

Communications to the Editor

Photoinduced Electron Transfer Mediated by a Shuttling Charge Carrier between Ruthenium and Iridium Trisbipyridyl Complexes Trapped in Sol-Gel Glasses

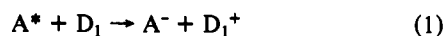
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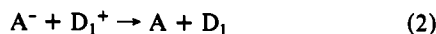
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As in the case of natural photosynthesis, the photochemical conversion of solar energy in artificial systems is based on a primary electron transfer process (reaction 1) between an excited acceptor A* (or donor) and an appropriate donor D₁ (or acceptor).



Reaction 1 should be followed by specific (catalyzed) reactions of the photogenerated radical ion pair (D₁⁺, A⁻), yielding useful chemicals such as H₂ and O₂.^{1,2} A basic objective of artificial photosynthetic devices is to inhibit the exothermic (energy-wasting) back reaction (reaction 2).¹⁻⁵



An important approach^{4,5} has been to overcome the difficulties encountered in two-component (D₁, A) systems by applying three (or more) molecules with proper redox properties, where, e.g., the primary donor D₁ acts as an intermediate charge carrier ("shuttler") to a secondary donor D₂, according to



followed by the back electron transfer:



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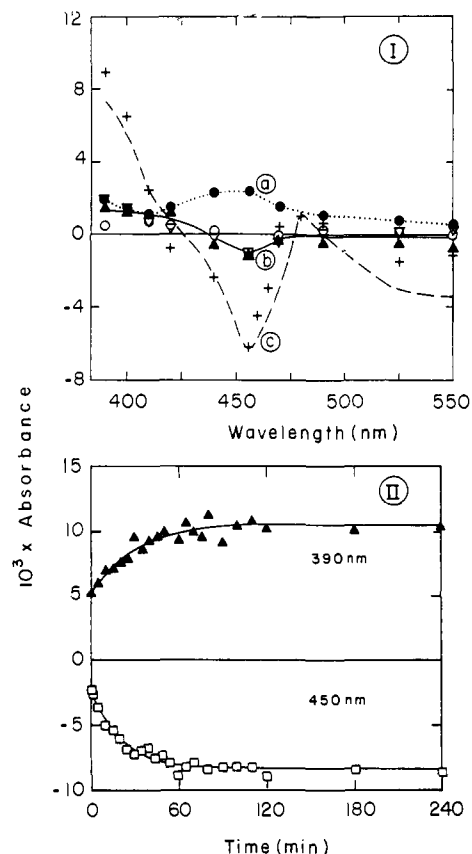


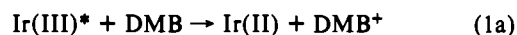
Figure 1. (I) Transient difference spectrum following pulsed N₂-laser excitation or continuous Hg-lamp illumination of the trapped Ir(III) systems in the presence of 4.5 mM DMB at pH = 2. (a) (●) Absorbance change recorded in the binary Ir(III)/DMB system 400 ms after the laser pulse (dotted line). (b) Curve constructed from the superposition of three difference spectra (full line): (1) (○) absorbance change recorded in the ternary system Ir(III)/DMB/Ru(II) 700 ms after the nitrogen laser pulse; (2) (▲) same, 10 s after continuous illumination; (3) (▽) the averaged difference spectrum [Ru(III) - Ru(II)] + [Ir(IV) - Ir(III)] obtained⁹ by separately carrying out the oxidation reactions of (sol-gel) glass-trapped Ru(II) and Ir(III) [Ru(II)* + Fe³⁺ $\xrightarrow{h\nu}$ Ru(III) + Fe²⁺; Ru(II)* + S₂O₈²⁻ $\xrightarrow{h\nu}$ Ru(III) + SO₄⁻ + SO₄²⁻; Ru(II) + Ce(IV) $\xrightarrow{h\nu}$ Ru(III) + Ce(III); Ir(III)* + S₂O₈²⁻ $\xrightarrow{h\nu}$ Ir(IV) + SO₄⁻ + SO₄²⁻]. (c) Dashed line, same as curve Ib2 but after 60 min. (d) The + points represent the Ru(III) - Ru(II) difference spectrum constructed by combining the three oxidation methods of glass-trapped Ru(II) described for curve Ib3. (II) Time dependence of the transient difference spectrum from Ib1 to Ic, attributed to the slow phase of Ru(III) formation via reactions 7 and 6 and/or via reaction 8. Most of the absorbance changes (growing-in at 390 nm and decay at 450 nm) are due to Ru(III) - Ru(II). Changes associated with Ir(II) - Ir(III) are not occurring in that time scale.

In the present work, we report the successful application of the above concept by inhibiting reaction 4 in a system where A and D₂ (and thus also A⁻ and D₂⁺) are completely immobilized by trapping in the three-dimensional network of a porous solid. D₁ is free to diffuse in the intrapore liquid phase, thus serving as a shuttling charge carrier between A and D₂. To achieve this goal, we have applied the relatively novel "sol-gel" technique⁶ which allows doping of porous inorganic glasses with organic and bio-

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logical molecules⁷ by room temperature polymerization of organic silanes. In a previous publication,⁸ we have shown that a trapped (excited) molecule, i.e., $A^* \equiv \text{Ir}[(\text{bpy})_2(\text{C}^3\text{N}'\text{bpy})]^{3+*}$, Ir(III)^* , undergoes interfacial electron transfer from an appropriate electron donor such as 1,4-dimethoxybenzene, DMB, which is present in the aqueous, intrapore, liquid phase. The reaction (which is based on a long-range electron-transfer mechanism between glass-embedded Ir(III)^* and DMB adsorbed at the solid-liquid interface⁹) leads to a charge-separated pair ($A^- \equiv \text{Ir(II)}$, $D^+ \equiv \text{DMB}^+$). A substantial fraction of this pair is highly stabilized by a variety of factors (primarily, long-range electron-transfer effects) discussed in refs 8 and 9. The specific, ternary system used in this work includes the same trapped photosensitizer and primary diffusible donor, but with $\text{Ru}(\text{bpy})_3^{2+}$ as the secondary (trapped) donor, D_2 .

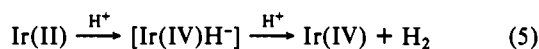
The initial transient absorbance (not shown) observed in the ternary system at pH = 2, $\sim 200 \mu\text{s}$ after N_2 -laser excitation, is similar to that measured in the absence of Ru(II) ⁸ and corresponds to the stoichiometric generation of Ir(II) and DMB^+ via reaction 1a. Analogously to the binary system which lacks Ru(II) , part



of this primary ion-pair population decays over several milliseconds via a fast second-order process (reaction 2b) ($k_{2b} = (5 \pm 2) \times$



$10^8 \text{ M}^{-1} \text{ s}^{-1}$, as compared to $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in homogeneous solutions) leading to a long-lived absorption characteristic of a residual Ir(II) , DMB^+ ion-pair population which escaped recombination via reaction 2b.⁸ In the binary system, at low pH, the latter absorption is replaced over several hundred milliseconds by the difference spectrum, Figure 1Ia, identified⁸ as the superimposed contribution of DMB^+ (450 nm) and of Ir(IV) generated via



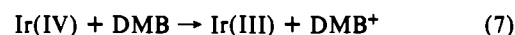
Reaction 5, which is first order with an overall rate of $\approx 4 \text{ s}^{-1}$ at pH = 1.3–2.0,⁸ is also observed in the present ternary system. This is in keeping with the detection of H_2 by gas chromatography with comparable yields in both systems ($\sim 1\%$).^{8,9} However, in the ternary system, the slow decay of Ir(II) (observed at 390 nm) via reaction 5 is accompanied by an additional first-order decay at 450 nm with k being proportional to the concentration of Ru(II) ($k = 2 \pm 1 \text{ s}^{-1}$, for $[\text{Ru(II)}] = 0.05 \mu\text{mol/g}$). The difference spectrum measured after 700 ms (Figure 1Ib1) lacks the 450-nm absorption band of DMB^+ and is identical with the superimposed difference absorbances: $[\text{Ir(IV)} - \text{Ir(III)}] + [\text{Ru(III)} - \text{Ru(II)}]$, determined by constructing this difference spectrum by oxidizing sol-gel trapped Ru(II) and Ir(III) via independent photochemical

and thermal processes⁹ (see Figure 1Ib3). These observations are interpreted in terms of the "shuttling" electron-transfer step,



($k_6 \sim 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), which protects DMB^+ from irreversible side reactions.⁸⁻¹⁰ The occurrence of the relatively slow reactions 5 and 6 is allowed by stabilization of the Ir(II) , DMB^+ pair due to the same factors discussed in ref 8 for the binary $\text{Ir(III)}/\text{DMB}$ system. It is important to note that due to reaction 5 the present system is not suitable for determining the recombination rate between the trapped A^- , i.e., Ir(II) , and D_2^+ , i.e., Ru(III) . (Our experiments can only set an upper limit of $\sim 5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the apparent rate of this process.) To achieve this goal a system should be designed in which neither A^- nor D_2^+ will react with the solvent.

The fate of the long-lived trapped photoproducts, Ir(IV) and Ru(III) , was investigated by using continuous irradiation with the 365-nm line of a Hg lamp, coupled with spectral measurements using an H.P. diode-array spectrophotometer. The transient difference spectrum measured 10 s after irradiation fits the 700-ms difference spectrum of the laser-induced experiments (Figure 1Ib1, I b2). Subsequently, a slow process is observed, taking place over a 50-min time scale, which is characterized by further bleaching at 450 nm and a growing-in at 390 nm (Figure 1II). The spectrum recorded after 60 min is shown in Figure 1Ic. Comparison with independent chemical and photochemical oxidation of Ru(II) (Figure 1Id) shows that it corresponds to the simple $[\text{Ru(III)} - \text{Ru(II)}]$ difference spectrum characterized by a pronounced "bleaching" around 450 nm. These observations are consistent either with (slow) reaction 7 (followed by generation



of another Ru(III) molecule by DMB^+ , via the faster reaction 6) or with a direct, long-range electron transfer through the matrix:



In conclusion, the present findings demonstrate the feasibility of photoinduced electron transfer by a diffusible electron carrier, from an immobilized photosensitizer (acceptor) to a secondary (immobilized) donor. Immobilization, achieved by trapping in a porous network, is generally applicable to other redox systems,⁹ avoiding the synthetic complications associated with covalent binding of the reactants to solid supports. The transparent and inert matrix is also free of numerous photochemical and thermal side reactions which characterize most organic or biological microenvironments.^{1,2} It carries the potential of generating photoinduced charge-separated pairs with lifetimes extending into time scales of minutes and hours. In the present specific system, the reduced $A^- \equiv \text{Ir(II)}$ moiety yields H_2 at low pH without requiring an additional catalyst. In homogeneous solutions, in the presence of appropriate catalysts, the oxidized $D_2^+ \equiv \text{Ru(III)}$ is known to evolve O_2 from water.^{1,2} The same procedure may, in principle, be applied in the present system by replacing the original solution, after irradiation, by one containing an appropriate catalyst for O_2 evolution.

Acknowledgment. This study was supported by the grants from the Materials Division of the U.S. Army (London), the U.S.–Israel BSF, the Israel NCRD, the E. Berman Solar Energy Foundation, and the Krupp Foundation. We are grateful to Prof. J. Rabani for most valuable discussions.

Registry No. 1,4-DMB, 150-78-7; 1,4-DMB⁺, 34478-03-0; $\text{Ru}(\text{bpy})_3^{2+}$, 15158-62-0; $\text{Ir}(\text{bpy})_3^{3+}$, 16788-86-6; $\text{Ru}(\text{bpy})_3^{3+}$, 18955-01-6; $\text{Ir}(\text{bpy})_3^{2+}$, 71818-70-7; SiO_2 , 7631-86-9; H_2 , 1333-74-0; H_2O , 7732-18-5.

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