# Intermolecular and Intramolecular Excited-State Electron Transfer Involving Electrode-Confined Rhenium Carbonyl Complexes: Toward Molecule-Based Systems for Light Absorption, Charge Separation, and Optical Energy Conversion

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We wish to report studies of excited-state electron transfer involving monolayer quantities of electrode-confined Re carbonyl complexes **1a** or **2a** with the aim of developing approaches to molecule-based photoelectrochemical devices. Surfaces derivatized with **1a** or **2a** have been characterized with respect to electrochemical, photophysical, and spectroscopic properties and compared to solution analogues **1b** and **2b**. Photoelectrochemical

1a, R = *n*-pr-SiCl₃
1b, R = allyl

2a, R = *n*-pr-SiCl₃
2b, R = allyl
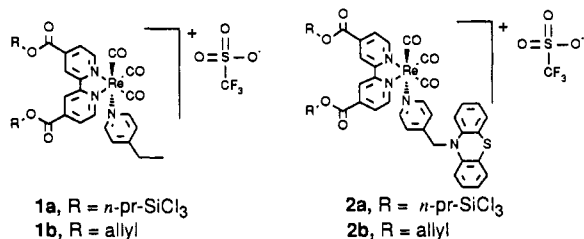
experiments show that sustained photooxidation of the sacrificial reagent triethanolamine, TEA, can be brought about as shown in part a or part b of Scheme I.

Possible applications to energy conversion are often cited to explain interest in excited-state electron transfer in multicomponent molecules. While reports of the synthesis and characterization of multicomponent molecules are abundant, reports concerning the application of such molecules to the energy conversion problem are scarce. The well characterized two-component molecule **2a** provides a good system to investigate the viability of a simple multicomponent molecular system in optical energy conversion and provides an important starting point from which more efficient systems can be designed.

Our overall aim is to generate an organized electrode-confined molecular assembly that achieves vectorial electron transfer as a result of light absorption. Efforts to mimic the mechanism of charge separation in natural photosynthetic systems have resulted in the synthesis and study of numerous multicomponent molecules.[1-5] A porphyrin-containing molecular pentad provides a striking example of a synthetic multicomponent molecule that efficiently yields a charge-separated state with a lifetime of 55

Scheme I

TEA ≡ N(C₂H₄OH)₃
∿∿∿ ≡ COVALENT LINKAGE
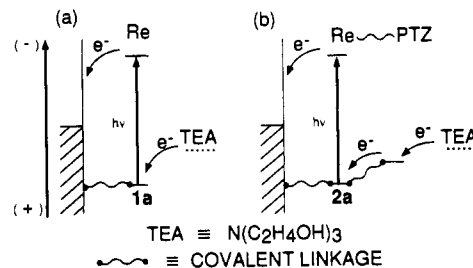
μs.[6] However, light-induced charge separation does not yield sustained energy conversion. Chromophore-containing multicomponent molecules have been immobilized on solid surfaces either by ion exchange[7] or as polymeric[8] or Langmuir-Blodgett films,[9] but few well-characterized examples have been *covalently* attached to electrode surfaces.[10] Use of covalent linkages can bring about a degree of orientation in multicomponent molecules, and covalent attachment may yield more durable systems than ones prepared by adsorption.

Our interest in **2a** stems from earlier work[3a] on intramolecular excited-state electron transfer showing the forward electron-transfer rate constant (k_f = 4 × 10⁹ s⁻¹, ΔG = –0.3 eV) for transfer from the pendant phenothiazine, PTZ, to the excited Re center is nearly 60 times faster than the reverse electron-transfer rate constant (k_b = 7 × 10⁷ s⁻¹, ΔG = –1.6 eV) for transfer from reduced bipyridine to oxidized PTZ, consistent with Marcus inverted region behavior.[11] A critical finding in our work is that the lowest excited state of the Re complex **1a** immobilized on conducting surfaces is sufficiently long-lived that intermolecular electron transfer can successfully compete with nonproductive quenching of the excited-state by the conductor. In addition, the charge-separated state of **2a** immobilized on conducting surfaces is effective in the photoassisted oxidation of triethanolamine.[12]

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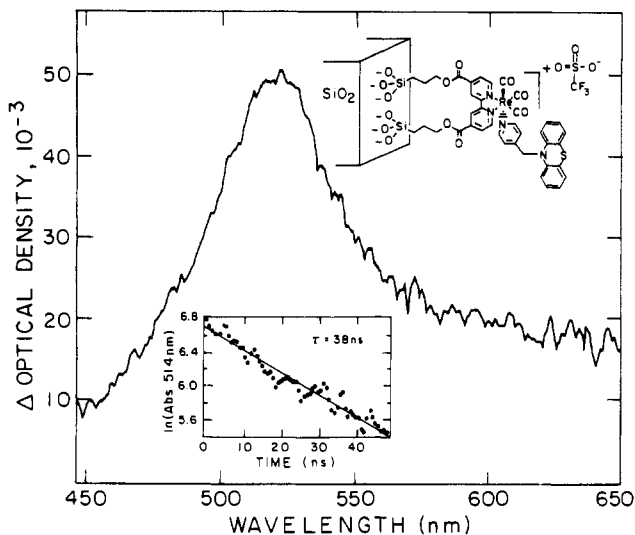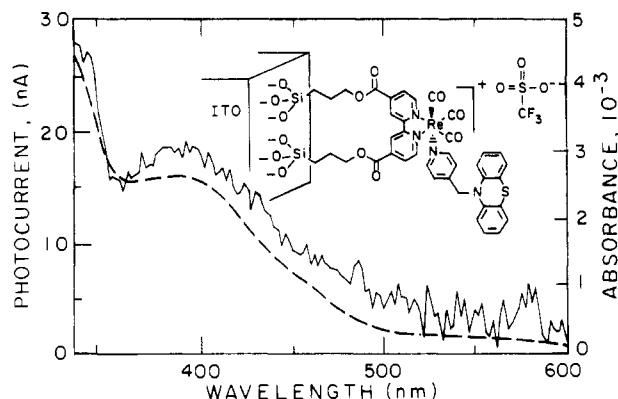
Figure 1. Transient absorption spectrum of **2a** immobilized on high surface area silica gel suspended in 0.1 M [*n*-Bu₄N]PF₆ in CH₂Cl₂ and recorded on an optical multichannel analyzer directly after a 5-ns laser pulse. Inset: Example of kinetic data for the decay of the charge-separated state of silica-confined **2a**.

1a and **2a** can be attached to high surface area silica gel, glass, and indium tin oxide (ITO) or platinum electrodes via the –SiCl₃ group.[13] ITO and Pt electrodes were derivatized by immersion in ∼1 mM CH₂Cl₂ solutions of **1a** or **2a** for at least 30 s. Cyclic voltammetry shows a reversible one-electron redox wave for the bipyridine–diester moiety at –0.75 V vs SCE for electrode-confined **1a** and **2a**, and for **2a** a second one-electron redox wave is observed at +0.78 V vs SCE, which is associated with the PTZ moiety. Integration of cyclic voltammetry waves for electrodes used in photophysical and photoelectrochemical studies show coverages for **1a** and **2a** of (3–15) × 10⁻¹⁰ mol/cm², corresponding to about one to five monolayers (assuming uniform coverage). Durability of the immobilized complexes upon reduction is less than desirable, but only 50% of the coverage is lost after scanning from –1.0 to +1.0 V at 200 mV/s for 30 min. However, derivatized electrodes are unchanged after storage in air for greater than one month at room temperature.

Excited-state lifetimes measured for **1b** and **1a** decrease in the following order: **1b** in solution (339 ns) > **1a**/glass (145 ns) ≈ **1a**/ITO (152 ns) > **1a**/Pt (35 ns).[14] Shorter lifetimes for **1a** on surfaces, in particular conductors, indicate that some excited-state quenching results from surface immobilization. Emission from **2a** on surfaces is very weak with a lifetime of <5 ns, consistent with rapid intramolecular electron transfer from pendant PTZ to the excited Re center.[3a] Transient absorption spectra recorded for **2a** immobilized on high surface area silica gel, Figure 1, shows formation of the charge-separated state on the surface. The lifetime of the charge-separated state of immobilized **2a** is 38 ns vs 17 ns for **2b** in solution.

In the presence of the sacrificial donor TEA, photoexcitation of **1a** or **2a** on Pt or ITO yields a sustained anodic photocurrent at potentials more positive than ∼–0.75 V vs SCE. Significantly, onset of anodic photocurrent for TEA oxidation occurs at a

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(14) All lifetimes were measured in degassed CH₂Cl₂ with 0.1 M [*n*-Bu₄N]-PF₆. Some scatter was observed in lifetime measurements. Error analysis would not be appropriate in describing these variations, since the value for each electrode results from the average of 20 laser shots. The variations are more likely the result of the effect of differing surface morphology. Therefore, the individual values are reported here: for ITO, 155, 159, 172, and 125 ns; for glass, 143, 127, 161, and 147 ns; and for Pt, 34, 40, 31, and 36 ns.

Figure 2. Comparison of photocurrent vs wavelength data (dashed line) with the absorption spectrum (solid line) of ITO-confined **2a**. The absorption spectrum correlates directly with the magnitude of the photocurrent.

potential ∼1 V more negative than for dark oxidation of TEA. At potentials positive of –0.6 V vs SCE the quantum yield for photocurrent is >0.1. Four independently prepared electrodes gave quantum yields of 0.14–0.39 at coverages of (1.4–5.1) × 10⁻¹⁰ mol/cm². The photoaction spectrum mimics the absorption spectrum of the Re complexes, Figure 2. The magnitude of the photocurrent increases linearly with light intensity, and at a given light intensity photocurrent depends on TEA concentration in a manner consistent with quenching by electron transfer from TEA to the excited state of **1a** or the charge-separated state of **2a**. Immobilized Re complexes do not yield stable photocurrents in the absence of TEA. Finally, anodic photocurrent ceases as the electrode reaches a potential where reduction of the bipyridine ligand begins to occur (∼–0.75 V vs SCE). This result is consistent with electron transfer from reduced bipyridine to the ITO electrode as a necessary step in the photocurrent process. Thus, part a or part b of Scheme I summarizes the events associated with photoelectrochemical oxidation of TEA. Since TEA is consumed, we cannot conclude that we can sustain conversion of light to electricity. However, we do conclude that we can sustain photoelectrochemical oxidation of TEA at potentials where oxidation does not occur in the dark.

In solution, the excited-state lifetime of the model complex **1b** is 339 ns, much longer than that of **1a** on electrode surfaces (145 ns/ITO, 35 ns/Pt). Shorter excited-state lifetimes for electrode-confined species show that excited-state quenching occurs; however, the excited state is long-lived enough to be efficiently quenched by TEA to give a photocurrent response similar to that of electrodes modified with **2a**. The similar photocurrent response for electrode-confined **1a** and **2a** shows that no advantage is obtained by using the two-component chromophore/donor complex **2a** for the photoelectrochemical oxidation of sacrificial donor TEA. In developing systems for sustained light to electrical energy conversion, reversible donors will be required and charge separation across long distances will likely be necessary to avoid back-electron-transfer. With TEA as donor, irreversible chemical reactions compete with back-electron-transfer. Our key finding is that Pt or ITO electrodes do not quench the excited state of the Re species at a rate that precludes efficient intermolecular, **1a**, or intramolecular, **2a**, electron transfer.