Artificial Photosynthesis: Mimicking Redox Asymmetry**

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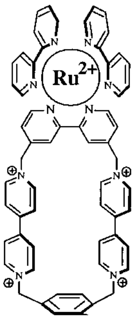
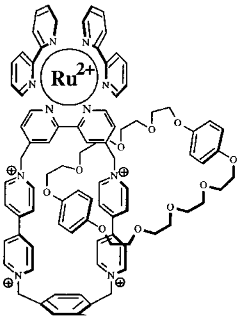
One intriguing aspect of the bacterial photosynthetic reaction center (RC) is the redox asymmetry of the cofactors: Electron transfer proceeds only along the L branch of an almost symmetrically twinned set of reagents.[1, 2] The M branch is apparently excluded, since the effective dielectric constant of the surrounding medium differs.[3, 4] A slightly higher polarity around the L branch favors electron transfer along this direction,[5] although the reaction can be made to proceed along the M branch in mutagenically modified RC complexes.[6] We now describe a model system that is similar to the RC complex: The two chemically identical electron acceptors bound to the primary donor have different reduction potentials because of their environment. This effect is achieved by wrapping an electron-donating crown ether around one of the acceptor moieties, thereby excluding access to polar solvent molecules and further attenuating its electron affinity with charge-transfer interactions.

Cyclophane **1** [functionalized with ruthenium(II) bis(2,2′-bipyridine)], the corresponding metalated [2]catenane **2**, and the free catenated ligand **3** were synthsized by standard procedures[7] and characterized by ^{1}H NMR spectroscopy and mass spectrometry. For **2** and **3**, as with analogous nonmetalated [2]catenanes, an electron-poor tetracationic 4,4′-bipyridinium-based cyclophane is interlocked with a complementary electron-donating macrocycle.[8]



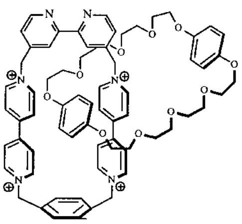
$6\,PF_6^-$

1



$6\,PF_6^-$

2



$4\,PF_6^-$

3

The structural feature that is most important to the present study is the asymmetry of the two 4,4′-bipyridinium dications bound to the metal complex in **2**. The absence of a suitable internal ^{1}H NMR probe prevented direct measurement of the rate at which the macrocycle migrates between these two cationic units. Such studies were possible for **3** in [D$_6$]acetone; in particular, signals for the degenerate 6,6′ protons of the 2,2′-bipyridine unit are readily observable from +25 to −60 °C. At the coalescence temperature ($T_c = -33\,°C$) the rate constant for this process was estimated as 88 s^{-1}, and the Gibbs energy of activation as 12.5 kcal mol^{-1}. The rate of interchange at the coalescence temperature, which corresponds to a lifetime of about 11 ms, indicates that the two interlocked rings in **2** are frozen on the time scale of the electron transfer.

Electrochemical studies of **2** in deoxygenated acetonitrile showed that the metal center undergoes a quasi-reversible one-electron oxidation with a half-wave potential E^0 of 1.29 ± 0.02 V versus the standard calomel electrode (SCE). At higher potentials, oxidation peaks can be resolved for the external ($E^0 = 1.44 \pm 0.02$ V vs. SCE) and internal ($E^0 = 1.73 \pm 0.04$ V vs. SCE) hydroquinol units of the crown ether. Upon reversing the scan, reduction peaks for the external ($E^0 = -0.32 \pm 0.01$ V vs. SCE) and internal ($E^0 = -0.45 \pm 0.01$ V vs. SCE) viologens were observed before the appearance of a two-electron peak ($E^0 = -0.85 \pm 0.03$ V vs. SCE) corresponding to formation of the neutral viologens. Similar electrochemical behavior was found for the nonmetalated **3** and for related [2]catenanes.[8, 9] The redox potentials for internal and external viologens differ because of a) the relative accessibility to polar solvent molecules and b) the interaction with electron-donating hydroquinol units. These factors combine to introduce significant (130 meV) redox asymmetry into **2**. The metal center in cyclophane **1** is oxidized at $E^0 = 1.29 \pm 0.02$ V vs. SCE, whereas the 4,4′-bipyridinium-based cyclophane undergoes one-electron reduction at $E^0 = -0.28 \pm 0.01$ V vs. SCE.

Because of the inherent redox asymmetry in **2**, we might expect light-induced electron transfer to occur selectively from the metal center to the external viologen in view of the more favorable thermodynamic driving force. To ensure that the rate of the forward electron transfer does indeed depend on the driving force, we first studied the noncatenated system **1**. Although **1** is not luminescent at room temperature, weak luminescence characteristic of the metal complex was observed at 77 K upon excitation at 565 nm. Transient absorption spectral studies at 20 °C indicate that the triplet excited state of the Ru^{II} complex, which is formed within the laser pulse, has a lifetime of (12 ± 2) ps; the parent compound tris(2,2′-bipyridine)ruthenium(II) has a lifetime of about 1 μs. After decay of the triplet state the spectra show the presence of a mixture of the Ru^{III} complex and the singly reduced form of the 4,4′-bipyridinium-based cyclophane. Decay of these redox intermediates occurred by first-order kinetics with a lifetime of (35 ± 3) ps. The overall reaction is fast because of the close proximity of the reactants; a similar conclusion was reached by Mallouk et al. for a related system that, however, was not part of a cyclophane.[10]

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The triplet energy of the metal complex was determined to be about 1.90 eV from the low-temperature emission spectrum. The thermodynamic driving force[11] for light-induced reduction of the viologen subunits in acetonitrile was estimated as $\Delta G^0 \approx -0.36$ eV, which indicates that the reaction is likely to fall within the "normal Marcus region".[12]

Charge recombination is much more favorable ($\Delta G^0 \approx -1.60$ eV) and is likely to occur within the "inverted Marcus region". These expectations were confirmed by measuring the rates of forward and reverse electron transfer between −30 and +65 °C. The activation energies E_A of (0.070 ± 0.002) and (0.010 ± 0.001) eV, respectively, were derived from the linear Arrhenius plots for forward and reverse electron transfer. The total reorganization energy λ for forward electron transfer was calculated to be about 0.85 eV based on Marcus theory [Eq. (1)].[12]

$$E_A = \left(\frac{(\lambda + \Delta G^0)^2}{4\lambda}\right) \qquad (1)$$

The rate constant for the forward electron transfer (k_{CS}), but not that of the charge recombination (k_{CR}), depends on the polarity of the surrounding solvent, as expressed in terms of the static dielectric constant ε_S. In highly polar solvents such as propylene carbonate ($\varepsilon_S = 62$), k_{CS} has an optimal value of about 10^{11} s^{-1} but decreases progressively as the polarity is reduced (Figure 1), subject to solubility restrictions. Because the electron transfer is under activation control (i.e., $-\Delta G^0 \approx 0.4\lambda$), we attribute the decreased rate to a smaller thermodynamic driving force in less polar solvents due to weaker solvation of reactants and products. The important conclusion of these studies is that k_{CS} increases with increasing solvent polarity and with increasing temperature.

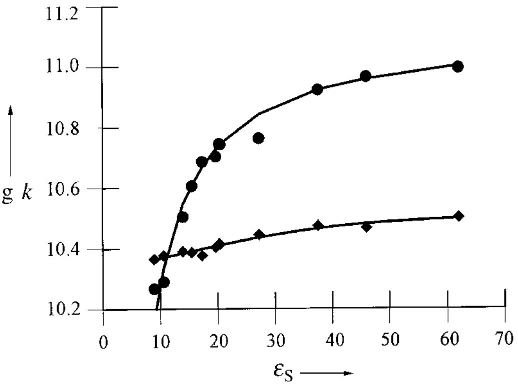

Figure 1. Effect of the dielectric constant on the rate constants for the forward electron transfer (●) and subsequent charge recombination (◆) measured for **1** after laser excitation at 565 nm. Solvents used (ε_S): propylene carbonate (62), dimethyl sulfoxide (46), acetonitrile (37.5), propionitrile (27.2), isobutyronitrile (20.4), butyronitrile (20.3), valeronitrile (19.7), hexanenitrile (17.3), 4-methylvaleronitrile (15.5), octanenitrile (13.9), 1,2-dichloroethane (10.6), dichloromethane (8.9).

Similar transient spectroscopic studies were made with the catenane **2**, whose two electron-poor arms show disparate reduction potentials in acetonitrile. Laser excitation resulted in immediate formation of the triplet excited state of the ruthenium(II) complex, which decayed by first-order kinetics with a lifetime of (17 ± 2) ps. The triplet state decayed by way of electron transfer to the adjacent cyclophane ($k_{CS} \approx 5.9 \times 10^{10}$ s^{-1}), as demonstrated by transient absorption spectroscopy (Figure 2), followed by subsequent charge recombination ($k_{CR} \approx 2.4 \times 10^{10}$ s^{-1}) to restore the ground state. The redox intermediates survive for about (42 ± 4) ps. By measuring the rate of the forward electron transfer in acetonitrile as a function of temperature, the activation energy for this process was found to be (0.062 ± 0.002) eV. In contrast, charge recombination, which must occur in the inverted Marcus region ($\Delta G^0 \approx -1.6$ eV), is almost activationless. Upon application of Equation (1), λ is estimated to be about 0.75 eV; the forward electron transfer lies in the normal Marcus region ($-\Delta G^0 \approx 0.4\lambda$), in which the rate increases with increasing driving force.

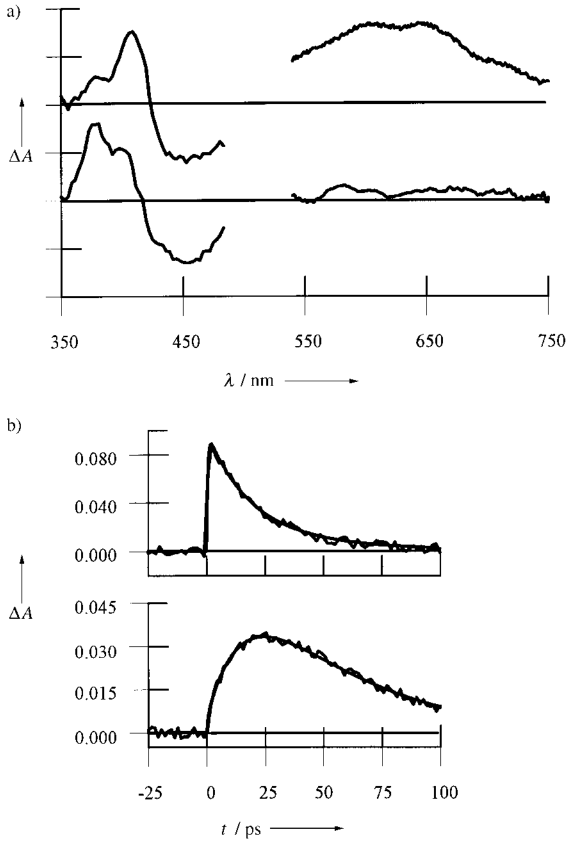

Figure 2. a) Transient differential absorption spectra recorded 1 ps (lower curve) and 25 ps (upper curve) after laser excitation of **2** in acetonitrile at 20 °C. b) Decay profiles showing formation and decay of the triplet state of the ruthenium(II) complex at 370 nm (top) and of the radical ion pair at 620 nm (bottom).

Consequently, the rate of electron transfer to the external viologen ($\Delta G^0 = -0.32$ eV) is expected to exceed that to the internal viologen ($\Delta G^0 = -0.19$ eV). Indeed, providing that λ and the electronic-coupling matrix element are identical for both viologens, a redox asymmetry of 130 meV would create a fivefold difference in rate. Therefore, electron transfer to the external viologen should account for about 85 % of the overall deactivation of the excited state. This remains a theoretical hypothesis, however, since the two viologens cannot be distinguished by spectroscopic means. Even so, it seems reasonable to anticipate that highly directional electron transfer can be induced by environmental effects of the type proposed here.

Experimental Section

The syntheses of **1**, **2**, and **3** starting from readily prepared 4,4′-bis-(methylene-4,4′-bipyridinium)-2,2′-bipyridyl bis(hexafluorophosphate) have been reported.[7] Solvents were purified by standard methods, and dielectric constants were taken from the literature.[13] For all laser spectroscopic studies, excitation was carried out at 565 nm with a 0.3-ps laser pulse delivered from a Nd-YAG pumped pyromethene dye laser similar to that described in ref. [14].

1: Yield: 64 mg, 70 %; ^{1}H NMR (360 MHz, CD_3COCD_3, 298 K): $\delta = 6.15$ (s, 4H), 6.25 (s, 4H), 7.55 – 7.79 (m, 12H), 7.90 (s, 4H), 7.91 – 8.11 (m, 4H), 8.23 (m, 4H), 8.51 (d, 4H, $J = 6.2$ Hz), 8.70 – 8.85 (m, 6H), 9.33 – 9.55 (m, 8H); FAB-MS (nitrobenzyl alcohol(NBA)/CH_3CN matrix): m/z: 1737 $[M - PF_6]^+$, 1591 $[M - 2PF_6]^+$, 1446 $[M - 3PF_6]^+$.

2: Yield: 40 mg, 68 %; ^{1}H NMR (360 MHz, CD_3COCD_3, 298 K): $\delta = 3.45$ – 3.48 (m, 4H), 3.61 – 3.63 (m, 8H), 3.69 – 3.72 (m, 8H), 3.79 – 3.85 (m, 12H), 3.93 – 4.10 (m, 4H), 6.10 (s, 4H), 6.23 (s, 4H), 6.26 (s, 4H), 7.57 – 7.73 (q, 4H, $J = 7.5$ Hz), 7.92 – 7.94 (d, 2H, $J = 6$ Hz), 7.98 (s, 4H), 8.00 – 8.02 (d, 2H, $J = 5.3$ Hz), 8.02 – 8.22 (m, 10H), 8.23 – 8.31 (q, 4H, $J = 7.8$ Hz), 8.34 – 8.36 (d, 2H, $J = 5.7$ Hz), 8.82 – 8.87 (m, 6H), 8.98 (m, 4H), 9.34 – 9.36 (d, 4H, $J = 5$ Hz); ES-MS ($CH_3CN/H_20/HCOOH$): m/z: 661 $[M - 3PF_6]^{3+}$, 460 $[M - 4PF_6]^{4+}$, 339 $[M - 5PF_6]^{5+}$.

3: Yield: 100 mg, 20 %; ^{1}H NMR (360 MHz, CD_3COCD_3, 298 K): $\delta = 3.46$ (m, 8H), 3.61 (m, 8H), 3.89 – 3.93 (m, 16H), 6.08 (s, 4H), 6.15 (s, 4H), 7.94 (m, 2H), 8.00 (s, 4H), 8.10 – 8.14 (2 × d, 8H, $J = 8$ Hz), 8.18 (m, 2H), 8.90 – 8.92 (d, 2H, $J = 5$ Hz), 9.27 – 9.29 (d, 4H, $J = 5.2$ Hz), 9.32 – 9.34 (d, 4H, $J = 7$ Hz); FAB-MS (NBA matrix): m/z: 1569 $[M - PF_6]^+$, 1425 $[M - 2PF_6]^+$, 1280 $[M - 3PF_6]^+$, 1135 $[M - 4PF_6]^+$.

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Solid-Phase Immobilization of a New Epoxidation Catalyst[**]

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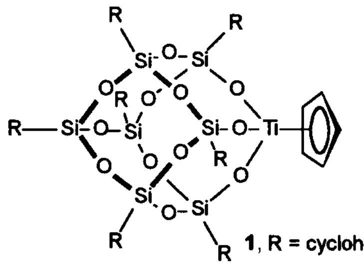
The heterogenization of homogeneous catalysts is an important topic in liquid-phase oxidation catalysis.[1] Recently we reported on the use of the titanium(IV) silsesquioxane $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}Ti(\eta^5\text{-}C_5H_5)]$ **1**[2] as an active and robust homogeneous catalyst for alkene epoxidation.[3] Under the catalytic conditions employed, **1** is stable and does not leach titanium, which makes it an attractive candidate for heterogenization. Here we report on the immobilization of **1** in an MCM-41 molecular sieve,[4] for which we especially exploited its strong adsorption in the MCM-41 channel. The resulting self-assembled materials are active, truly heterogeneous, and recyclable catalysts for alkene epoxidation in the liquid phase.



1, R = cyclohexyl

The adsorption of the silsesquioxane **1** from hexane into an MCM-41 molecular sieve occurs quickly and can be followed easily by UV/Vis spectroscopy in solution by monitoring its intense 216 nm band. We investigated MCM-41 molecular sieves with Si/Al ratios of 42, 125, and ∞. The adsorption kinetics of **1** are typical for "single-file diffusion",[5] indicating that its actual adsorption takes place inside the MCM-41 channels. Because of this fast and complete adsorption, the loading of **1** can be adjusted easily by varying its total amount in solution. The maximum loading for the MCM-41 host with a Si/Al ratio of 42 was found to be 97 milligrams of **1** per gram

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