Photoinduced Charge Separation in Multilayer Thin Films Grown by Sequential Adsorption of Polyelectrolytes

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A central problem in the design of artificial photosynthetic systems is control of supramolecular structure. The best systems, in terms of the overall quantum yield for charge separation, are those in which the branching ratio between forward and back electron transfer rates is high at each successive step.[1] Because these rates vary exponentially with intermolecular distance, a good strategy is to arrange all the components at fixed distances, and in roughly a straight line. For example, supermolecules containing up to five different redox-active subunits, all of which participate in the multistep charge separation reaction, have been synthesized.[2] Through judicious attention to the strength of electronic coupling and the thermodynamic driving force for each successive electron transfer step in these pentads, very high charge separation quantum yields (>80%) and lifetimes (55 μs) have been achieved.[3] Precise tuning of ground- and excited-state energetics in related fixed-distance dyad and triad molecules has yielded compounds that rival bacterial photosynthetic reaction centers in terms of rapid, activationless charge separation, slow charge recombination, and very high overall quantum efficiency.[4]

These elegant supermolecules effectively mimic the initial charge separation events of photosynthesis. However, their synthesis is generally daunting, and they are not easily coupled to catalytic particles that might be used to convert their transiently stored energy into chemical form. To overcome these problems, other synthetic strategies have been devised in which redox chains are organized in space by solid supports, such as sol–gel glasses,[5] zeolites,[6] and layered compounds.[7] We demonstrate in this paper a different approach, based on sequential polyelectrolyte adsorption, that enables one to
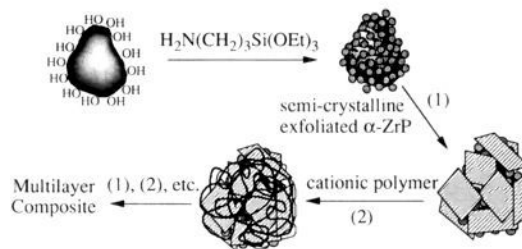

Figure 1. Schematic procedure for the preparation of the composite multilayers on high surface area silica. Transmission electron micrographs show some degree of agglomeration both in the Cab-O-Sil SiO₂ starting material and in the anchored composites, which are omitted in this idealized picture.

juxtapose electron donors and acceptors at fixed distances for photoinduced electron transfer reactions. The advantage of this technique is that redox-active layers are easily grown in any sequence, and therefore electron transfer chains containing several components are synthesized painlessly from the appropriate homopolymers.

The procedure used to prepare these redox assemblies is shown in Figure 1. It is based on a technique originally developed by Decher and others,[8–12] for growing multilayer films of polyelectrolytes, which was subsequently adapted in our laboratory[13] and elsewhere[14] to the preparation of films containing inorganic, two-dimensional sheets. Here we extend this technique to the construction of inorganic–organic multilayers on high surface area silica. Polycations **1** and **2** were grown as monolayers, separated by single, anionic inorganic sheets of zirconium phosphate. These ca. 8 Å thick insulating sheets confine the two redox polymers to separate layers and are thin enough to allow electron transfer between them.

These "onion-like" redox structures were prepared by first derivatizing fumed silica (Cab-O-Sil) particles with an aminoalkoxysilane,[15] and then suspending the solid in water in order to protonate the amine terminus and create a cationic

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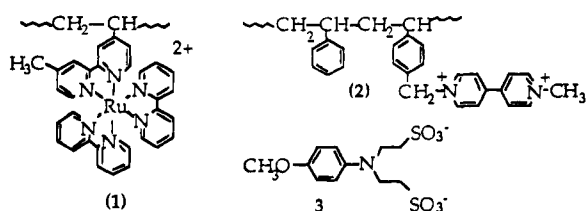
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(15) In a typical derivatization procedure, 5.0 g of Cab-O-Sil (Kodak; 150 m²/g) was suspended in 150 mL of anhydrous toluene in a poly(tetrafluoroethylene) bottle, to which was added 5 mL of (3-aminopropyl)triethoxysilane (Aldrich). The solution was deaerated with flowing Ar and the bottle sealed and heated with stirring at 60 °C for 72 h. The derivatized silica was isolated by centrifugation with intermittent washings with toluene, methanol, and finally water and dried in air at 80 °C. The solid was stirred in a suspension of exfoliated α-ZrP (10 mequiv/L) for 3–6 h, isolated by centrifugation with several intermittent washings, and dried in air at 70 °C. The redox polymers (as chloride salts) were deposited from 10⁻⁴ M aqueous solutions, alternately with α-ZrP. Thicker layers of viologen polymer **2** (38 ± 4 Å) could be obtained by depositing it in a coiled conformation from 10⁻⁴ M **2**/1 M NaCl solutions.

surface. Semicrystalline α-Zr(HPO$_4$)$_2$·H$_2$O[16] (α-ZrP) was ex-

Figure 2. Transient diffuse reflectance spectra for 1/2/SiO$_2$ composite with 3.5 mM **3** in solution at 10 μs (●) and 40 μs (□) following 532 nm, 7 ns laser excitation. The inset shows the transient signal of MV$^{•+}$ recorded at 400 nm and a 2nd order fit to the data (—). Spectra were corrected empirically for the diffuse reflectance geometry; see ref 23.

foliated using 0.15 M tetrabutylammonium hydroxide to yield a suspension of constant pH (8.0−8.5) containing 100−200 × 8 Å sheets. Details of the synthesis and characterization of redox polymers **1** and **2** and the electron donor **3** (MDESA^{2-}) will be given elsewhere.[17] Ellipsometric data from films grown under identical conditions on planar Si/SiO$_x$ substrates gave reproducible thicknesses of 12−13 and 8−9 Å for **1** and α-ZrP. The thickness of **2** was 9−10 Å when monolayers were grown in the absence of added salt, and it was 38 ± 4 Å when the polymer was deposited in a coiled conformation from 1 M NaCl solution.[8d]

When the dyad composite system **1/2/SiO$_2$** (slash marks indicate a layer of α-ZrP) is photoexcited at 532 nm in the absence of solution phase electron donor **3**,[18] there is no transient signal associated with reduced **2**,[19] expected from reaction 1, and the lifetime (600 ns) of the MLCT state is similar to that measured for **1/SiO$_2$** alone. In this configuration, *Ru(II) cannot

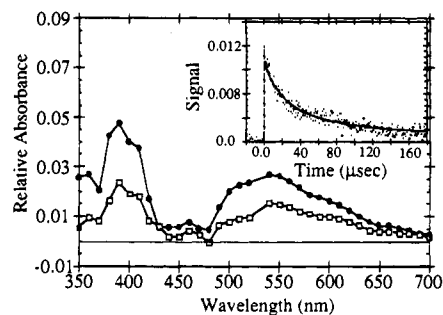$$*\text{Ru(II)} + \text{MV}^{2+} \;\not\rightarrow\; \text{MV}^{•+} + \text{Ru(III)} \qquad (1)$$

reduce the viologen groups in the adjacent layer, presumably because of the separation imposed by the intervening α-ZrP sheet. However, when the reversible electron donor **3** is added to the solution, a new electron transfer pathway is created via reaction 2.[20] In the absence of the electron acceptor polymer

$$\text{MDESA}^{2-} + \text{Ru(II)}* \rightarrow \text{MDESA}^{•-} + \text{Ru(I)} \qquad (2)$$

2, spectral features attributed to Ru(I) and MDESA$^{•-}$ (360 and 510 nm) are observed in transient diffuse reflectance spectra. Emission intensities and lifetimes (both monitored at 630 nm) reveal that quenching of **1*** by **3** is ca. 50% complete, and that both static and dynamic components are involved in the reductive quenching reaction (2).

The reduced form of **1** (formally Ru(I)) is a more powerful reducing agent than *Ru(II) by *ca.* 400 mV, and this additional driving force accelerates electron transfer from **1** to the viologen polymer **2**:

$$\text{Ru(I)} + \text{MV}^{2+} \rightarrow \text{MV}^{•+} + \text{Ru(II)} \qquad (3)$$
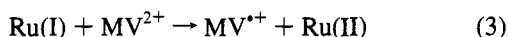
Reaction 3 follows reaction 2 sufficiently rapidly that the rise of signals from MV$^{•+}$ cannot be temporally resolved from the disappearance of *Ru(II). Figure 2 shows transient spectra of **1/2/SiO$_2$** suspended in a 3.5 mM aqueous solution of **3**. The *Ru(II) absorbance at 360 nm[21] is replaced by a 390 nm peak,

characteristic of the viologen radical cation; the broad peak around 550 nm is also attributed to reduced **2** in aggregated form. Additionally, there is a long-lived species that absorbs near 510 nm, which is assigned to the radical anion of oxidized **3**. These spectral features are consistent with a charge-separated state composed of oxidized solution-phase **3** and reduced **2**, which is "buried" in the inner layer of the composite.

The quantum yield for the formation of the **2−3** charge-separated state is ~30%. This quantum yield is quite high when one considers that quenching of *Ru(II) is incomplete, and that MDESA$^{•-}$ must escape from the cationic surface in order to be detected on the microsecond time scale. The second-order kinetics of charge recombination ($k = 1 \times 10^9$ M^{-1} s^{-1}) is consistent with cage escape of MDESA$^{•-}$, following reaction 2, and subsequent diffusion to a reduced MV$^{•+}$ site. The magnitude of the rate constant may be attributed in part to the high driving force (ca. 1.3 eV) and to the weak distance dependence of very exoergic electron transfer reactions.[22] While recombination of radical pairs at defect sites that expose MV$^{•+}$ to the solution cannot be ruled out, the inertness of the **2/1/SiO$_2$** composite in solutions of **3** argues against this model.

Control experiments in which the order of polymer deposition is reversed (i.e., **2/1/SiO$_2$**) show no evidence for electron transfer quenching of *Ru(II) by **3**, or for interlayer electron transfer between excited state **1** and **2**. Additional control experiments underscore the importance of the "onion" layer structure for the efficient formation and long lifetime of the charge-separated state. Replacing the α-ZrP sheets with poly(styrenesulfonate) (PSS) monolayers[8−12] has the effect of shutting off reaction 2. The photosensitizer polymer **1** is apparently intertwined with and covered by PSS to such an extent that it is inaccessible to electron donor **3**. Eliminating the silica support and the α-ZrP layers, i.e., dissolving **1**, **2**, and **3** in solution, allows reaction 2 to proceed but not reaction 3, presumably because of electrostatic repulsion between the two polycations. Finally, replacing **1** with poly(allylamine), a non-photoactive polycation, eliminates the photochemical response entirely. Therefore, ground-state interaction of **2** and **3** does not contribute significantly to the photochemistry.

We are currently preparing more complex "onion-like" structures, containing additional layers of donors and acceptors, in the hopes of further separating the ultimately oxidized and reduced species in these systems.

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