption features to their original ground-state positions (Figure 2, inset).[20] On the basis of these observations and similar findings in other porphyrins,[21] we assign the transient present at 10 ps as a vibrationally or conformationally unrelaxed form of the electronic ground state of the Q-substituted porphyrin monomer.

**Zn⌒$H_2$ and Zn–$H_2$–HQ Dimers.** The ultrafast dynamics of the quinone-free porphyrin dimer Zn⌒$H_2$ in 2-MTHF are illustrated in Figure 4. The bleachings near 500 and 540 nm in the 1-ps spectrum roughly reflect the ground-state spectral intensities and show the presence of complexes in which there is a localized

---

[19] To our knowledge an *authentic* spectrum of $H_2OEP^+$ has not been reported. However, $H_2TPP^+$, like metallo-TPP cations, shows absorption in the 650–750-nm region.[19a] On the basis of these analogies and the similar results found here for the $H_2$ and Zn porphyrin monomers, we assign the 710-nm band found immediately after excitation of the Ph–$H_2$–Q monomer as Ph–$H_2^+$–$Q^-$. (a) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1985**, *24*, 2440–2447.

[20] The combination of the charge recombination process between the reduced quinone and the adjacent oxidized porphyrin ($\tau$ = 3–6 ps) and the ~10-ps vibrational/conformational relaxation in the electronic ground state leads to a wavelength dependence of the apparent time constant in the Soret and Q-band regions. Furthermore, the vibrational relaxation process itself will give rise to a wavelength variation of the apparent time constant measured across the broad transient absorption to the red of the ground-state bleachings, as described elsewhere.[21a]

[21] (a) Rodriguez, J.; Holten, D. *J. Chem. Phys.* **1989**, *91*, 3525–3532. (b) Rodriguez, J.; Holten, D. *J. Chem. Phys.* **1990**, *92*, 5944–5950. (c) Bilsel, O.; Rodriguez, J.; Holten, D. *J. Chem. Phys.* **1990**, *94*, 3508–3512. (d) Rodriguez, J.; Kirmaier, C.; Holten, D. *J. Chem. Phys.*, in press.

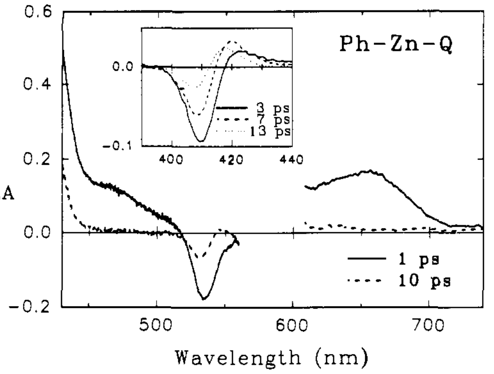


Figure 2. Absorption difference spectra for the Ph–Zn–Q porphyrin monomer in toluene at two key delay times at 295 K. The inset shows spectra in the Soret region for a sample of 30-fold lower concentration. In this and the following figures, the 570–610-nm region is omitted due to 582-nm excitation light. Each spectrum is the average of ~300 spectra acquired in overlapping 150-nm intervals; concatenation of the spectra acquired at closely spaced time delays compensates for dispersion in the pump/probe delay time (which is a few picoseconds between 450 and 550 nm). Each spectrum has a typical standard deviation in $\Delta A$ of 0.005.

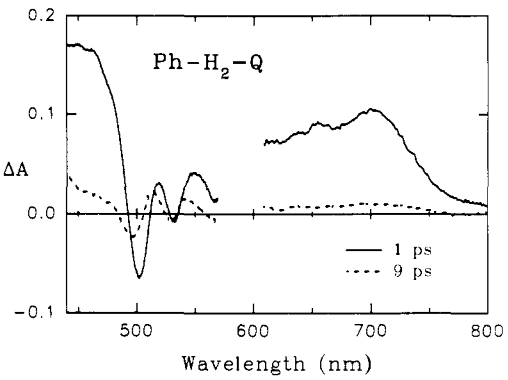


Figure 3. Absorption difference spectra for monomer Ph–$H_2$–Q in toluene at 295 K.

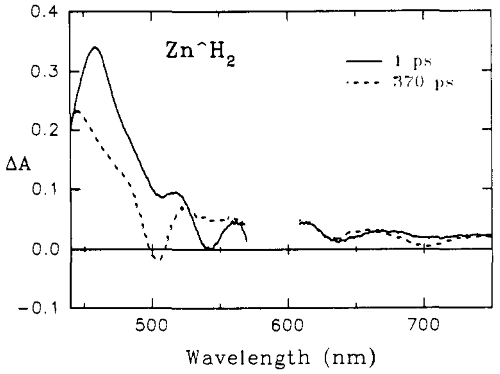


Figure 4. Absorption difference spectra for the $Zn^\frown H_2$ dimer in 2-MTHF at 295 K. The 1-ps spectrum evolves into the spectrum at 370 ps with $\tau$ ~ 15 ps, with no further change to >2 ns.

excitation on either the Zn or $H_2$ subunit. This is not unexpected since the 582-nm pump pulse significantly overlaps both the Zn subunit's Q(0,0) band and the $H_2$ subunit's $Q_X(1,0)$ band.[22] The

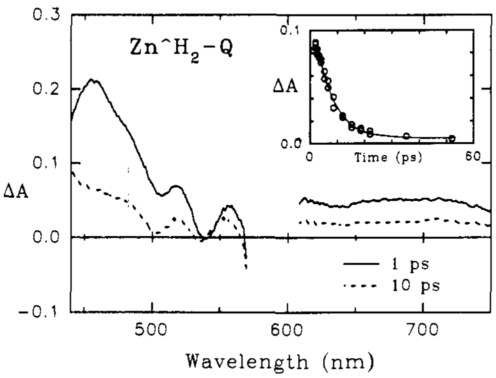


Figure 5. Absorption difference spectra for the $Zn^\frown H_2$–Q gable porphyrin dimer in toluene at 295 K. The inset shows the kinetics at 700–710 nm and a dual-exponential fit giving time constants of 1.7 and 6.1 ps.

bleaching at 535 nm due mainly to the Zn subunit recovers substantially with $\tau$ = 14 ± 1 ps, while the bleaching at 500 nm due mainly to the $H_2$ subunit grows, as does the 710-nm (0,1) stimulated emission from the $H_2$ subunit ($\tau$ = 17 ± 2 ps). During this time the weak (0,1) stimulated emission from the Zn subunit near 650 nm disappears. The resulting spectrum, shown at 370 ps in Figure 4, contains the expected[14] characteristics of the $^1(\pi,\pi^*)$ state of a free-base octaalkylporphyrin: strong absorption in the vicinity of 450 nm, bleaching in the $Q_X(1,0)$ and $Q_X(0,0)$ bands near 500 and 535 nm, and flat absorption to the red of 600 nm broken by the combined (0,0) bleaching/stimulated emission band at 635 nm and the (0,1) stimulated emission band at 710 nm.

The straightforward interpretation of these results is that, in the fraction of the complexes in which the excitation is initially localized at the Zn subunit, energy transfer occurs to the $H_2$ subunit at a rate of ~15 $ps^{-1}$.[23] This supplements the fraction of the dimers in which the $H_2$ porphyrin was originally excited to give a spectrum that, consistent with the ~10-ns lifetime of the $^1(\pi,\pi^*)$ state of the $H_2$ subunit,[13] does not change appreciably on the 3-ns time scale of the experiments. This interpretation is consistent with the finding that the fluorescence emission spectrum of $Zn^\frown H_2$ is essentially the same as that of the free-base monomer.[13] Similar results are found for $Zn^\frown H_2$ in toluene and for Zn–$H_2$–HQ in 2-MTHF (HQ is hydroquinone); in the latter complex, energy transfer from the excited Zn to $H_2$ subunit has $\tau$ = 13 ± 2 ps.

**$Zn^\frown H_2$–Q and Zn–$H_2$–Q Dimers.** Transient absorption data for the quinone-substituted gable dimer $Zn^\frown H_2$–Q are shown in Figure 5. (The flat dimer Zn–$H_2$–Q gives very similar results.) The 1-ps spectrum in the 400–550-nm region is similar to that for $Zn^\frown H_2$ (Figure 4), suggesting that the initial spectrum reflects a mixture of transients resulting from excitation of either the Zn or $H_2$ subunit. Considering our results for $Zn^\frown H_2$ and monomer Ph–$H_2$–Q, it is likely that the initial spectrum for $Zn^\frown H_2$–Q contains both $Zn^{*\frown} H_2$–Q and $Zn^\frown H_2^+$–$Q^-$ (the latter forming from $Zn^\frown H_2^*$–Q during the flash).

The evolution of the transient absorption centered near 700 nm (Figure 5 inset) is not well described by a single exponential (as it is in Ph–$H_2$–Q and Ph–Zn–Q). A dual-exponential fit gives time constants of 1.7 ± 1.3 and 6.1 ± 1.0 ps. The former may reflect decay of $Zn^{*\frown} H_2$–Q via energy/electron transfer, while the latter has the proper time constant for CR in Zn–$H_2^+$–$Q^-$ on the basis of the data on monomer Ph–$H_2$–Q. As in the Q-substituted monomers, the blue region kinetics are further complicated by the <15-ps vibrational/conformational relaxations following

---

[22] Selective excitation also does not occur because the Q bands are built on a broad background that appears to be a tail of the Soret band. Such a tail appears to be present in a variety of porphyrin dimers. (See ref 21b and Yan, X.; Holten, D. *J. Phys. Chem.* **1988**, *92*, 409–414.) Since the Soret involves strongly coupled transitions of the two monomeric subunits, excitation into a tail of the Soret is likely to yield excitations on either the Zn or $H_2$ subunit after internal conversion from the Soret to the Q, or lowest $^1(\pi,\pi^*)$, manifold. In keeping with this, shifting the wavelength of the 350-fs excitation pulse to 620 nm (to the red of the Q(0,0) band of the Zn subunit) still results in bleaching in the Q bands of both subunits.

[23] Similar 10–15-ps lifetime Zn* → $H_2$ porphyrin-based energy-transfer behavior has been observed independently in fluorescence lifetime studies of related covalently linked heterodimers: (a) Chardon-Noblat, S.; Sauvage, J.-P.; Mathis, P. *Angew. Chem.* **1989**, *101*, 631–633; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 593–595. (c) Meier, H.; Kobuke, Y.; Kugimiya, S. *J. Chem. Soc., Chem. Commun.* **1989**, 923–924. (d) Osuka, A.; Maruyama, K.; Yamazaki, I.; Tamai, N. *Chem. Phys. Lett.* **1990**, *165*, 392–396. See also ref 6a.

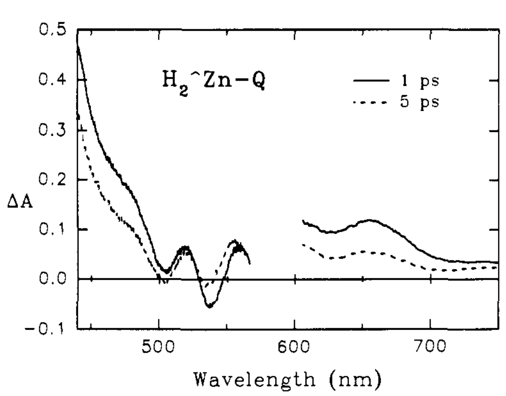


**Figure 6.** Absorption difference spectra for the $H_2\frown Zn$–Q gable porphyrin dimer in toluene at 295 K. The same spectral behavior is found for $H_2$–Zn–Q.

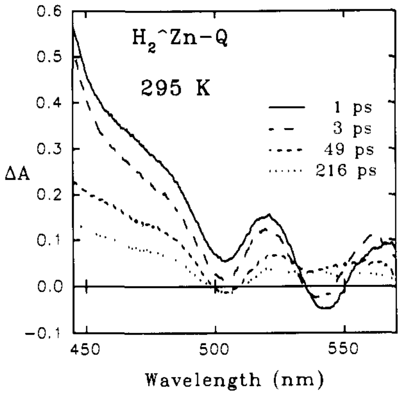


**Figure 7.** Absorption difference spectra for $H_2\frown Zn$–Q in 2-MTHF at 295 K. Spectra at >600 nm are essentially the same as in Figure 6.

CR. Similar behavior is observed for Zn–$H_2$–Q in toluene and for $Zn\frown H_2$–Q in benzonitrile and 2-MTHF.

**$H_2\frown Zn$–Q and $H_2$–Zn–Q Dimers.** These two monometalated dimers have very similar transient behavior to one another. The 1-ps spectrum for the gable complex in Figure 6 can be associated with two transient states: (i) Bleaching of the 500-nm $Q_X(1,0)$ band of the $H_2$ subunit and bleaching in both the $Q_X(0,0)$ and Q(1,0) bands of the $H_2$ and Zn moieties near 535 nm, respectively, indicates the presence of transients derived from excitation of either the Zn or $H_2$ subunit. (ii) A prominant absorption feature centered at 660 nm (similar to the feature observed at 1 ps for Ph–Zn–Q and attributed to Ph–$Zn^+$–$Q^-$; Figure 1) indicates the formation of $H_2\frown Zn^+$–$Q^-$ via subpicosecond ET from Zn* to Q. (iii) $H_2$ subunit (0,0) bleaching/stimulated emission at 635 nm and (0,1) stimulated emission near 710 nm indicated the presence of the $^1(\pi,\pi^*)$ state $H_2{}^*\frown Zn$–Q.

The transient absorption decay at 660 nm is dual exponential with time constants of 3.2 ± 0.4 and 62 ± 3 ps for the gable dimer and 2.8 ± 0.3 and 73 ± 6 ps for the flat dimer in toluene at 295 K. Similar time constants are found in the 450–550-nm region. The fast phase is accompanied by decay of the 660-nm peak to a flat absorption interrupted by troughs near 635 and 710 nm, and by decay of a fraction of the bleaching near 535 nm. Upon comparison with the results for monomer Ph–Zn–Q, the ~3-ps process for $H_2\frown Zn$–Q (or $H_2$–Zn–Q) can be ascribed to CR in $H_2\frown Zn^+$–$Q^-$ (or $H_2$–$Zn^+$–$Q^-$). The spectrum remaining after this fast step (see spectra at 5 ps in Figure 6 and at longer times in Figures 7 and 8) is characteristic of the $^1(\pi,\pi^*)$ state of a free-base porphyrin, namely, $H_2{}^*\frown Zn$–Q (or $H_2{}^*$–Zn–Q). The lifetime of the excited $H_2$ porphyrin thus accounts for the slow (60–75 ps) component.

Similar behavior was found for $H_2\frown Zn$–Q in benzonitrile at 295 K, where the slow process has $\tau$ = 55 ± 11 ps. The temperature dependence of the kinetics for $H_2\frown Zn$–Q was studied in 2-MTHF (Figures 7 and 8); the decay of the 450–460-nm absorption is dual exponential with time constants of 2.2 ± 0.2 and 55 ± 6 ps at 295 K and 4.1 ± 0.7 and 106 ± 23 ps at 77 K.

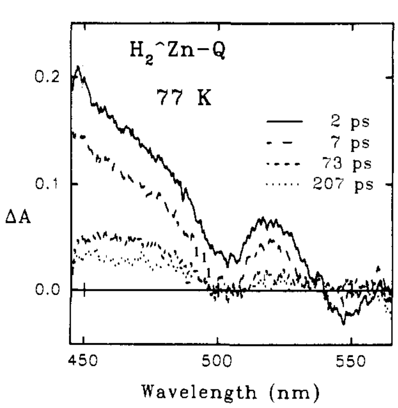


**Figure 8.** Absorption difference spectra for $H_2\frown Zn$–Q in 2-MTHF glass at 77 K.

## Discussion

**Porphyrin Monomer Systems.** The transient absorption spectra observed immediately after excitation of the quinone-substituted monomers Ph–Zn–Q, Ph–$H_2$–Q, and $H_2$–Q do not show the characteristic features of the porphyrin lowest $^1(\pi,\pi^*)$ state. Rather, the features can be assigned to a porphyrin cation radical, namely, a charge-separated state involving the oxidized porphyrin and the reduced quinone. This implies a subpicosecond $^1(\pi,\pi^*)$ lifetime, which corroborates the conclusion drawn from the fluorescence quenching data[13] that ET is very efficient in these systems. The spectral and kinetic behavior of Ph–Zn–Q, Ph–$H_2$–Q, and $H_2$–Q can be ascribed to rapid (<350 fs) exergonic charge separation ($-\Delta G \approx$ 1.0, 0.69, and 0.75 eV for the three compounds, respectively; Figure 1) followed by fast (3–6 ps) exergonic CR ($-\Delta G \approx$ 1.1, 1.3, and 1.2 eV) to regenerate the electronic ground state (eq 1; P = Zn or $H_2$ porphyrin).

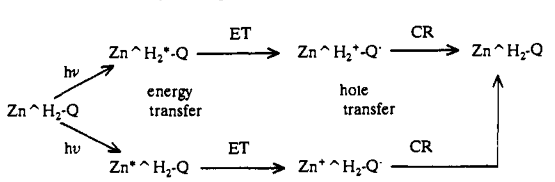
$$\text{P-Q} \xrightarrow{h\nu} \text{P*-Q} \xrightarrow[<350\ \text{fs}]{\text{ET}} \text{P}^{+}\text{-Q}^{-} \xrightarrow[\sim 5\ \text{ps}]{\text{CR}} \text{P-Q} \qquad (1)$$

Our findings are in contrast to those reported previously for a free-base porphyrin directly linked to one or four quinones.[10] In that study, the results were interpreted in terms of ultrafast (<7 ps) formation of the porphyrin $^3(\pi,\pi^*)$ excited state followed by ET to the quinone(s) to give a small yield of a charge-separated state with a long lifetime (>1 ns). We see no evidence for $^3(\pi,\pi^*)$ or long-lived ionic products.

In discussing the absolute rates of ET and CR, it is important to appreciate that the ultrafast (3–6 ps) CR process apparently does not regenerate the same ground state in terms of the overall nuclear configuration that existed prior to excitation. A nonelectronic relaxation is shown by the ~10-ps kinetic phase that is accompanied by the blue shifting and narrowing of the transient absorption immediately to the red of the bleachings in the ground-state Soret and Q bands. Such behavior has been found in a number of porphyrins—the excited and deligated states of Ni(II) complexes and in the ground state of Ce(IV) porphyrin sandwich complexes (in a variety of solvents and at low temperature)—when substantial electronic energy must be dissipated after an ultrafast deactivation process.[21] Vibrational, conformational, and solvent dynamics have been considered for this behavior and it is believed that a unifying process such as vibrational relaxation makes a substantial contribution. The excess vibrational energy must be equilibrated among the internal modes of the porphyrin (probably not a subpicosecond event) and the internal energy must flow into the solvent (apparently requiring on the order of 10 ps).[21] A conformational change (e.g., involving the porphyrin/quinone separation) also will necessarily be followed by vibrational relaxation.

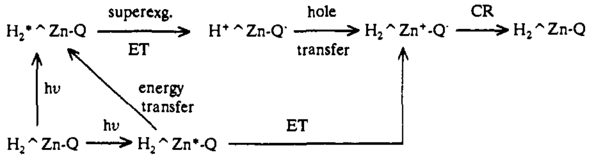
Since the nonelectronic relaxation is observed upon CR in 3–6 ps, it becomes reasonable to question whether the actual CR step, which itself follows a highly exergonic charge-separation process, involves vibrationally equilibrated states of the system. Additionally, since charge separation occurs within the 350-fs flash (and from preliminary studies, within a 150-fs flash), it is questionable whether the initial ET reaction occurs from a vibrationally equilibrated $^1(\pi,\pi^*)$ state.

**Quinone-Substituted Dimers $\mathrm{Zn}\frown\mathrm{H_2}$–Q and Zn–$H_2$–Q.** Excitation of $\mathrm{Zn}\frown\mathrm{H_2}$–Q at 582 nm is expected to produce both $\mathrm{Zn}\frown\mathrm{H_2}^*$–Q and $\mathrm{Zn}^*\frown\mathrm{H_2}$–Q.[22] In the first case, we expect dynamics essentially identical with that observed for the monomer Ph–$H_2$–Q: ultrafast (<1 ps) ET from $H_2^*$ to the quinone (to give $\mathrm{Zn}\frown\mathrm{H_2}^+$–$Q^-$) and subsequent CR in ~5 ps to regenerate the ground state (top pathway in eq 2). More complex behavior is initiated in $\mathrm{Zn}^*\frown\mathrm{H_2}$–Q since Zn* can decay via two routes: (i) energy transfer to the $H_2$ subunit (which in $\mathrm{Zn}\frown\mathrm{H_2}$ requires ~15 ps) or (ii) ET to the quinone (possibly superexchange mediated by $\mathrm{Zn}\frown\mathrm{H_2}^*$–Q or $\mathrm{Zn}^+\frown\mathrm{H_2}^-$–Q). CR in any $\mathrm{Zn}^+\frown\mathrm{H_2}$–$Q^-$ formed could involve $\mathrm{Zn}\frown\mathrm{H_2}^+$–$Q^-$ as an intermediate or via superexchange (lower routes in eq 2). Unfortunately, the complexity introduced by parallel dynamics involving $H_2^*$ does not allow us to distinguish these possibilities. A key point for both $\mathrm{Zn}\frown\mathrm{H_2}$–Q and Zn–$H_2$–Q, however, is that ground-state recovery is complete in <15 ps.



(2)

**Dimers $\mathrm{H_2}\frown\mathrm{Zn}$–Q and $H_2$–Zn–Q.** These dimers reveal a novel process not seen in the $\mathrm{Zn}\frown\mathrm{H_2}$–Q and Zn–$H_2$–Q analogues. Specifically, in the gable complex $\mathrm{H_2}\frown\mathrm{Zn}$–Q excitation in toluene, benzonitrile, or 2-MTHF at 295 K yields, in addition to the <15-ps charge-separation/recombination kinetics found in $\mathrm{Zn}\frown\mathrm{H_2}$–Q (and monomer Ph–$H_2$–Q), a longer lived (55–75 ps) transient state. The transient can be assigned on the basis of characteristic spectral features as the $^1(\pi,\pi^*)$ state of the distal $H_2$ subunit, $\mathrm{H_2}^*\frown\mathrm{Zn}$–Q. Since the quinone-free analogues $\mathrm{H_2}\frown\mathrm{Zn}$, $\mathrm{H_2}\frown\mathrm{H_2}$, and $\mathrm{Zn}\frown\mathrm{Zn}$ have $^1(\pi,\pi^*)$ lifetimes of 8.6, 10, and 1.9 ns, respectively,[13] the 55–75-ps decay of $\mathrm{H_2}^*\frown\mathrm{Zn}$–Q *must necessarily* reflect ET to the quinone mediated by the higher energy intervening Zn porphyrin.



(3)

The excited $H_2$ subunit arises predominantly from direct photoexcitation. Although $\mathrm{H_2}^*\frown\mathrm{Zn}$–Q also could be produced via energy transfer in those complexes in which the Zn subunit is photoexcited, the most likely fate of Zn* is ultrafast (<1 ps) ET to the adjacent quinone followed by CR in ~5 ps; this is expected from our results on the Ph–Zn–Q monomer and accounts well for the <15-ps kinetics observed for $\mathrm{H_2}\frown\mathrm{Zn}$–Q.

We believe that the slower 55–75-ps process involving ET from $H_2^*$ to the quinone is mediated by the intervening Zn porphyrin via a superexchange mechanism, as discussed below. Once formed, the charge-separated state $\mathrm{H_2}^+\frown\mathrm{Zn}$–$Q^-$ evidently returns to the ground state by a nonradiative process at a rate equal to or faster than that associated with charge separation. Although not determined by the data, we consider it likely on the basis of energetics (Figure 1) that this process occurs by fast exergonic hole transfer to give $\mathrm{H_2}\frown\mathrm{Zn}^+$–$Q^-$, followed by rapid (~5 ps) CR. The general scheme in eq 3 also applies to the flat dimer $H_2$–Zn–Q since similar behavior is observed.

The lifetime of the relatively long lived transient assigned as $\mathrm{H_2}^*\frown\mathrm{Zn}$–Q is only weakly dependent on temperature: The time constant increases in 2-MTHF from 55 ps at 295 K to 106 ps at 77 K. This observation is supported by static emission experiments, which show only a small (~3-fold) increase in the fluorescence yield of $\mathrm{H_2}\frown\mathrm{Zn}$–Q in 2-MTHF at 77 vs 295 K.[13] These critical results show that the decay of $\mathrm{H_2}^*\frown\mathrm{Zn}$–Q (or $H_2^*$–Zn–Q) does not involve a thermally activated step such as ET to the Zn subunit ($\mathrm{H_2}^*\frown\mathrm{Zn}$–Q → $\mathrm{H_2}^+\frown\mathrm{Zn}^-$–Q) or energy transfer ($\mathrm{H_2}^*\frown\mathrm{Zn}$–Q → $\mathrm{H_2}\frown\mathrm{Zn}^*$–Q); these processes are endergonic by 0.5 and 0.17 eV (Figure 1) and would be manifested by a decrease in the decay rate of $>10^8$ between 295 and 77 K.

It is important to realize that the nature of the particular stepwise mechanism for an activated process (i.e., energy or electron transfer) is not important. Even "uphill" Förster-type energy transfer is expected (in the absence of tunneling or superexchange) to display a strong temperature dependence, in accordance with the constraints of detailed balance. Indeed, a strong temperature dependence is expected in the Förster theory because of the temperature dependence of the absorption and emission homogeneous line shapes; the overlap of these spectra becomes very small at low temperature if the donor state is lower in energy than the acceptor state, as is observed in the porphyrin dimers under study.[24] The proposed superexchange mechanism could, in fact, be completely temperature independent as long as the temperature dependence of the Franck–Condon factor for ET is small.

The simplest possibility for a temperature-independent Franck–Condon factor for the proposed superexchange-mediated process $\mathrm{H_2}^*\frown\mathrm{Zn}$–Q → $\mathrm{H_2}^+\frown\mathrm{Zn}$–$Q^-$ is if $\Delta G$ and the reorganization energy ($\lambda$) are approximately equal (the activationless condition in semiclassical Marcus theory[25a]). We do not favor this possibility, especially since the observed time constant is insensitive to the dielectric properties of the solvent (62 ps in toluene, 55 ps in benzonitrile, and 55 ps in 2-MTHF at 295 K), requiring that all three solvents contribute about equally to $\Delta G$ and $\lambda$.[26] (Solvent-insensitive rates have been found recently in two other porphyrin–quinone systems.[8a,9]) Rather, the process is likely in the inverted region (especially in nonpolar media),[26] and a more fundamental reason for a relatively temperature independent Franck–Condon factor can be gleaned from nonadiabatic treatments.[25] In particular, temperature-insensitive behavior is expected if there is minimal coupling to low-frequency quantum modes whose thermal population would change significantly over the temperature range of interest (i.e., modes of <100 $cm^{-1}$). That ET is most strongly coupled to medium- and high-frequency modes of the donor and acceptor has been expressed for temperature-independent ET in the reaction center (several processes appearing to lie in the inverted region),[27] in another porphyrin–quinone system,[8a] and for inverted-region ET in a non-porphyrin-based donor–acceptor complex.[11a] Since the early-time behavior of $\mathrm{H_2}\frown\mathrm{Zn}$–Q, which largely reflects CR between $Zn^+$ and $Q^-$ (eq 3) as in the monomers (eq 1), is also relatively insensitive to temperature (2.2 vs 4.1 ps in 2-MTHF at 295 vs 77 K), this

---

(24) Absorption and emission spectra at 77 K have been reported for these compounds[13] and show the expected sharpening of the bands and a decreased overlap between the Zn emission and $H_2$ absorption bands in the mixed $\mathrm{Zn}\frown\mathrm{H_2}$ and Zn–$H_2$ heterodimers.

(25) (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322. (b) Kakitani, T.; Kakitani, H. *Biochim. Biophys. Acta* **1981**, *635*, 498–514. (c) Sarai, A. *Biochim. Biophys. Acta* **1980**, *589*, 71–83. (d) Bixon, M.; Jortner, J. *Chem. Phys. Lett.* **1989**, *159*, 17–20. Warshel, A.; Chu, Z. T.; Parson, W. W. *Science* **1989**, *246*, 112–116. (e) Lin, S. H. *J. Chem. Phys.* **1989**, *90*, 7103–7113.

(26) The free energy for the process is expected to be $-\Delta G \sim 0.75$ eV in $CH_2Cl_2$ based on the redox potentials in this solvent (Figure 1). The internal $\lambda$ for a tetrapyrrole is expected to be small (~0.1 eV), and that for the quinone to be somewhat larger (~0.2 eV),[25b,d,26a,b,27] giving a total internal $\lambda$ of ~0.3 eV. Thus, for the Marcus activationless condition[25a] $-\Delta G \sim \lambda$ to be satisfied the solvent $\lambda$ must be ~0.45 eV. This is not likely in toluene but is possible in the more polar benzonitrile. Note that the solvent $\lambda$ estimated from dielectric continuum theory is not likely to be as large as in smaller systems due to substantial delocalization of charge over the porphyrin (and to a lesser extent the quinone). The solvent insensitivity of the proposed superexchange-mediated process (and for ET in two other porphyrin–quinone systems[8a,9]) may reflect a less steep dependence of the rate on free energy than predicted by semiclassical or single-mode quantum theory, as has been discussed for the reaction center.[2f,27] (a) Warshel, A. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 3105–3109. (b) Kirmaier, C.; Holten, D.; Parson, W. W. *Biochim. Biophys. Acta* **1985**, *810*, 33–48.

(27) (a) Gunner, M. R.; Dutton, P. L. *J. Am. Chem. Soc.* **1989**, *111*, 3400–3412. (b) McDowell, L. M.; Kirmaier, C.; Holten, D. *J. Phys. Chem.*, submitted. See also ref 4c. Kirmaier, C.; Gaul, D.; Debey, R.; Holten, D.; Schenck, C. C. *Science*, in press.

description is likely appropriate for all our systems.

At present, we are not aware of any other reasonable mechanistic alternatives to the proposed superexchange mechanism that can account for the observed decay behavior of $\mathrm{H_2^{*}\frown Zn{-}Q}$ and $\mathrm{H_2^{*}{-}Zn{-}Q}$. Superexchange involving the bridge linking the donor and acceptor has been proposed for a number of systems.[7-11b-d] The observed time constant of 55–110 ps is significantly faster than expected for a 12–14-Å edge-to-edge distance if ET proceeds through the solvent, as discussed on the basis of the fluorescence data.[13] Additionally, in our monometalated dimers, the 55–110-ps time constant is much faster than that observed for ET over about the same distance (and with about the same driving force) from an excited porphyrin to a benzoquinone linked by a bisbicyclooctyl spacer.[6i] This suggests that the mediating Zn–porphyrin subunit provides an excellent superexchange bridge, perhaps due to the conjugated $\pi$-electron system or to the energies of the relevant orbitals. In any case, we have presented here a key, and we believe clear, example, which demonstrates that a porphyrin can serve very effectively as a superexchange mediator in well-defined complexes containing close electronic and structural relatives of the cofactors in the bacterial reaction center.

Aside from the specific question of superexchange, the observation of highly efficient low-temperature charge separation is of interest in its own right. There are only a few other examples of porphyrin-based photosynthetic model systems in which this has been observed.[8] Indeed, there has been considerable discussion as to whether low-temperature charge separation can be effected in model systems without the benefit of unusual structure or energetics (i.e., driving force).[8c] Both the time-resolved results reported here and the supporting low-temperature fluorescence emission studies[13] indicate, in fact, that ET in covalently linked porphyrin–quinone systems can take place efficiently at low temperature (and in nonpolar solvents), as it does in the reaction center.[28] Apparently, one of the factors that is needed is a rigid, temperature-independent structure: If the model system is floppy, then at room temperature ET may occur efficiently only in geometries where the donor and acceptor subunits closely approach. These favorable geometries may not be accessible in a frozen solvent and the ET efficiency would be expected to decrease. To the extent that ET occurs predominantly through the bonds in the bridge separating the donor and acceptor, one would expect to observe efficient low-temperature photoinduced ET in a wide variety of model systems. Our results on structurally rigid and well-defined quinone-substituted porphyrin complexes are consistent with this point of view.

**Acknowledgment.** This work was supported by a grant from the Robert A. Welch Foundation (F-1018 to J.L.S., the Dreyfus Foundation (New Faculty Grant 1984 and Teacher–Scholar Award 1988–1992 to J.L.S.; Teacher–Scholar Award 1987–1991 to R.A.F.), the National Science Foundation (PYI Award 1986 to J.L.S.), and National Institutes of Health Grants (GM 34685 to D.H. and GM 41657 to J.L.S.). R.A.F. also acknowledges receipt of a Research Career Development Award from the NIH, Institute of General Medical Sciences.

---

[28] Temperature-insensitive electron transfer in the bacterial reaction center is discussed in refs 2a,b,e,4c,25,26b, and 27.

---

# Preparation and Reactions of $Mn_2(CO)_9(\eta^1$-aldehyde) Complexes

**R. Morris Bullock* and Brian J. Rappoli**

*Contribution from the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973.*

*Received July 24, 1990*

**Abstract:** The reaction of $HMn(CO)_5$ with $RMn(CO)_5$ ($R = CH_3$, $p$-$CH_3C_6H_4$, or $CH_2CH_2CH{=}C(Ph)CH_3$) gives $Mn_2(CO)_9(\eta^1$-RCHO) complexes. It is suggested that these $Mn_2(CO)_9(\eta^1$-aldehyde) complexes may provide a model for a previously unobserved intermediate in the formation of aldehydes from the hydroformylation of olefins. The $\eta^1$-aldehyde ligand is weakly bound to the manganese, as evidenced by its facile displacement by ligands such as CO, $PPh_3$, and $CH_3CN$. The kinetics of the reaction of $HMn(CO)_5$ with $(CO)_5Mn(CH_2CH_2CH{=}C(Ph)CH_3)$ were studied by $^1H$ NMR at 25 °C in $C_6D_6$. The reaction is first-order in the manganese alkyl complex, and the rate of the reaction decreases slightly with increasing concentration of $HMn(CO)_5$. A negligible isotope effect ($k_H/k_D = 1.04 \pm 0.09$) was found for the reaction of $(CO)_5Mn(CH_2CH_2CH{=}C(Ph)CH_3)$ with $DMn(CO)_5$. The reaction of $Mn_2(CO)_9(\eta^1$-$CH_3CHO)$ with excess $HMn(CO)_5$ takes several days at room temperature and produces ethanol and the manganese cluster complex $Mn_3(CO)_9(\mu_3$-$OEt)_2(\mu_2$-OEt).

Aldehyde and ketone complexes of transition metals have been known for many years, but detailed studies of the formation and reactions of such complexes have only recently been reported.[1] Both aldehydes and ketones can bond to metal centers by either $\eta^1$- or $\eta^2$-bonding modes (Figure 1), and several examples of both of these have been crystallographically characterized.

In a few cases, isolable aldehyde and ketone complexes have been utilized in organic synthesis. Gladysz and co-workers have prepared optically active $\eta^2$-aldehyde complexes of Re and have converted them into optically active alcohols.[2] Hersh and co-workers have structurally characterized a cationic W $\eta^1$-aldehyde complex and have demonstrated that it is an excellent catalyst for the Diels–Alder reaction between dienes and $\alpha,\beta$-unsaturated enones.[3] In other cases, aldehyde complexes are not directly observed but have been postulated as key intermediates in metal-mediated organic syntheses. For example, Faller and co-workers

---

[1] (a) For a review of aldehyde and ketone complexes of transition metals, see: Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298–303. (b) For a review treating both transition-metal and main-group Lewis acid complexes of aldehydes, ketones, etc., see: Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256–272.

[2] (a) Fernández, J. M.; Emerson, K.; Larsen, R. H.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8268–8270. (b) Garner, C. M.; Quirós Méndez, N.; Kowalczyk, J. J.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146–5160.

[3] Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070–6081. (b) Honeychuck, R. V.; Bonnesen, P. V.; Farahi, J.; Hersh, W. H. *J. Org. Chem.* **1987**, *52*, 5293–5296.

0002-7863/91/1513-1659$02.50/0 © 1991 American Chemical Society