Chemical Approaches to Artificial Photosynthesis

THOMAS J. MEYER

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514

Received May 4, 1987 (Revised Manuscript Received November 14, 1988)

In artificial photosynthesis, the goal is to mimic the ability of green plants and other photosynthetic organisms in their use of sunlight to make high-energy chemicals. This is a difficult problem chemically, which accounts for much of the complexity of the natural photosynthetic apparatus.[1] Nonetheless, a number of promising approaches have appeared in recent years based on semiconductors, membranes, vesicles, and molecular systems.[2] In this Account I will describe some of the approaches that my own group has taken to the design of chemical systems for artificial photosynthesis.

An example of a target reaction is shown in Scheme I. In the scheme, molecular-level excitation of a ground state (GS) leads to an excited state (ES). In subsequent steps, the excited-state energy is converted into the stored chemical energy of the photoproducts, here O_2 and formic acid. The net reaction, eq 1, is an oxidation–reduction reaction. It consists of two half-reactions, one involving the reduction of CO_2,
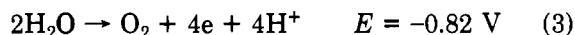
$$2CO_2(g) + 2H_2O(l) \rightarrow 2HCO_2H(aq) + \tfrac{1}{2}O_2(g) \quad (1)$$

$$E^\circ = -1.43 \text{ V } (\Delta G^\circ = +5.72 \text{ eV})$$
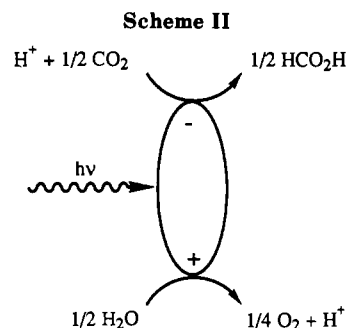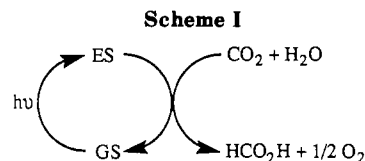
tions, one involving the reduction of CO_2,

$$CO_2 + 2H^+ + 2e \rightarrow HCO_2H \quad E = -0.61 \text{ V} \quad (2)$$

and the other, the oxidation of water. The potentials cited are at pH = 7 vs the NHE reference electrode.

$$2H_2O \rightarrow O_2 + 4e + 4H^+ \quad E = -0.82 \text{ V} \quad (3)$$

What is clear from the half-reactions is that, in order for the net reaction to occur, electrons must be transferred from H_2O to CO_2 in a reaction that is thermo-

Scheme I

Scheme II

dynamically uphill by 1.43 V. The way that this is achieved in photosynthesis is by a series of electron transfers which occur after light is absorbed.[1] A related strategy for an artificial system is adopted in the cartoon in Scheme II. In this strategy, light absorption at the molecular level is followed by excited-state electron transfer. The electron transfers that are induced must lead to spatially separated oxidative and reductive equivalents. They must stay separated long enough for the reductive equivalents to be transferred (as electrons) to a catalyst where CO_2 is reduced. The oxidative equivalents must be transferred to a second catalyst where water is oxidized. The energy requirement for the reaction is 5.72 eV, and the half-reactions involve 4e changes. Since an absorbed photon can only

Thomas J. Meyer is W. R. Kenan Professor and Chairman of the Department of Chemistry at the University of North Carolina. He received his B.S. degree at Ohio University in 1963 and the Ph.D. at Stanford University in 1966 under the direction of Henry Taube. After a NATO postdoctoral year in 1967 with Sir R. S. Nyholm at University College London, he joined the faculty of the Department of Chemistry at The University of North Carolina.
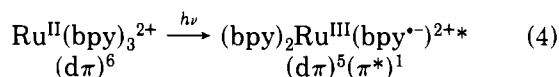
(1) (a) Barber, J. *Photosynthesis in Relation to Model Systems*; Elsevier: New York, 1979. (b) Clayton, R. K. *Photosynthesis: Physical Mechanisms and Chemical Patterns*; Cambridge University Press: London, 1980.

(2) Grätzel, M., Ed. *Energy Resources Through Photochemistry and Catalysis*; Academic Press: New York, 1983.

give a single oxidant–reductant pair, the light absorption–electron transfer apparatus must be utilized four times in order to achieve a single reaction turnover.

Scheme II, or rather the attempt to achieve it, provides an outline for the remainder of this account. I will try to introduce in a systematic way the molecular components and processes that are required and, at the end, to introduce some strategies for combining them in complex molecular assemblies.

Light Absorption. The absorption of light is the energy input step that must trigger the photosynthetic reaction. When light is absorbed at the molecular level, the incident light energy is converted into the transient, stored chemical energy of the excited state. In photosynthesis, the chlorophylls play a major role in the light-harvesting cycle, and synthetic porphyrins have been used extensively in artificial systems.[1,2] Even more popular have been polypyridyl complexes such as [Ru(bpy)$_3$]$^{2+}$ (bpy is 2,2'-bipyridine). In these complexes, the absorption of light comes from metal to ligand charge transfer (MLCT) transitions. An electron is promoted from a metal-based dπ orbital (t$_{2g}$ in O_h symmetry) to a low-lying π^* level on the polypyridyl ligand, e.g., eq 4.[3,4]

$$Ru^{II}(bpy)_3{}^{2+} \xrightarrow{h\nu} (bpy)_2Ru^{III}(bpy^{\bullet-})^{2+*} \quad (4)$$
$$(d\pi)^6 \qquad\qquad (d\pi)^5(\pi^*)^1$$

The MLCT excited states that result have several desirable features: (1) they can be quite stable; (2) there are adjacent oxidized and reduced forms, e.g., [Ru(bpy)$_3$]$^{3+}$ and [Ru(bpy)$_3$]$^+$; (3) their lifetimes can be sufficiently long to exploit with ease in chemical reactions; (4) the underlying ground-state synthetic chemistry is available to make families of related complexes. Examples include [(phen)M(CO)$_4$] (M = Cr, Mo, W; phen is 1,10-phenanthroline), [(bpy)Re(CO)$_3$Cl], [M(bpy)$_3$]$^{2+}$ (M = Fe, Ru, Os), and [M(bpy)$_2$Cl$_2$]$^+$ (M = Rh, Ir).
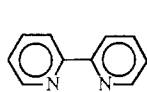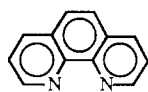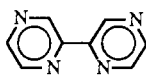
2,2'-bipyridine   1,10-phenanthroline   2,2'-bipyrazine
(bpy)   (phen)   (bpyz)

The energy range in which these complexes absorb light can be extended from the near infrared to the ultraviolet by using changes in the metal or the surrounding ligands to vary the relative energies of the dπ and π^* levels.[3-5]

The actual spectra are quite complex.[6] Bands arising from a series of MLCT transitions appear because low molecular symmetries lift the degeneracy of the dπ

levels, and the polypyridyl ligands have a series of π^* acceptor levels. Further complications arise because each individual MLCT transition has vibronic components, and spin–orbit coupling "mixes" MLCT states that are "singlet" in character, e.g., (^{1}[(dπ)^5(π^*)^1]), with lower lying "triplet" states (^{3}[(dπ)^5(π^*)^1]).[7] The combination of multiple MLCT transitions, vibronic progressions, and solvent broadening allows the (dπ)^6 polypyridyl complexes to absorb light over a wide energy range. In addition, the range in which light can be absorbed can be tuned systematically by adjusting the relative energies of the dπ and π^* levels by making chemical changes.

MLCT Excited States. In order to be useful, an excited state must (1) be reached with high efficiency following light absorption; (2) last long enough to undergo a chemical reaction; (3) be stable so that the system can be recycled. Excitation of [Ru(bpy)$_3$]$^{2+}$ throughout the near UV and visible gives, independent of wavelength, the MLCT excited state. It appears rapidly (<10 ps) and with high efficiency (quantum yield, $\phi \sim 1$).[8] This "state" is actually a combination of three low-energy, closely spaced MLCT states that are in thermal equilibrium. Kinetically, they behave as a single, averaged state near room temperature. It is this averaged MLCT "state" of [Ru(bpy)$_3$]$^{2+}$ and related complexes that provides the basis for the oxidation–reduction chemistry that follows.

The photochemistry of these complexes is somewhat complicated. Higher lying states exist which can provide additional decay channels.[3c,10-12] The most important are low-lying dd states. Typically, they are reached by a thermally activated electron transfer in which the excited electron initially in π^*(bpy) is transferred to a dσ^* orbital (e$_g$ in O_h symmetry), (dπ)^5(π^*)$^1 \rightarrow$ (dπ)^5(dσ^*)^{1}.[11] The dσ^* orbitals are antibonding with regard to the metal–ligand bonds. Once they are populated, dd states tend to be shortlived, and because of their antibonding character, they can lead to the loss of ligands and decomposition of the complex.

Some successful attempts have been made to eliminate dd states by synthetic design. The most straightforward approach has been to turn to the third transition series where, in complexes of Os(II), the splitting between the dπ and dσ^* levels is 30% greater than for Ru(II). With the higher dπ–dσ^* energy gap, the dd states are too high in energy to play a role in determining excited-state properties at room temperature except for unusual cases.[3c] For polypyridyl complexes of Fe(II), the dπ–dσ^* separation is smaller by

(3) (a) Crosby, G. A. *Acc. Chem. Res.* 1975, 8, 231. (b) Ferguson, J.; Herren, F.; Krausz, E. R.; Vrbanich, J. *Coord. Chem. Rev.* 1985, 64, 21. (c) Meyer, T. J. *Pure Appl. Chem.* 1986, 58, 1193.

(4) (a) Balzani, V.; Bolleta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* 1978, 75, 1. (b) Kalyanasundaram, K. *Coord. Chem. Rev.* 1982, 46, 159. (c) Juris, A.; Barigelletti, F.; Campagna, S.; Balzani, V.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* 1988, 84, 85.

(5) (a) Balzani, V.; Juris, A.; Barigelletti, F.; Belser, P.; von Zelewsky, A. *Proc. Riken Int. Symp. Photochem. Metal Complexes*, Sci. Papers Inst. of Phys. and Chem. Res. 1984, 78 and references therein. (b) Cook, M. J.; Lewis, A. P.; Thomson, A. J. *J. Chem. Soc., Perkin Trans. 2* 1984, 1293. (c) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* 1985, 24, 2755.
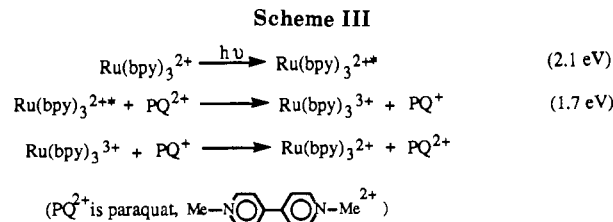
(6) (a) Decurtins, S.; Felix, F.; Ferguson, J.; Gudel, H. U.; Ludi, A. *J. Am. Chem. Soc.* 1980, 102, 4102. (b) Yersin, H.; Gallhuber, E. *J. Am. Chem. Soc.* 1984, 106, 6582. (c) Hensler, G.; Gallhuber, E.; Yersin, H. *Inorg. Chem.* 1987, 26, 1641; *J. Am. Chem. Soc.* 1987, 109, 4814.

(7) (a) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* 1982, 21, 3967; 1983, 22, 1614. (b) Ferguson, J.; Herren, F. *Chem. Phys.* 1983, 76, 45.

(8) (a) Kirk, A. D.; Hoggard, P. E.; Porter, G. B.; Rockley, M. G.; Windsor, M. W. *Chem. Phys. Lett.* 1976, 37, 199. (b) Demas, J. N.; Taylor, D. G. *Inorg. Chem.* 1979, 18, 3177.

(9) (a) Lacky, D. E.; Pankuch, B. J.; Crosby, G. A. *J. Phys. Chem.* 1980, 84, 2068. (b) Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J.; Carrassiti, V.; Traverso, O. *J. Chem. Soc., Faraday Trans. 1* 1979, 75, 353.

(10) Lumpkin, R. S.; Worl, L. A.; Murtaza, Z.; Kober, E. M.; Meyer, T. J. *J. Phys. Chem.*, in press.

(11) (a) Van Houten, J.; Watts, R. J. *Inorg. Chem.* 1978, 17, 3381. (b) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* 1982, 104, 4803. (c) Gleria, M.; Minto, F.; Baggiato, G.; Bartolus, P. *J. Chem. Soc., Chem. Commun.* 1978, 285. (d) Winkler, J. R.; Sutin, N. *Inorg. Chem.* 1987, 26, 220; Creutz, C.; Chou, M.; Netzel, T. L.; Okamura, M.; Sutin, N. *J. Am. Chem. Soc.* 1980, 102, 309.

(12) (a) Barigeletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* 1983, 22, 3335. (b) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* 1984, 106, 2613. (c) Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* 1986, 25, 227.

$\sim 30\%$. The dd states are even lower in energy, and they dominate the photochemistry. Consequently, complexes of Fe(II) have not been of value in energy-conversion applications.[11d] A second strategy, which has been successfully employed, is based on mixed chelates. For example, the low-lying π^* levels of the bpyz ligand in $[Ru(bpy)_2(bpyz)]^{2+}$ introduce a MLCT state that is sufficiently low in energy that the dd states are not accessible at room temperature.[12]

The photochemical and photophysical properties of the MLCT excited states of many complexes have been investigated by temperature dependent emission, lifetime, and quantum yield measurements.[3,4] From studies on the family of complexes $[(bpy)Os^{II}(L)_4]^{2+}$, where only the nonchromophoric ligands, L, are varied, trends emerge in excited-state properties that can be surprisingly systematic.[3c] For example, variations in L (L = $^1/_2$bpy, CH_3CN, PR_3, AsR_3,...) lead to systematic changes in the energy gap between the excited and ground states and a range in emission energies that exceeds 1 eV. The qualitative "energy gap law" for nonradiative decay predicts that ln k_{nr} should decrease linearly with the emission energy, E_{em}.[13] This prediction has been verified experimentally by using changes in the nonchromophoric ligands,[14] the solvent,[15a] the counterion in an ion pair,[15b] or the glass to fluid transition in an ethanol/methanol glass[15c] to vary E_{em}. From resonance Raman and emission spectral fitting studies, the energy released when the excited states undergo nonradiative decay appears (>90%) in seven medium-frequency (1000–1600 cm^{-1}) polypyridyl ring stretching modes. Lesser amounts of energy are dissipated into low-frequency metal to ligand stretching modes and into the solvent.[14,16] Vibrational structure appears in low-temperature emission spectra. Based on a Franck–Condon analysis of the structure, the average bond length changes that occur at the bpy ligand in the excited state have been calculated.[16b] The same parameters derived from the Franck–Condon analysis have been used to calculate relative rate constants for nonradiative decay.[14]

Although individual nuances most certainly exist within the family of Os complexes, the carryover in properties is remarkable. When combined with the underlying synthetic chemistry, a basis exists for the preparation of a series of "designer excited states" where such properties as lifetime and emission energy can be tailor-made to meet the demands of a specific application.

Energy Conversion by Electron-Transfer Quenching. In order for the energy stored in a molecular excited state to be utilized chemically, the excited state must undergo a reaction before it decays to the ground state. The chemistry of the half-reactions

Scheme III

Ru(bpy)$_3^{2+}$ $\xrightarrow{h\nu}$ Ru(bpy)$_3^{2+*}$　　　　(2.1 eV)

Ru(bpy)$_3^{2+*}$ + PQ^{2+} $\longrightarrow$ Ru(bpy)$_3^{3+}$ + PQ$^+$　　(1.7 eV)

Ru(bpy)$_3^{3+}$ + PQ$^+$ $\longrightarrow$ Ru(bpy)$_3^{2+}$ + PQ^{2+}

(PQ^{2+} is paraquat, Me–N◯–◯N–Me^{2+})

in eq 2 and 3 involves net electron transfer. Electron-transfer chemistry also provides a basis for utilizing the energy stored in molecular excited states. For example, MLCT excited states are known to undergo rapid electron-transfer reactions.[17,18] An outer-sphere example is shown in Scheme III, where electron-transfer quenching leads to the oxidant $[Ru(bpy)_3]^{3+}$ ($E°'$(Ru(bpy)$_3)^{3+/2+}$) = 1.3 V vs NHE) and the reductant PQ$^+$ ($E°'$(PQ$^{2+/+}$) = -0.4 V). Similarly, reductive electron transfer quenching,

$$Ru(bpy)_3^{2+*} + Me_2NPh \rightarrow Ru(bpy)_3^+ + Me_2NPh^+$$
(5)
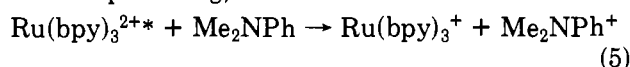
leads to $[Ru(bpy)_3]^+$, which is a powerful reducing agent ($E°'$(Ru(bpy)$_3^{2+/+}$) = -1.3 V vs SCE in CH_3CN).[19]

The sequence of reactions in Scheme III is potentially exploitable in energy conversion processes. In the sequence, the initial energy of the excited state (2.1 eV) is converted into the redox energy of the oxidant/reductant pair, $[Ru(bpy)_3]^{3+}$ + PQ$^+$ (1.7 eV). Such schemes, based on outer-sphere electron transfer, are primitive in a chemical sense. After the oxidant/reductant pair is produced photochemically, their translational motions are uncorrelated and cannot be controlled. They undergo recombination by back electron transfer (k_b in Scheme III) at a rate near the diffusion-controlled limit.

Nonetheless, much has been learned about excitation/electron-transfer sequences involving MLCT excited states that is transferable to the more complex intramolecular systems that will be described below. For example, $[Ru(bpy)_3]^{2+*}$ has been shown to undergo facile, oxidative or reductive electron-transfer quenching with a variety of oxidants or reductants.[4,17] The magnitudes of the quenching rate constants can be understood on the basis of contemporary theories of electron transfer.[4,17,20] Electron transfer is rapid because the differences in structure that exist between $[Ru(bpy)_3]^{2+*}$ and $[Ru(bpy)_3]^{3+}$ or $[Ru(bpy)_3]^+$ are small. This minimizes the barrier to electron transfer that arises from intramolecular structural changes. The barrier to electron transfer arising from the reorientation of solvent dipoles is also small because the com-

(13) (a) Avouris, P.; Gelbart, W. M.; El-Sayed, M. A. *Chem. Rev.*, 1977, 77, 793. (b) Freed, K. F. *Acc. Chem. Res.* 1978, 11, 74. (c) Lin, S. H. *Radiationless Transitions*; Academic Press: New York, 1980.

(14) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* 1986, 90, 3722.

(15) (a) Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Chem. Phys. Lett.* 1982, 91, 91. Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* 1983, 105, 5583. (b) Vining, W. J.; Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* 1985, 89, 1095. (c) Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* 1986, 90, 5307.

(16) (a) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* 1981, 103, 7441. (b) Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. *J. Am. Chem. Soc.* 1984, 106, 3492.

(17) (a) Meyer, T. J. *Acc. Chem. Res.* 1978, 11, 94; *Prog. Inorg. Chem.* 1983, 30, 389. (b) Sutin, N.; Creutz, C. *Pure Appl. Chem.* 1980, 52, 2717. (c) Balzani, V.; Scandola, F. In *Energy Resources Through Photochemistry and Catalysis*; Gratzel, M., Ed.; Academic Press: 1983; Chapter 1. (d) *Supramolecular Photochemistry*; Balzani, V., Ed.; D. Reidel Pub. Co.: Dordrecht, Holland, 1987.

(18) (a) Gafney, H. D.; Adamson, A. W. *J. Am. Chem. Soc.* 1972, 94, 8238. Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* 1973, 95, 5159. (b) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* 1974, 96, 4710. Young, R. C.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* 1975, 97, 4781. (c) Navon, G.; Sutin, N. *Inorg. Chem.* 1974, 13, 2159.

(19) (a) Anderson, C. P.; Salmon, D. J.; Meyer, T. J.; Young, R. C. *J. Am. Chem. Soc.* 1977, 99, 1980. (b) Maestri, M.; Gratzel, M. *Ber. Bunsen-Ges. Phys. Chem.* 1977, 81, 504.
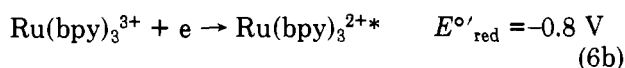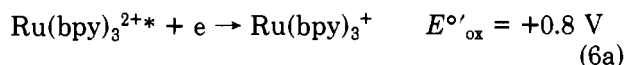
(20) (a) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* 1979, 101, 4815. (b) Rehn, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* 1969, 73, 834; *Isr. J. Chem.* 1970, 8, 259. (c) Kim, H. B.; Kitamura, N.; Kawanishi, Y.; Tazuke, S. *J. Am. Chem. Soc.* 1987, 109, 2500.

Chart I
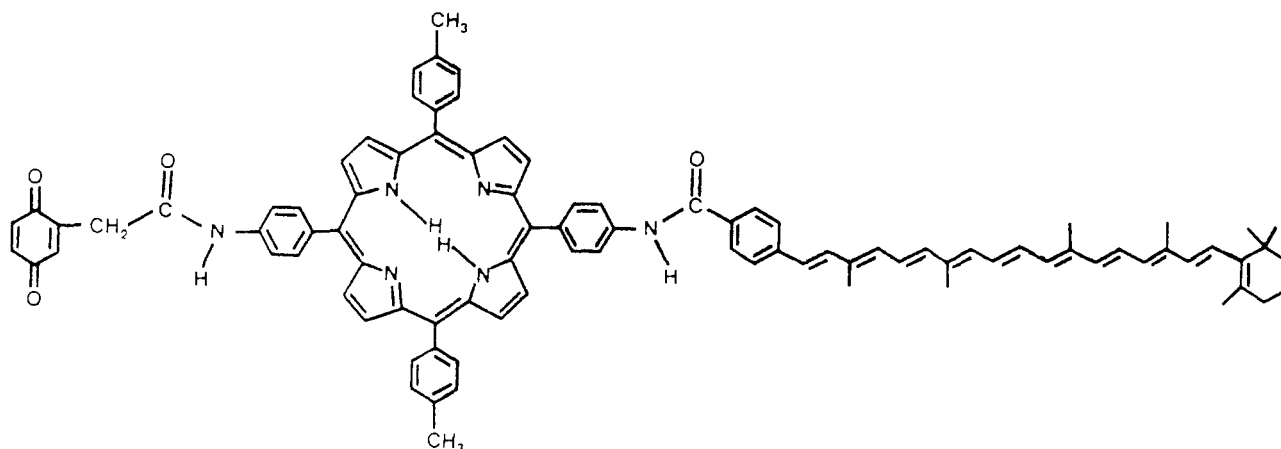
plexes are large. The molecular radius of $[Ru(bpy)_3]^{2+}$ is ~ 7 Å.

In fact, when combined with an appropriate kinetic analysis, quenching rate constants have been used to estimate redox potentials for MLCT excited states acting as oxidants or reductants.[4,20a] For $[Ru(bpy)_3^{2+}]^*$ in water, the potentials (vs NHE) are shown in eq 6.

$$Ru(bpy)_3^{2+*} + e \rightarrow Ru(bpy)_3^+ \qquad E^{\circ\prime}_{ox} = +0.8 \text{ V}$$
$$(6a)$$

$$Ru(bpy)_3^{3+} + e \rightarrow Ru(bpy)_3^{2+*} \qquad E^{\circ\prime}_{red} = -0.8 \text{ V}$$
$$(6b)$$

For the series of complexes $[(bpy)Os^{II}(L)_4]^{2+}$ which were mentioned earlier, it has been shown that the variations made in L lead to a family of excited states where the range in $E^{\circ\prime}_{ox}$ values is more than 1 V.[5c]

Intramolecular Control of Light-Induced Electron Transfer. The Design of Artificial Reaction Centers. Schemes based on bimolecular electron transfer, such as the one shown in Scheme III, can be carried out with high efficiency but at a cost. The cost is that there is no spatial control of the photoproduced oxidant/reductant pair. Recombination by back electron transfer is an uncontrollable event. As implied by the cartoon in Scheme II, a means must be found for directing the oxidative and reductive equivalents in a spatially selective way toward different catalysts. At the molecular level, that requires that a *directional* charge-transfer character be built into the system.

In photosynthesis, the equivalent of the electron transfer quenching scheme in Scheme III occurs, but at the "reaction center". The reaction center is held in a fixed position in the photosynthetic membrane. The underlying molecular structure is formed in such a way that, following optical excitation and electron-transfer quenching, a chemical potential gradient exists toward intramolecular electron transfer. The gradient separates the photochemically produced oxidative and reductive equivalents by electron transfer and directs them to different places in the structure. Once produced, the redox equivalents are directed away from the reaction center by electron transfer hopping along separate electron-transport chains within the membrane. The chains lead to different places in the membrane where catalytic sites exist for the reduction of CO_2 or the oxidation of H_2O.

The photochemically induced separation of oxidative and reductive equivalents has been accomplished in

Chart II
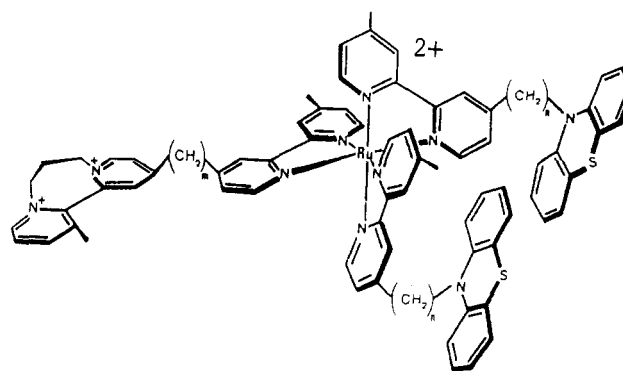
Scheme IV
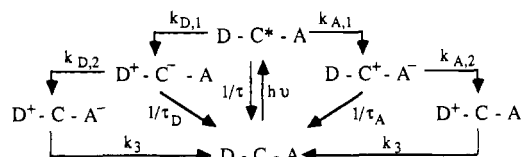
synthetic molecules that contain a light absorber or chromophore (C), and electron-transfer donors (D) and acceptors (A) held in appropriate spatial arrays. Two examples are illustrated, the first (Chart I) based on the $\pi-\pi^*$ chromophore of a porphine derivative,[23] and the second (Chart II) based on a MLCT chromophore.[24] The important feature in either case is the presence of both electron-transfer donors and acceptors which are chemically attached to the chromophore at spatially separated sites. In such molecular arrays, optical excitation, quenching, and subsequent electron transfer (Scheme IV) provide the basis for converting the incident photon energy into transiently stored, spatially separated oxidative (D^+) and reductive (A^-) redox equivalents. The light-induced redox splitting is directional at the molecular level because of the existence of an intramolecular free-energy gradient. The gradient arises from the differences in redox potentials between

(21) *Antenna and Reaction Centers of Photosynthetic Bacteria*; Springer Ser. Chem. Phys. Vol. 42; Michel-Beyerle, M. E., Ed.; Springer-Verlag: New York, 1985.

(22) (a) Diesenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385. (b) Diesenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *Nature* **1985**, *318*, 618.

(23) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J. C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Lidell, P. A.; Lehman, W. R.; Nemeth, G. A.; Moore, A. L. *Nature* **1984**, *307*, 630.

(24) Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519.
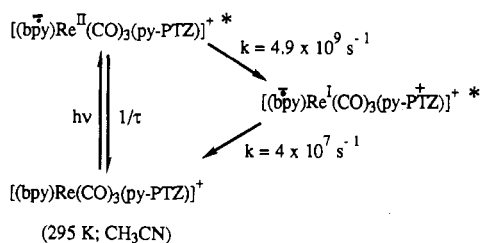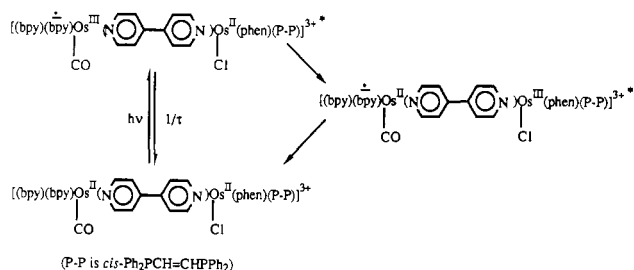
Chart III

$[(b\overline{py})Re^{II}(CO)_3(py\text{-}PTZ)]^{+\,*}$

$k = 4.9 \times 10^9 \text{ s}^{-1}$

$hv \quad 1/\tau$

$[(b\overline{py})Re^{I}(CO)_3(py\text{-}P\overset{+}{T}Z)]^{+\,*}$

$k = 4 \times 10^7 \text{ s}^{-1}$

$[(bpy)Re(CO)_3(py\text{-}PTZ)]^{+}$

(295 K; CH₃CN)

Chart IV

$[(bpy)(\dot{bpy})Os^{III}(N \bigcirc\!\!-\!\!\bigcirc N)Os^{II}(phen)(P\text{-}P)]^{3+\,*}$

$hv \quad 1/\tau$

$[(bpy)(\dot{bpy})Os^{II}(N\bigcirc\!\!-\!\!\bigcirc N)Os^{III}(phen)(P\text{-}P)]^{3+\,*}$

$[(bpy)(\dot{bpy})Os^{II}(N\bigcirc\!\!-\!\!\bigcirc N)Os^{II}(phen)(P\text{-}P)]^{3+}$

(P-P is *cis*-Ph₂PCH=CHPPh₂)

the excited state couples and the quencher couples.

As illustrated in Scheme IV, the redox separated (RS) state, D⁺–C–A⁻, can be reached by two different channels, either by initial oxidative quenching ($k_{A,1}$) or by reductive quenching ($k_{D,1}$) followed by a second intramolecular electron transfer step. Even in the absence of direct electronic coupling between D⁺ and A⁻ and slow back electron transfer by k_3, the lifetime of the RS state is limited by the reversal of the electron-transfer chains and the decay of the excited state in D–C*–A.

Inspired, in part, by attempts to mimic the light harvesting–electron transfer quenching apparatus of the reaction center, a series of interesting chromophore–quencher complexes have been prepared, based on porphyrins and metalloporphyrins.[23,25] Some of the individual steps in Scheme IV and related reactions involving energy transfer have also been demonstrated for MLCT-based chromophore–quencher complexes. Although the synthetic challenges can be formidable, cases are known where either oxidative, e.g., [(bpy)₂-(CO)Os(MQ⁺)]³⁺,[26] or reductive, [(bpy)Re(CO)₃(py-PTZ)]⁺,[27] quenchers have been chemically linked to

$N\bigcirc\!\!-\!\!\bigcirc\overset{+}{N}\!\!-\!CH_3$

(MQ⁺)

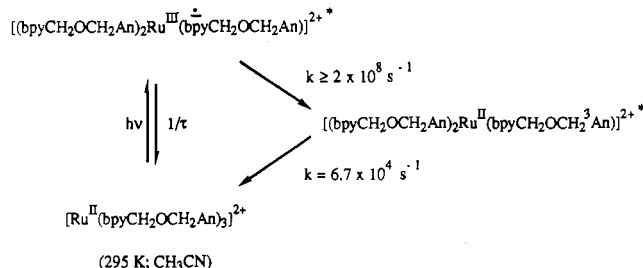$N\bigcirc\!\!-\!CH_2\!\!-\!N$

(py-PTZ)
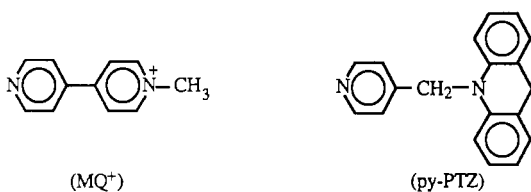
MLCT chromophores. On the basis of transient absorbance and emission changes induced by laser flash photolysis, it has been shown that initial MLCT excitation is followed by rapid intramolecular quenching to give the expected RS states, as transients, e.g., Chart III.[27]

(25) (a) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562. (b) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571. (c) Siemiarczuk, A.; McIntosh, A. R.; Ho, T.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 7224.

(26) Westmoreland, T. D.; LeBozec, H.; Murray, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5952.

(27) (a) Westmoreland, T. D.; Schanze, K. S.; Neveux, P. E., Jr.; Danielson, E.; Sullivan, B. P.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2596. (b) Chen, P. Y.; Westmoreland, T. D.; Schanze, K. S.; Athon, D.; Neveux, P. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1116.

Chart V

$[(bpyCH_2OCH_2An)_2Ru^{III}(b\dot{py}CH_2OCH_2An)]^{2+\,*}$

$k \geq 2 \times 10^8 \text{ s}^{-1}$

$hv \quad 1/\tau$

$[(bpyCH_2OCH_2An)_2Ru^{II}(bpyCH_2OC\overset{3}{H}_2An)]^{2+\,*}$

$k = 6.7 \times 10^4 \text{ s}^{-1}$

$[Ru^{II}(bpyCH_2OCH_2An)_3]^{2+}$

(295 K; CH₃CN)

Ligand-bridged complexes have been prepared in which MLCT excitation is followed by electron transfer across the ligand bridge to give a "remote" MLCT excited state (Chart IV).[28] In the remote excited state, the reducing and oxidizing equivalents are separated by ~13 Å. In the complex [Ru(bpyCH₂OCH₂An)₃]²⁺, visible light absorption at the Ru-bpy chromophore is followed by rapid (<5 ns) intramolecular energy transfer to give the corresponding anthracene triplet (Chart V).
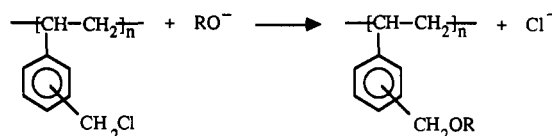
$CH_3\text{-}\bigcirc_N\!\!-\!\!\bigcirc_N\text{-}CH_2\text{-}O\text{-}CH_2\text{-}\bigcirc$

[(bpy-CH₂OCH₂An)]
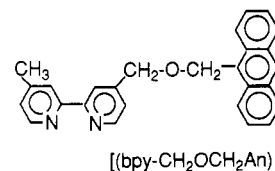
The triplet once formed has an extended lifetime (15 μs) and undergoes oxidative quenching by PQ²⁺.[29] Work of this kind is giving insight into molecular processes and molecular building blocks. When they are properly accounted for and assembled, the basis will exist for controlling the flow of electrons and energy within complex molecules in exquisite detail.

A second approach to achieving photochemically induced redox splitting at the molecular level is to take advantage of the multiple sites on a polymer as a basis for assembling combinations of chromophores and quenchers.[30,31] In our own work we have utilized a soluble 1:1 styrene chloromethylstyrene copolymer.

$\text{-}\!\!+\!CH\text{-}CH_2\text{-}CH\text{-}CH_2\!\!+\!\!_n$

$\bigcirc \qquad \bigcirc\text{-}CH_2Cl$
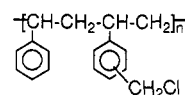
For this polymer a general synthetic strategy is available for adding groups, based on the nucleophilic displacement of chloride with the concomitant formation of ester, amine, pyridinium, or ether links,[32] e.g.,

$\text{-}\!\!+\!CH\text{-}CH_2\!\!+\!\!_n + RO^- \longrightarrow \text{-}\!\!+\!CH\text{-}CH_2\!\!+\!\!_n + Cl^-$

$\bigcirc\text{-}CH_2Cl \qquad\qquad \bigcirc\text{-}CH_2OR$

We have been able to prepare metal complex containing

(28) (a) Schanze, K. S.; Neyhart, G. A.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 2182. (b) Curtis, J. C.; Bernstein, J. S.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 385.

(29) Boyde, S.; Jones, W.; Meyer, T. J., submitted.

(30) (a) Webber, S. E. In *New Trends in the Photochemistry of Polymers*; Allen, N. S., Rabek, J. E., Eds.; Elsevier: New York, 1985; Chapter 1. (b) Phillips, D. In *Polymer Photophysics*; Phillips, D., Ed.; Chapman and Hall: New York, 1985; Chapter 1. (c) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: New York, Chapter 9.

(31) (a) Sassoon, R. E.; Rabani, J. *J. Phys. Chem.* **1985**, *89*, 5500. (b) Matsuo, T.; Sakamoto, T.; Takuna, K.; Sakura, K.; Ohsako, T. *J. Phys. Chem.* **1981**, *85*, 1277.

(32) (a) Margerum, L. D.; Meyer, T. J.; Murray, R. W. *J. Phys. Chem.* **1986**, *90*, 2696. (b) McClanahan, S.; Younathan, J.; Meyer, T. J. *Macromolecules*, in press.

Scheme V
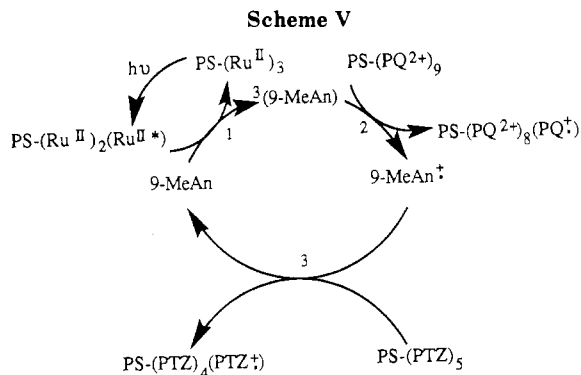
polymers by using as bases [(bpy)$_2$Ru(4,4'-(CO$_2^-$)$_2$-bpy)], [(bpy)$_2$Ru(4-Me-4'-(CH$_2$O$^-$)-bpy)]$^+$, or their Os equivalents. Similarly, MQ$^+$, PTZ$^-$, or AnCH$_2$O$^-$ as bases

[4,4'-(CO$_2^-$)bpy]   [4-Me-4'-(CH$_2$O$^-$)bpy]
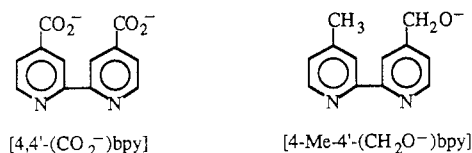
have led to the attachment of the oxidative or reductive quenchers PQ^{2+} or PTZ or of anthryl derivatives which can act as energy-transfer quenchers and carriers.

(AnCH$_2$O$^-$; R = H, Me, Ph)   (PTZ$^-$)
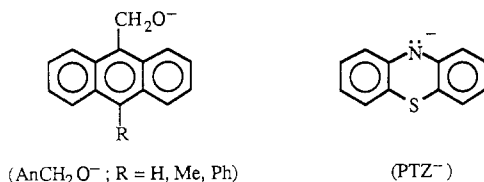
In one application, flash photolysis of a solution containing a Ru-bpy chromophore, PQ^{2+}, and PTZ all on separate polymeric strands led to no excited-state quenching. Quenching is inhibited because diffusion of the quencher containing macromolecules is relatively slow. However, the addition of unbound 9-methylanthracene (9-MeAn) to the same solution leads to the series of rapid bimolecular reactions shown in Scheme V. In Scheme V the compositions of the individual polymers are shown as the number of sites occupied by PQ^{2+}, PTZ, or the Ru-bpy chromophore, Ru^{II}, per 30 chloromethylstyryl sites available on the polymer. The first reaction in Scheme V is energy-transfer quenching of the polymer-bound Ru-bpy excited state by 9-MeAN. This is followed by two sequential electron-transfer steps. The first involves oxidative quenching of ^{3}An, and the second, reduction of An$^+$ by PTZ.[33]

When the three-stage 9-MeAn shuttle is finished, ~1.3 eV of the initial MLCT excited state energy has been converted into the oxidizing and reducing equivalents of PQ$^+$ and PTZ$^+$ on separated polymeric strands. The net reaction is shown in eq 7.

$$\text{PS-(PQ}^{2+})_9 + \text{PS-(PTZ)}_5 \xrightarrow{h\nu}$$
$$\text{PS-(PQ}^{2+})_8(\text{PQ}^+) + \text{PS-(PTZ)}_4(\text{PTZ}^+) \quad (7)$$
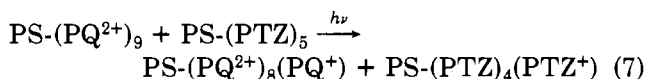
As a bonus, compared to simple molecular quenchers in solution, recombination by back electron transfer is slowed considerably because of slow diffusion of the macromolecules.[31a,32a,34]
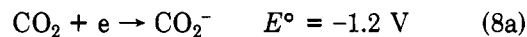
(33) Olmsted, J.; McClanahan, S.; Danielson, E.; Younathan, J.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3297.

(34) Younathan, J.; Danielson, E.; Strouse, G.; Worl, L. A., manuscript in preparation.

In a second application, a mixed-function polymer containing light loadings of [M(bpy)$_2$(4-Me-4'-(CH$_2$O$^-$)bpy)]$^{2+}$ (M = Ru, Os) (three out of 30 sites) and a high loading of an anthryl derivative (15 out of 30 sites) has been prepared. In the polymer, the ordering of excited-state energies is MLCT(Ru) > ^{3}An > MLCT(Os). We have been able to show that, following MLCT excitation at Ru(II), rapid, efficient long-range energy transfer occurs to Os(II) by an intramolecular energy transfer shuttle.[34]
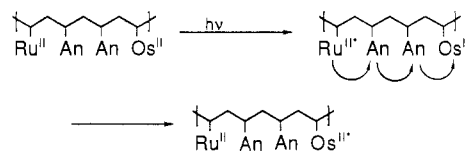

Catalysis. Reactions such as the oxidation of water to dioxygen or the reduction of CO$_2$ to HCO$_2$H are simple in terms of the numbers of atoms involved. However, they are difficult to carry out at reasonable rates near the thermodynamic potentials of the two couples. The problem is mechanistic. One-electron couples involving H$_2$O or CO$_2$ are highly unfavorable thermodynamically because they involve the formation of high-energy intermediates such as OH or CO$_2^-$, reaction 8 at pH = 7 vs NHE. These intermediates are

$$\text{CO}_2 + \text{e} \rightarrow \text{CO}_2^- \qquad E^\circ = -1.2 \text{ V} \qquad (8a)$$

$$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH} + \text{e} \qquad E^\circ = -2.4 \text{ V} \qquad (8b)$$

unacceptable because they demand reductants that are too reducing or oxidants that are too oxidizing. For example, the *minimum* energy needed to drive the reaction CO$_2$ + H$_2$O $\rightarrow$ CO$_2^-$ + H$^+$ + OH is 3.6 eV or 340 nm, which is beyond the visible region of the spectrum.

In order to solve the reactivity problem, redox reagents must be designed that carry out the oxidation of water or the reduction of CO$_2$, but in synchronous, *multielectron* steps near the thermodynamic potentials of the CO$_2$/HCO$_2$H or O$_2$/H$_2$O couples. The multielectron chemistry should be triggered following a series of simple electron transfers, and it should be possible to use these reagents many times so that they can be used as catalysts.

It is possible to design such reagents. In the oxidation of water to dioxygen, four electrons and four protons must be lost from two water molecules with the formation of the O–O bond of O$_2$. In the μ-oxo complex, [(bpy)$_2$(H$_2$O)Ru^{III}ORu^{III}(H$_2$O)(bpy)$_2$]$^{4+}$, the two water molecules are held in relatively close proximity across an oxo bridge. Upon chemical or electrochemical oxidation, the complex becomes more acidic and a proton is lost at pH > 4 to give [(bpy)$_2$(OH)Ru^{IV}ORu^{III}-(H$_2$O)(bpy)$_2$]$^{4+}$. Further oxidation and proton loss leads to the four electron oxidized complex [(bpy)$_2$(O)Ru^{V}O-Ru^V(O)(bpy)$_2$]$^{4+}$. This complex does oxidize water to dioxygen and, far more rapidly, Cl$^-$ to Cl$_2$/HOCl. The catalytic cycle for water oxidation is shown below.[35]
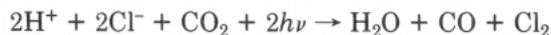
Scheme VI
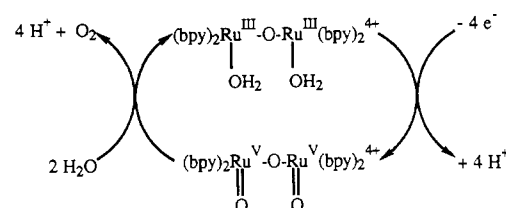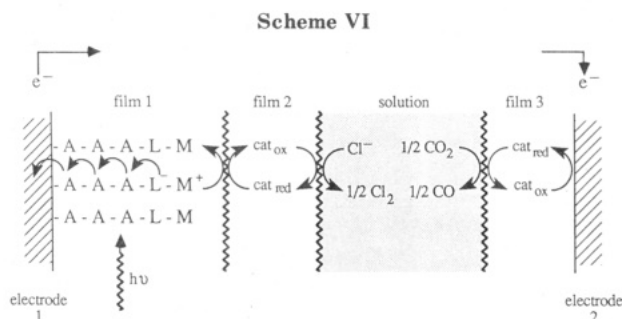
A number of transition-metal complexes have also been identified which are electrocatalysts for the reduction of CO_2.[36]   For example, electrochemical reduction of $[(bpy)Re(CO)_3Cl]$ leads first to $[(bpy)Re(CO)_3]$ after loss of Cl^- and, at more negative potentials, to $[(bpy)Re(CO)_3]^-$. Both reduce CO_2 to CO but by different pathways.[36b,c]

Assembly. Polymeric Films on Electrodes. The photochemical properties of the complex molecules and polymers described here show that there are legitimate approaches to achieving light induced redox separation at the molecular level. In either case, the underlying synthetic chemistry is available, at least in principle, to prepare more complex systems in which chemically attached oxidative or reductive catalysts are added to the chromophore–quencher/electron-transport apparatus. Perhaps in a single giant molecule or on separate polymeric strands with electron- or energy-transfer connections, such assemblies would contain the ingredients required for artificial photosynthesis. If so, they will appear at the cost of some very challenging synthetic chemistry.

Natural photosynthesis uses membranes, and there are other, more general approaches to assembling the required components based on membranes and molecular films. Some very interesting results have been obtained in artificial systems where chromophore–quencher assemblies have been incorporated into membranes, micelles, or vesicles.[1,37,38]

Another approach is to assemble the required structures in thin polymeric films on conducting electrodes in order to exploit some of the advantages offered by electrochemical devices. An example is shown in Scheme VI, where the net reaction,

$$2H^+ + 2Cl^- + CO_2 + 2h\nu \rightarrow H_2O + CO + Cl_2$$

occurs at the two separate electrodes of a photoelectrochemical cell. The key features in the film structure are the molecular apparatus for excitation and redox splitting, the intrafilm electron transport chain to the electrode in film 1, and the "bilayer" structure at the

photoelectrode in which the catalyst for Cl^- oxidation is incorporated into film 2. Film 2 is layered atop film 1. One advantage to such a hybrid photoelectrochemical approach is that it separates the net reaction into its two component half-reactions. The half-reactions occur at separate electrodes and can be dealt with separately, which decreases the complexity of the assembly problem by a factor of 2.

Although the device shown in Scheme VI is elaborate, it is not far-fetched. Synthetic approaches are available for incorporating polypyridyl-based complexes into thin polymeric films on electrodes where, to a large extent, they retain their light-absorbing and redox properties.[39] The H_2O and Cl^- oxidation catalyst $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$ has been shown to retain its catalytic ability toward the oxidation of Cl^- to Cl_2 in polymeric films.[35b]   The CO_2 reduction catalyst $[(bpy)Re(CO)_3Cl]$ has been incorporated into thin polymeric films by reductive electrochemical polymerization of $[(vbpy)Re(CO)_3Cl]$ (vbpy is 4-methyl-4'-vinyl-2,2'-bipyridine)[40a] or by oxidative electropolymerization of $[(pyr-bpy)Re(CO)_3Cl]$ (pyr-bpy is 4-(4-pyrrol-1-ylbutyl)-4'-methyl-2,2'-bipyridine).[40b] Both the rate at which the Re complex reduces CO_2 and its stability as a catalyst are greatly improved in the film environment.

(vbpy)   (pyr-bpy)
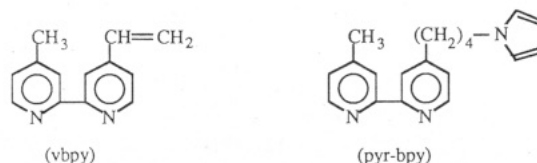
The problem remains of how to construct a photochemical apparatus for producing oxidative and reductive redox equivalents and then directing them to different places in the film structure. We have been exploring various approaches to synthesizing controlled microstructures within polymeric films with this thought in mind. In one approach, organic and/or inorganic chromophores have been incorporated into precast films of chemically reactive chlorosulfonated polystyrene ($[-CH_2CH(p-C_6H_4SO_2Cl)-]_n$; $PS-SO_2Cl$). In the attachment chemistry, nucleophilic displacement of chloride occurs with sulfonamide bond formation, e.g.,[41]

(9)

(5-NH_2phen is 5-amino-1,10-phenanthroline)

(35) (a) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R., Jr.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855. (b) Vining, W. J.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2023. (c) Rotzinger, F. P.; Munavalli, S.; Conte, P.; Hurst, J. K.; Gratzel, M.; Peru, F.-J.; Frank, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 6619. (d) Meyer, T. J. In Metal Oxo Complexes and Oxygen Activation. In *Oxygen Complexes And Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1988, p 33.

(36) (a) Eisenberg, R.; Fisher, B. *J. Am. Chem. Soc.* **1980**, *102*, 7363. (b) Hawecker, J.; Lehn, J.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328. Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414. (c) Sullivan, B. P.; Bruce, M. R.; O'Toole, T. R.; Bolinger, C. M.; Megehee, E.; Thorp, H.; Meyer, T. J. In *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988.

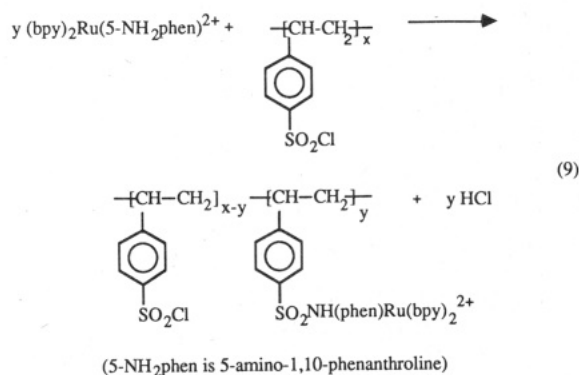(37) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.

(38) Fendler, J. H. *J. Phys. Chem.* **1985**, *89*, 2730.

(39) (a) Abruna, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1. (b) Murray, R. W. Chemically Modified Electrodes. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; M. Dekker: New York, 1984; Vol. 13.

(40) (a) O'Toole, T. R.; Margerum, L. D.; Westmoreland, T. D.; Vining, W. J.; Murray, R. W.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1416. O'Toole, T. R.; Margerum, L. D.; Sullivan, B. P.; Murray, R. W.; Meyer, T. J. *J. Electroanal. Chem.*, in press. (b) Bidan, G.; DeRonzier, A.; Moutet, J.-C. *Nouv. J. Chim.* **1984**, *8*, 501.

Scheme VII
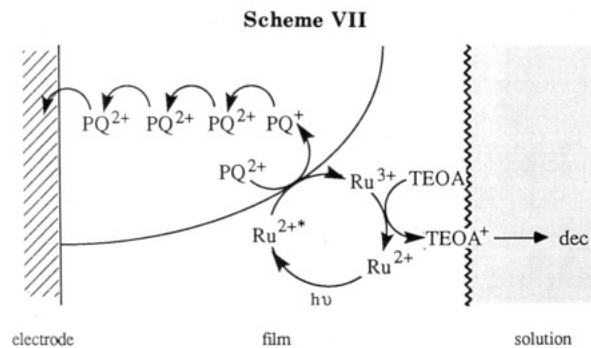
The polypyridyl complex in reaction 9 is large; its molecular radius is ~ 7 Å. It occupies only a limited number of the available chlorosulfonated sites. In thin films the remainder of the sites can be used to bind smaller molecules. Alternatively, partial hydrolysis of the remaining sites via $PS\text{-}SO_2Cl + 2OH^- \rightarrow PS\text{-}SO_3^- + H_2O + Cl^-$ provides an ion-exchange environment for incorporating cationic quenchers like PQ^{2+}.[41]

In the step where the complex is added to the film, an electrode coated with $PS\text{-}SO_2Cl$ is soaked in a solution containing the chromophore. Sulfonamide bond formation starts at the outside of the film, at the film–solution interface, and works its way in toward the electrode. Because of the outside-in nature of the attachment chemistry, a *concentration gradient* of the complex forms within the films with the concentration decreasing from the outside to the inside.[42]

In partly hydrolyzed films with PQ^{2+} and the irreversible oxidative scavenger triethanolamine (TEOA) in the external solution, the components are in place for a photoelectrode whose operation is shown in Scheme VII.[43] The concentration gradient of Ru^{2+} from inside to outside is suggested by the curved line.

Excitation of the fixed chromophore and oxidative quenching by PQ^{2+} produces PQ^+. It is a mobile carrier whose reducing equivalents are carried to the inner electrode by diffusion–electron-transfer hopping. The chemically fixed oxidative equivalents are returned to the Ru(II) state by electron transfer from TEOA, which decomposes irreversibly following one-electron oxidation. From the results of concentration-dependent lifetime and photocurrent measurements on the films, the photocurrents arise by diffusional quenching of Ru^{2+*} sites that lie near sulfonate ion channels produced in the hydrolysis step. Per photon absorbed quantum yields for photocurrent production of up to ~ 0.14 have been achieved at high added TEOA.

We are currently investigating ways to modify the chlorosulfonated polystyrene films so as to create separate conduction channels for oxidative equivalents to reach the outside of the films and reductive equivalents to reach the inside.

We are also investigating alternate approaches to the microstructure problem. One is the construction of "molecular wires" from the surface of derivatized carbon electrodes. This work is being conducted in collaboration with Professor Bruce Erickson and his group at UNC. In the wires there will be a controlled spatial array of electron-transfer acceptors (A), donors (D), and chromophores (C). The most promising lead synthetically is to utilize synthetic amino acids and the Merrifield technique to construct molecular chains. The molecular chains will consist of spatially ordered chromophore–quencher combinations held by peptide links. The electrode will act as the ultimate electron donor,
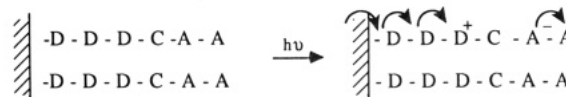
or acceptor,
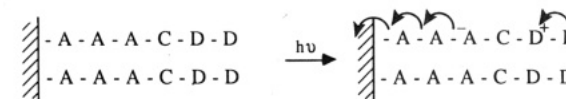
In still another approach, we are exploring structures where there are discrete, separated layers that contain donors in one layer, acceptors in another layer, and the chromophore in a middle layer. The idea is to produce separated oxidative and reductive equivalents at the two different chromophore–quencher film interfaces.

The chemical approaches to artificial photosynthesis described here are based on a series of well-established chemical principles, the development of an extensive supporting synthetic chemistry, and the discovery of new catalytic systems and the principles by which they operate. It is impressive that nearly all of the background chemistry and photochemistry has appeared within the past 10–15 years. It seems inevitable that, with continued progress in this area, devices of the type implied here, or at least having some of their features, will be successfully constructed. Even if they have no economic value, the ability to incorporate the broadly based set of ideas required to deal with making them will be an impressive demonstration of the growing "high technology" capabilities of modern chemistry.

(41) Ellis, C. D.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1748.

(42) Surridge, N. A.; Linton, R. W.; Hupp, J. T.; Bryan, S. R.; Meyer, T. J. *Anal. Chem.* **1986**, *58*, 2443.

(43) (a) Hupp, J. T.; Otruba, J. P.; Parus, S. J.; Meyer, T. J. *J. Electroanal. Chem.* **1985**, *190*, 287. (b) Surridge, N.; Hupp, J. T.; McClanahan, S.; Gould, S.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 294. (c) Surridge, N.; Hupp, J. T.; Danielson, E.; McClanahan, S.; Gould, S.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 304.