Supplementary Material Available: 500-MHz ^1H (including proton–proton decoupled) and 125-MHz ^{13}C NMR spectra of 1 in acetone-d_6, comparison of 500-MHz ^1H NMR spectra of 1 and tolyporphin *O,O*-diacetate in $CDCl_3$, and HMBC spectrum of 1 in acetone-d_6 (10 pages). Ordering information is given on any current masthead page.

Intramolecular Electron Transfer in Rigid Media at Room Temperature

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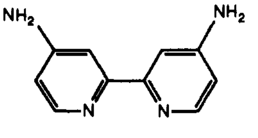
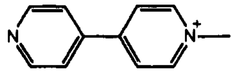
The study of intramolecular photochemical electron transfer in fluid solution is a rapidly expanding area with important implications for fundamental processes, artificial photosynthesis, and molecular-level devices.[1] One limitation is that electron transfer is typically inhibited in rigid media because of restricted reorientation in the surrounding solvent dipoles. Recently, we showed that intramolecular electron transfer could occur in low-temperature glasses if the free energy change were sufficiently favorable.[2] Wasielewski et al. have made related observations based on modified porphyrins,[3] and earlier work by several groups has shown that *intermolecular* electron transfer could occur in rigid matrices.[4] We demonstrate here that the earlier results are more generally applicable to both electron transfer and energy transfer in rigid polymeric media or in the solid state at room temperature.

Solid solutions of metal complexes have been prepared previously as thin films in poly(methyl methacrylate) (PMMA), polystyrene (PS), or poly(vinyl alcohol) (PVA).[5] We have used similar techniques to prepare ~1-mm-thick, free-standing films of PMMA containing ~0.2% of the salts $[Re(bpy)(CO)_3(MQ^+)](PF_6)_2$ (bpy is 2,2′-bipyridine) and $[Re(4,4'\text{-}(NH_2)_2bpy)(CO)_3(MQ^+)](PF_6)_2$. Earlier work based on these complexes[2] showed that at 77 K in frozen glasses $d\pi \rightarrow \pi^*$ (4,4′-$(NH_2)_2$bpy) excitation in the amino derivative was followed by rapid intramolecular electron transfer, eq 1, but that an equivalent process did not occur for the bpy complex. From



(4,4′-(NH₂)₂bpy)



(MQ+)

$$\xrightarrow{h\nu} [(4,4'\text{-}(NH_2)_2bpy^{\bullet-})Re^{II}(CO)_3(MQ^+)]^{2+*} \rightarrow [(4,4'\text{-}(NH_2)_2bpy)Re^{II}(CO)_3(MQ^{\bullet})]^{2+*} \quad (1)$$

electrochemical measurements in CH_3CN at 295 K, the driving forces for intramolecular electron transfer are 1.0 V for the amino derivative and 0.49 V for the bpy complex.

The same difference in behavior is observed in PMMA at room temperature. Emission from samples containing $[Re(bpy)(CO)_3(MQ^+)](PF_6)_2$ is nearly superimposable on that from $[Re(bpy)(CO)_3(4\text{-}Etpy)](PF_6)$(4-Etpy is 4-ethylpyridine) (λ_{max} ~525 nm), but with evidence for a weak component on the low-energy side of the spectrum for the MQ^+ complex. By contrast, emission from $[Re(4,4'\text{-}(NH_2)_2bpy)(CO)_3(MQ^+)](PF_6)_2$ is decreased by >90% compared to that from $[Re(4,4'\text{-}(NH_2)_2bpy)(CO)_3(4\text{-}Etpy)](PF_6)$ and red-shifted from 503 to 578 nm. In transient absorption difference spectra, Figure 1C, a strong absorption feature appears, within the laser pulse (<10 ns), for the amino derivative at 610 nm which arises from a $\pi \rightarrow \pi^*$ transition at $MQ^{\bullet}$.[6] Subsequent decay to the ground state was independent of monitoring wavelength and fit satisfactorily to the Williams–Watts (Kolrausch) function,[7] eq 2, with $k_1 = 8.3 \times 10^5$ s^{-1}, $\beta = 0.53$, and $\langle\tau\rangle = 2.2$ μs.[8] This is an increase of 42× over the 52-ns lifetime for decay found in CH_2ClCH_2Cl at 295 K.

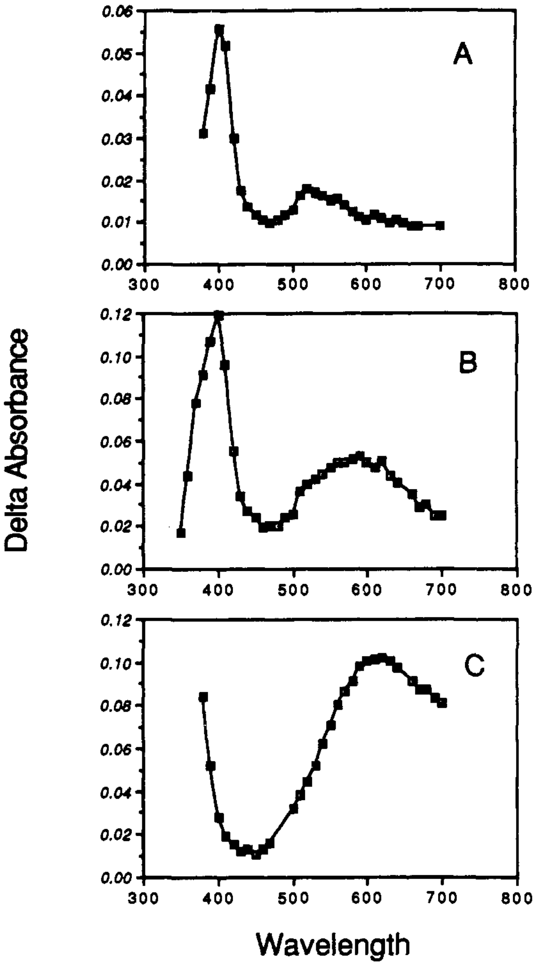


Figure 1. Transient absorption difference spectra for (A) $[Re(bpy)(CO)_3(4\text{-}Etpy)](PF_6)$, (B) $[Re(bpy)(CO)_3(MQ^+)](PF_6)_2$, and (C) $[Re(4,4'\text{-}(NH_2)_2bpy)(CO)_3(MQ^+)](PF_6)_2$ in PMMA acquired 100 ns after 420-nm excitation (<4 mJ/pulse).

$$I(t) = I_0 e^{-(k_1 t)^{\beta}} \quad (2)$$

For $[Re(bpy)(CO)_3(MQ^+)](PF_6)_2$ in PMMA, the characteristic absorption features for the $Re^{II}(bpy^{\bullet-})$ excited state appear at 370 and 540 nm within the laser pulse, along with the feature at 610 nm, the latter being greatly diminished in intensity, Figure 1B.

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(1) (a) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chichester, 1991. (b) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*(5), 163. (c) Fox, M. A., Chanon, M., Eds. *Photoinduced Electron Transfer*; Elsevier: New York, 1988. (d) Wrighton, M. S. *Comments Inorg. Chem.* **1985**, *4*, 269.

(2) Chen, P.; Danielson, E.; Meyer, T. J. *J. Phys. Chem.* **1988**, *92*, 3708.

(3) (a) Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 719. (b) Wasielewski, M. R.; Johson, D. G.; Svec, W. A.; Kersey, K. M.; Minsek, D. W. *J. Am. Chem. Soc.* **1988**, *110*, 7219.

(4) (a) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057. (b) Strauch, S.; McLendon, G.; McGuire, M.; Guarr, T. *J. Phys. Chem.* **1983**, *87*, 3579. (c) Kira, A.; Imamura, M. *J. Phys. Chem.* **1984**, *88*, 1865.

(5) For early examples involving transition-metal complexes, see: (a) Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1275. (b) Hager, G. D.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7031.

(6) (a) Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381. (b) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(7) (a) Williams, G.; Watts, S. B.; North, A. M. *Trans. Faraday Soc.* **1977**, *67*, 1323. (b) Williams, G.; Watts, S. B. *Trans. Faraday Soc.* **1970**, *66*, 80.

(8) If $I(t)$ is considered as arising from a superposition of exponentials, $\langle\tau\rangle = (k_1\beta)^{-1}\,\Gamma(1/\beta)$, where $\Gamma(n)$ is the gamma function and $\langle\tau\rangle$ is the average relaxation time. (Lindsey, C. P.; Patterson, G. D. *J. Chem. Phys.* **1980**, *73*, 3348.)

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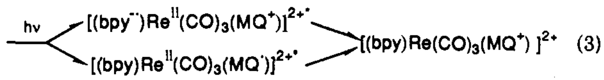
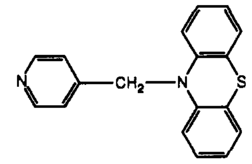
Decay to the ground state was dependent on the monitoring wavelength. It could be fit to eq 2 with $k_1 = 4.1 \times 10^6$ s^{-1}, $\beta = 0.32$, and $\langle\tau\rangle = 1.8$ μs at 610 nm. The small amount of $[Re^{II}(bpy)(CO)_3(MQ^{\bullet})]^{2+*}$ that is formed appears to arise from direct excitation and *not* by intramolecular electron transfer after Re → bpy excitation, eq 3. The appearance of the two states is excitation wavelength dependent, but difficult to deconvolute since the Re → bpy and Re → MQ^+ absorptions are badly overlapped.



$$\xrightarrow{h\nu} \begin{cases} [(bpy^{\bullet-})Re^{II}(CO)_3(MQ^+)]^{2+*} \\ [(bpy)Re^{II}(CO)_3(MQ^{\bullet})]^{2+*} \end{cases} \longrightarrow [(bpy)Re(CO)_3(MQ^+)]^{2+} \quad (3)$$

Qualitatively similar behavior was observed for salts of the complexes in the solid state. The emission maxima for powdered samples appeared at 630 nm for $[Re(4,4'\text{-}(NH_2)_2bpy)(CO)_3(MQ^+)](PF_6)_2$ and at 520 nm for $[(bpy)Re(CO)_3(MQ^+)](PF_6)_2$.

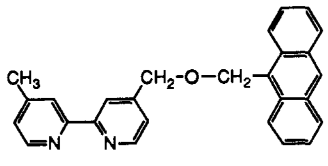
Similar effects were observed for reductive electron transfer in $[Re(4,4'\text{-}(X)_2bpy)(CO)_3(py\text{-}PTZ)](PF_6)$ (X = H or CO_2Et)[9] in PMMA. In $[(bpy)Re(CO)_3(py\text{-}PTZ)](PF_6)$ there was no evidence for quenching of the $Re^{II}(bpy^{\bullet-})$ emission. Emission quenching does occur for X = CO_2Et, and the characteristic $\pi \rightarrow \pi^*$ transition for PTZ^+ at 517 nm[10] appears within the 420-nm laser pulse in transient absorption experiments.[11] These observations are consistent with intramolecular electron transfer for X = CO_2Et, eq 4, but not for X = H. The driving forces for intramolecular electron transfer from PTZ to Re^{II} are 0.59 V (X = CO_2Et) and 0.36 V (X = H) in CH_3CN at 298 K. In transient absorption experiments, decay to the ground state was independent of monitoring wavelength and satisfactorily fit to eq 2 with $k_1 = 2.7 \times 10^6$ s^{-1}, $\beta = 0.73$, and $\langle\tau\rangle = 620$ ns. This compares to $\tau = 25$ ns for the same process in CH_2ClCH_2Cl at 296 K.



(py-PTZ)

$$\xrightarrow{h\nu} [(4,4'\text{-}(CO_2Et)_2bpy^{\bullet-})Re^{II}(CO)_3(py\text{-}PTZ)]^{+*} \rightarrow [(4,4'\text{-}(CO_2Et)_2bpy^{\bullet-})Re^{I}(CO)_3(py\text{-}PTZ^{\bullet+})]^{+} \quad (4)$$

In a PMMA sample containing the salt $[Ru(bpy)_2(bpy\text{-}CH_2\text{-}O\text{-}CH_2\text{-}An)](PF_6)_2$,[12] >80% quenching of the $Ru^{II}(bpy^{\bullet-})$-based emission occurred, accompanied by the appearance of the characteristic $\pi \rightarrow \pi^*$ transition for ^3An at 430 nm in the transient absorption difference spectrum.[13] Energy transfer is favored by 0.3 eV.



(bpy-CH₂-O-CH₂-An)

These results provide a new avenue in the study of electron transfer. They show that, with sufficient driving force, oxidative or reductive intramolecular electron transfer or energy transfer can occur in rigid media at room temperature. When combined with the large optical density changes that occur upon near-UV excitation, these properties may be of value in the design of molecular-level optical devices. For back electron transfer or nonradiative decay to the ground state, there is a decrease in k of as much as 42×. The decrease is due, at least in part, to the frozen dipole orientations in the polymer matrix. This causes an increase in the energy gaps between the redox-separated or excited states and their ground states, and a concomitant decrease in the rate constants for electron transfer or nonradiative decay.[2,3,9,14]

Acknowledgment. Financial support for this work from the NSF under Grants CHE-8806664 and CHE-9022493 is gratefully acknowledged. We also thank G. F. Strouse for supplying the sample of $[Ru(bpy)_2(bpy\text{-}CH_2\text{-}O\text{-}CH_2\text{-}An)](PF_6)_2$.

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(9) (a) Chen, P.; Duesing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 5850. (b) Chen, P.; Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8305.

(10) (a) Biehl, E. R.; Chiou, H.; Keepers, J.; Kennard, S.; Reeves, P. C. *J. Heterocycl. Chem.* **1975**, *12*, 397. (b) Alkaitis, S. A.; Beck, G.; Grätzel, M. *J. Am. Chem. Soc.* **1975**, *97*, 5723.

(11) The PTZ-containing samples gave evidence of sample decomposition after extended photolysis, >100 laser shots at 420 nm (3 mJ/pulse). The decomposition led to permanent color changes and changes in the transient decay characteristics observed after laser flash photolysis.

(12) (a) Boyde, S.; Strouse, G. F.; Jones, W. E., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7448. (b) G. F. Strouse, work in progress.

(13) (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970. (b) Turro, N. J. *Molecular Photochemistry*; W. A. Benjamin: New York, 1967.

(14) (a) Freed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272. (b) Fong, F. K. *Theory of Molecular Relaxation*; Wiley: New York, 1975. (c) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.

Molecular Recognition via Base Pairing: Photoinduced Electron Transfer in Hydrogen-Bonded Zinc Porphyrin–Benzoquinone Conjugates

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Various combinations of porphyrin derivatives and quinones act as key electron-transfer mediators in natural photosynthetic processes,[1] and many covalently-linked porphyrin–quinone compounds have evolved as potential models for the natural apparatus.[2] An alternative approach to photosynthetic modeling, which may be more biomimetic, involves preorganized supramolecular porphyrin–quinone aggregates that are not covalently-linked. Here, we report the construction of a new, noncovalent photosynthetic model that relies on spontaneous cytosine–guanine base-pairing[3] for its preorganization (Figure 1).[4]

Synthesis of the free-base form (**3**) of the zinc(II) porphyrin-guanine compound **1** was communicated previously.[5] The quinone–cytosine molecule **2** was synthesized as illustrated in Scheme I. The known trityl-protected (aminoethyl)cytosine derivative **4**[3d] was converted to its solubilized analogue **5** and coupled reductively with dibenzoylbenzaldehyde to give **6**. Treatment of **6** with KOH/CH_3OH provided the hydroquinone derivative **7**, which, following detritylation and DDQ oxidation, gave **2**. Control molecules **8** and **9** were derived, respectively, from **6** and **7**. Compounds **10** and **11** were prepared as before.[3c] All new com-

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(1) (a) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385. (b) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *Nature* **1985**, *318*, 618. (c) Deisenhofer, J.; Michel, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 829.

(2) Connolly, J. S.; Bolton, J. R. In *Photoinduced Electron Transfer Part D*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; pp 303–393.

(3) (a) Furuta, H.; Magda, D.; Sessler, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 978. (b) Sessler, J. L.; Magda, D.; Hugdahl, J. *J. Inclusion Phenom.* **1989**, *7*, 19. (c) Harriman, A.; Magda, D.; Sessler, J. L. *J. Phys. Chem.* **1991**, *95*, 1530. (d) Harriman, A.; Magda, D. J.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 345.

(4) (a) Tecilla, P.; Dixon, R. P.; Slobodkin, G.; Alavi, D. S.; Waldeck, D. H.; Hamilton, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 9408. (b) Aoyama, Y.; Asakawa, M.; Matsui, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1991**, *113*, 6233.

(5) See refs 3b and 3c. Compound **3** was converted to its zinc(II) complex **1** by treatment with $Zn(OAc)_2 \cdot H_2O$.

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