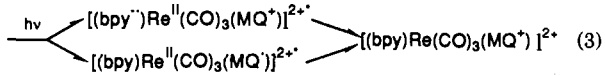
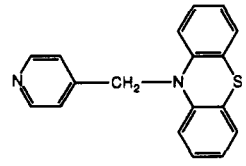
Decay to the ground state was dependent on the monitoring wavelength. It could be fit to eq 2 with $k_1 = 4.1 \times 10^6\ s^{-1}$, $\beta = 0.32$, and $\langle\tau\rangle = 1.8\ \mu s$ at 610 nm. The small amount of $[Re^{II}(bpy)(CO)_3(MQ^{\bullet})]^{2+*}$ that is formed appears to arise from direct 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.



(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



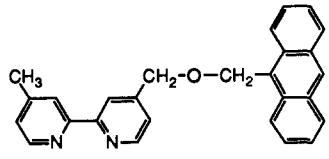
(py-PTZ)

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

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

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.

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-CH_2-O-CH_2-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 $[Ru(bpy)_2(bpy\text{-}CH_2\text{-}O\text{-}CH_2\text{-}An)](PF_6)_2$.

(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

Anthony Harriman,* Yuji Kubo,† and Jonathan L. Sessler*

Department of Chemistry & Biochemistry and Center for Fast Kinetics Research The University of Texas at Austin Austin, Texas 78712

Received August 30, 1991

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-

† Permanent address: Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780, Japan.

(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 $Zn(OAc)_2 \cdot H_2O$.

0002-7863/92/1514-388$03.00/0

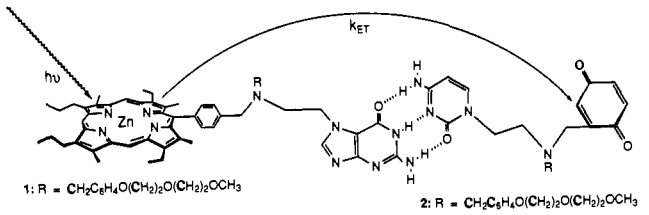
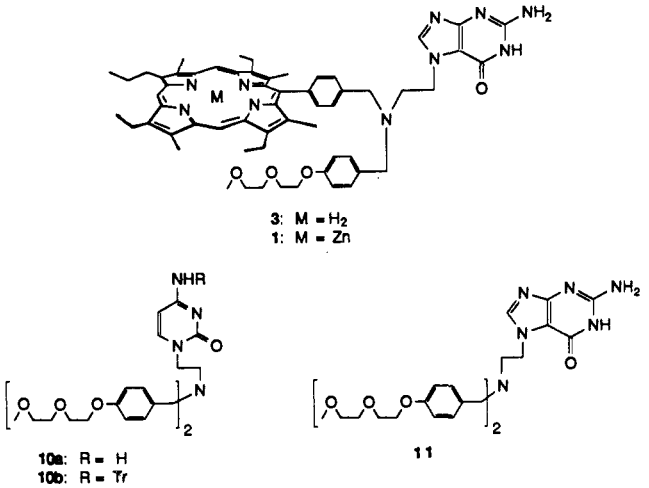


Figure 1. Schematic representation of photoinduced electron transfer across the hydrogen-bonded conjugate formed between **1** and **2** in aprotic solvents. Due to the flexibility of the components, many conformations are possible.

pounds gave satisfactory spectroscopic data (see supplementary material).



Upon mixing in CH_2Cl_2 solution, the above nucleobases may associate by way of complementary three-point hydrogen bonds[6] to produce assemblies in which, from CPK models, the subunits are separated by <20 Å edge-to-edge with many conformations of this or smaller separations being possible (Figure 1). ^{1}H-NMR studies,[7] performed in CD_2Cl_2, gave an association constant (K) of (3100 ± 470) M^{-1} for guanine and cytosine derivatives **10a** and **11** and confirmed that the principal interactive mode involved hydrogen bonding between the bases.[8] There were no (^{1}H-NMR or UV/vis) spectral shifts that could be attributed to π-stacking between porphyrin and/or quinone subunits, even at the highest available concentrations.

In CH_2Cl_2, fluorescence from the porphyrin subunit in **1** was quenched upon addition of high concentrations of **2**. The fluorescence quantum yield decreased with increasing concentration of **2** until a limiting value, corresponding to ≈35% quenching, was reached (Figure 2). Time-resolved fluorescence studies[9] indicated that the decay profiles, initially single exponential with τ_s = (1.5 ± 0.2) ns, became biphasic in the presence of **2**. The derived lifetimes (τ_1 = (1.5 ± 0.2) ns; τ_2 = (0.94 ± 0.07) ns)[10] remained constant, but the relative contribution of τ_2 increased with increasing concentration of **2**. At the highest available concentration (0.012 M) of **2**, τ_1 contributed ca. 5% to the initial emission intensity. Addition of ethanol (2% v/v), which competes for hydrogen-bonding sites, restored the porphyrin fluorescence.

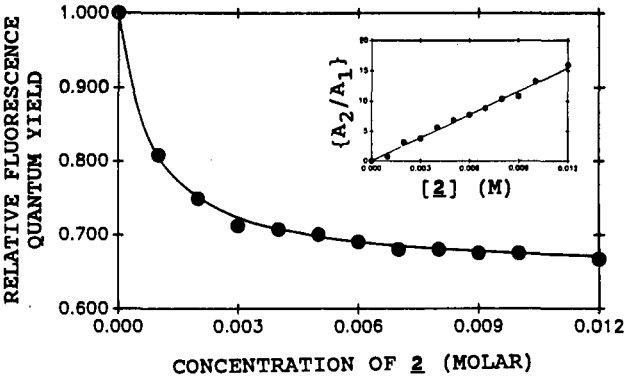
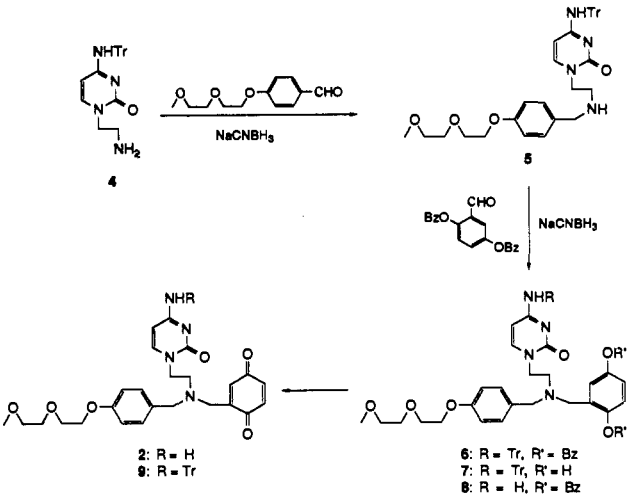


Figure 2. Effect of concentration of **2** on the relative fluorescence yield of **1** ([**1**] = 60 μM). The solid curve drawn through the data points represents a theoretical fit to a linear combination of relative fluorescence yields of free (Φ_f = 1.00) and hydrogen-bonded (Φ_f = 0.65) **1** using an association constant of 1290 M^{-1}. The insert shows a plot of the ratio of the fractional amplitudes of the shorter-lived (A_2) and longer-lived (A_1) components versus the concentration of **2**, as derived from time-correlated single-photon-counting studies (see refs 3c, 3d, and 10).

Scheme I



No fluorescence quenching was observed when **2** was replaced with either **8** or 2-methylbenzo-1,4-quinone (<0.02 M). Furthermore, fluorescence from zinc octaethylporphyrin was not quenched by **2** at concentrations <0.02 M.

These results are consistent with a model in which electron transfer occurs from excited zinc porphyrin to quinone within the confines of a preorganized base-paired array formed from **1** and **2** (Figure 1). The derived rate constant is (4.2 ± 0.7) × 10^8 s^{-1} ($\Delta G° \approx -96$ kJ mol^{-1}),[11] which, from interpolation of the data obtained for related porphyrin–spacer–quinone compounds,[12] corresponds to a through-bond electron transfer across 12 Å, assuming identical attenuation factors and electronic coupling

(6) Williams, L. D.; Chawla, B.; Shaw, B. R. *Biopolymers* **1987**, *26*, 591.
(7) ^{1}H-NMR binding studies were effected[3a] by monitoring chemical shift changes for the guanine imino protons as a function of relative concentration using a least-squares NMR curve-fitting program provided by Professor Eric Anslyn, and we thank Dr. Katsuhiko Ariga for his assistance in performing these analyses.
(8) Katz, L.; Penman, S. *J. Mol. Biol.* **1966**, *15*, 220.
(9) A mode-locked, synchronously-pumped, cavity-dumped Rhodamine 6G dye laser with excitation at 575 nm and single-photon-counting detection (FWHM 70 ps) was used. Solutions containing **1** (60 μM) and **2** (0–12 mM) in aerated CH_2Cl_2 were illuminated in a microcell having an optical path length of 10 μm.
(10) (a) In the presence of **2**, the data could be fit satisfactorily to the sum of two exponentials: $I_f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_1 refers to the unperturbed porphyrin fluorescence lifetime and τ_2 is the lifetime shortened by electron transfer to an adjacent quinone. Reanalyzing the shorter-lived component in terms of a "stretched" or "extended" exponential[10b] and allowing for displacement of the reactants[10c] improved somewhat the quality of the analytical fit but did not change the magnitude of the derived "averaged" rate constant for electron transfer. (b) Marshall, D. B. *Anal. Chem.* **1989**, *61*, 660. (c) Mataga, N. In *Molecular Dynamics in Restricted Geometries*; Klafter, J., Drake, J. M., Eds.; Wiley: New York, 1989; pp 23–37.
(11) The rate constant was derived as $k = [(1/\tau_2) - (1/\tau_1)]$. Redox potentials for one-electron oxidation of zinc octaethylporphyrin ($E°$ = 0.72 V vs SCE) and reduction of 3-methylbenzo-1,4-quinone ($E°$ = −0.40 V vs SCE) were measured by cyclic voltammetry in CH_2Cl_2 solution.
(12) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090.

elements. From time-resolved fluorescence studies,[3c] K was estimated to be (1290 ± 230) M^{-1} for interaction between **1** and **2**. This value is comparable to that obtained with **10a** and **11** and is consistent with the steady-state data (Figure 2). Blocking the cytosine amino group (i.e., using **9** with **1**) reduces K to (410 ± 70) M^{-1} but does not alter the photochemical behavior; the derived rate constant for electron transfer is (3.7 ± 0.8) × 10^8 s^{-1}. Since "blocking" reduces the observed binding constant for cytosine–guanine base-pairing between **10b** and **11** (K = (180 ± 30) M^{-1}), these data are further consistent with the model presented in Figure 1. Thus, the present study introduces a base-paired system capable of effecting specific, but noncovalent, long-range electron-transfer processes.

Acknowledgment. J.L.S. thanks the National Science Foundation (PYI, 1986), the Camille and Henry Dreyfus Foundation (Teacher-Scholar, 1988), the Sloan Foundation (Sloan Fellowship, 1989), the Robert A. Welch Foundation (F-1018), and the National Institutes of Health (GM 41657). A.H. thanks the National Science Foundation (CHE 9102657). The Center for Fast Kinetics Research is supported jointly by the National Institutes of Health (RR00886) and The University of Texas at Austin.

Supplementary Material Available: Synthetic details for the preparation of compounds **1**, **2**, and **4–11** and ^{1}H-NMR experimental data for binding studies with **10** and **11** (8 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Dicyclopenta[*ef*,*kl*]heptalene (Azupyrene) Chemistry. Electrophilic Monosubstitution. Theory and Experiment [*J. Am. Chem. Soc.* **1985**, *107*, 1896–1899]. ARTHUR G. ANDERSON, JR.,* ERNEST R. DAVIDSON, EDWARD D. DAUGS, L. GLENN KAO, RICHARD L. LINDQUIST, and KRISTINE A. QUENEMOEN

Page 1898, right column under the subsection Azupyrene (**1**): The reference of the paper by Jutz was omitted. The reference is the following: Jutz, C. J.; Schweiger, E. *Synthesis* **1974**, 193.

Page 1899, right column, line 13: ^{1}H NMR absorption at δ 9.80 should read (s, 2, H-3, H-5).

*Book Reviews**

Chemical Aspects of Enzyme Biotechnology: Fundamentals. Edited by Thomas O. Baldwin, Frank M. Raushel, and A. Ian Scott (Texas A&M University). Plenum Press: New York and London. 1990. ix + 359 pp. $85.00. ISBN 0-306-43815-1.

This book contains the proceedings of the 8th Industry–University Cooperative Chemistry Program symposium held at Texas A&M University, March 19–22, 1990. It consists of 25 chapters, in typescript form, organized under the following headings: Enzyme Mechanisms; Protein Folding; Design and Redesign of Enzymes and Proteins; New Drugs Based on Enzyme Mechanisms; Organic Synthesis with Enzymes; and Vitamin B12. An appendix contains a list of the 15 posters presented at the meeting. There is a brief subject index.

Structure–Activity and Selectivity Relationships in Heterogeneous Catalysis. Edited by R. K. Grasselli (Mobil Central Research Laboratory) and A. W. Sleight (Oregon State University). Elsevier: Amsterdam, Oxford, New York, Tokyo. 1991. x + 364 pp. $180.00. ISBN 0-444-88942-6.

This book contains the proceedings of the ACS symposium on the title subject held in Boston, MA, April 22–27, 1990. This work represents Volume 67 in the series *Studies in Surface Science and Catalysis*. It consists of a preface and 32 chapters in typescript form organized under the following headings: Oxidation; Hydrogenation; Zeolite Catalysis; and Surface Science and Modeling. There is an author index and a list of the previous volumes in the series.

Cell Separation Science and Technology. ACS Symposium Series 464. Edited by Dhinakar S. Kompala (University of Colorado) and Paul Todd (National Institute of Standards and Technology). American Chemical Society: Washington, DC. 1991. ix + 301 pp. $69.95. ISBN 0-8412-2090-5.

This book was developed from a symposium sponsored by the Divisions of Industrial and Engineering Chemistry, Inc., and Biochemical Technology at the 199th National Meeting of the ACS in Boston, MA, April 22–27, 1990. It consists of 17 chapters organized, after an introductory chapter, under the following headings: Flow Sorting and Optical Methods; Sedimentation and Flow; Affinity Adsorption and Extraction Methods; and Electrophoretic and Magnetic Methods. There are indexes of authors, their affiliations, and subjects.

Enzymes in Carbohydrate Synthesis. ACS Symposium Series 466. Edited by Mark D. Bednarski and Ethan S. Simon (University of California, Berkeley, and Rohm and Haas, respectively). American Chemical Society: Washington, DC. 1991. xi + 131 pp. $34.95. ISBN 0-8412-2097-2.

This book was developed from a symposium sponsored by the Division of Carbohydrate Chemistry at the 199th National Meeting of the ACS at Boston, MA, April 22–27, 1990. It consists of a preface, nine chapters, an appendix classifying the enzymes referred to in the volume, and author, affiliation, and subject indexes.

Polymeric Drugs and Drug Delivery Systems. ACS Symposium Series 469. Edited by Richard L. Dunn (Atrix Laboratories) and Raphael M. Ottenbrite (Virginia Commonwealth University). American Chemical Society: Washington, DC. 1991. xii + 313 pp. $74.95. ISBN 0-8412-2105-7.

This book was developed from a symposium sponsored by the Division of Polymer Chemistry, Inc. at the 200th National Meeting of the ACS in Washington, DC, August 26–31, 1990. It consists of a preface by the editors and 25 chapters organized under the following headings: Drug Delivery Systems; Polymeric Drugs and Drug Conjugates; Polymeric Drug Delivery; and Liposomal Drug Delivery. There are indexes of authors, their affiliations, and subjects.

*Unsigned book reviews are by the Book Review Editor.