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# Long-Distance Electron Transfer Across Molecule−Nanocrystalline Semiconductor Interfaces

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Tremendous insights into the mechanisms for electron transfer have been gained over the last 15 years by studying donor−spacer−acceptor model systems of varying complexity.[1] Important and classic experiments involving redox active molecules separated by hydrocarbon,[2,3] peptidic,[4] protein,[5] and DNA[6] spacers, have thoroughly revealed the distance dependence for electron-transfer processes in fluid solutions. Related studies of surface-mediated electron transfer have utilized molecules positioned at variable distances from planar surfaces and electrodes by means of self-assembled monolayers,[7] inert gas spacers,[8] and Langmuir−Blodgett films.[9]

To date, however, no systematic studies have been performed of fixed-distance electron transfer across semiconductor nanoparticles. Electronic interactions across molecule−nanoparticle interfaces are finding applications in several emerging fields of chemistry and provide the basis for new classes of molecular devices.[10] Control over the distance between molecules and nanoparticles will ultimately lead to a deeper understanding of interfacial electron transfer. Previous researches have attempted to fix the distance with limited success.[11,12] Here we report a new strategy for studying fixed-distance electron transfer at nanoparticle interfaces and the first experiments with metal oxide nanocrystallites that have resulted in rapid ($k_{et} > 10^8$ s$^{-1}$) interfacial electron transfer over an 18 Å distance.[13]

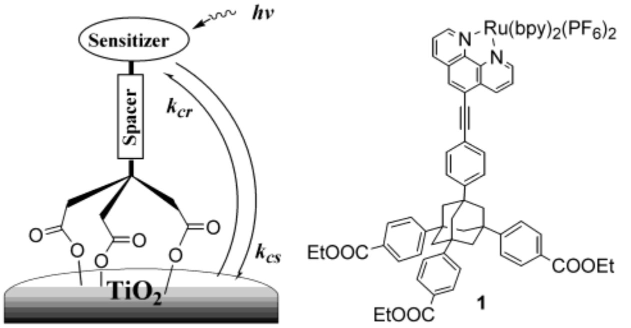

**Figure 1.** Schematic representation of a surface-bound molecular tripod (left) and structure of Ru(Ad-Ph-E-phen)(bpy)$_2$(PF$_6$)$_2$ **1** (right).

The general strategy is to utilize a tripod-shaped organic molecule as a rigid, three-point anchor that can position a redox active molecule at a variable, yet fixed distance with respect to the surface of a semiconductor nanoparticle, Figure 1.[13,14] By incorporating three surface-binding groups into one molecule, the orientation shown in Figure 1 is thermodynamically favored.[15] A chromophoric electron donor was employed so that the kinetic rate constants for interfacial electron transfer to, $k_{cs}$, and from, $k_{cr}$, a semiconductor nanocrystallite can be quantified spectroscopically after selective light excitation.

The first "molecular tripod" prepared, Ru(Ad-Ph-E-phen)(bpy)$_2$(PF$_6$)$_2$,[16] **1**, is an adamantane derivative having three phenyl arms each terminating with an ester group and a fourth phenylethynyl arm bearing the sensitizer, Ru(phen)(bpy)$_2$(PF$_6$)$_2$. The Ru complex **1** was prepared from the ligand Ad-Ph-E-phen, which was recently synthesized in our laboratories.[17]

Infrared measurements of **1** revealed a single asymmetric CO stretch at 1708 cm$^{-1}$. An acetonitrile solution of **1** displayed the expected metal-to-ligand charge transfer, MLCT, band in the visible region ($\lambda_{max} = 450$ nm, $\epsilon = 16\,200$ M$^{-1}$ cm$^{-1}$) and room-temperature photoluminescence ($\lambda_{max} = 624$ nm) with a long excited-state lifetime, $\tau = 1.44$ $\mu$s. Tripod **1** was bound to mesoporous thin films of anatase TiO$_2$ or, for some experiments, insulating ZrO$_2$ particles. For brevity, surface-bound **1** is abbreviated as **1**/TiO$_2$ or **1**/ZrO$_2$. The TiO$_2$ nanocrystallites were approximately 20 nm in diameter and were deposited as ~10 $\mu$m thick, mesoporous films on tin-oxide coated glass, glass, or sapphire substrates. Spectroscopic, electrochemical, and photo-

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[13] This is the distance of the Ru center from the plane defined by the three surface-bound O (the footprint). This distance is therefore most appropriate for interfacial charge recombination since interfacial charge separation occurs from an electron localized on a ligand in the MLCT excited state.

[14] The footprint of **1** is ~70 Å$^2$, which covers about five Ti atoms on the (001) face of anatase TiO$_2$.

[15] As surface-binding groups were chosen esters, that are known to form strong bonds to TiO$_2$ with high adduct formation constants, $K_{ad} = (2-10) \times 10^4$ M$^{-1}$: (a) Nazeeruddin, M. K.; Liska, P.; Moser, J.; Vlachopoulos, N.; Grätzel, M. *Helv. Chim. Acta* **1990**, *73*, 1788. (b) Péchy, P.; Rotzinger, F. P.; Nazeeruddin, M. K.; Kohle, O.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M. *Chem. Commun.* **1995**, 65.

[16] Abbreviations used in this paper: bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline; Ad-Ph-E-phen = 1-[4-(5-(1,10-phenanthrolinyl)ethynyl)phenyl]-3,5,7-(4-carboethoxyphenyl)adamantane; dcb = 4,4′-(COOH)$_2$-2,2′-bipyridine; deeb = 4,4′-(COOEt)$_2$-2,2′-bipyridine.

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electrochemical measurements were made as previously described.[18]

Surface binding of **1** to $TiO_2$ follows the Langmuir adsorption isotherm model from which an adduct formation constant was obtained, $K_{ad} = 3 \times 10^6\ M^{-1}$, which is about 2 orders of magnitude larger than those reported for binding of Ru(II) sensitizers through deeb ligands.[15] The limiting surface coverage is $3 \times 10^{-8}$ mol $cm^{-2}$ and is typical of other Ru(II) compounds. Infrared measurements of **1**/$TiO_2$ revealed an asymmetric C═O stretch at 1720 $cm^{-1}$. The ~12 wavenumber shift to higher energy upon surface binding is consistent with ester-type linkages,[19] and the appearance of just one stretch indicates that all three groups bind in a similar fashion. The UV−vis absorption spectra of **1**/$TiO_2$ and **1** in solution were unchanged, consistently with weak electronic coupling between the Ru(II) sensitizer and the semiconductor. Finally, **1**/$TiO_2$ could be reversibly oxidized electrochemically in $CH_3CN$ electrolyte at + 1.29 V vs Ag/AgCl. In summary, the spectroscopic and electrochemical properties of **1**/$TiO_2$ are consistent with the surface attachment geometry represented in Figure 1.

Time-resolved absorption spectroscopy was used to characterize the excited states of **1**/$ZrO_2$ and to measure the yields and rate constants of interfacial electron transfer in **1**/$TiO_2$. On insulating $ZrO_2$, the absorbance difference spectra measured after pulsed 532.5 nm light excitation were identical to that measured in fluid solution and are typical of MLCT excited states. The long excited-state lifetime of **1** compared to $Ru(phen)(bpy)_2^{2+}$ ($\tau = 1.20\ \mu s$), suggests electronic delocalization of the excited state onto the phenylethynyl spacer.[20] Calculations indicate that in **1** the ligand-centered LUMO is delocalized over the phenylethynyl spacer.[21]

The absorption difference spectra observed for **1**/$TiO_2$ are shown in Figure 2. There is no evidence for the presence of excited states, and the spectra are due to an interfacial charge-separated state with an oxidized **1** and an electron in $TiO_2$. Remarkably, this state forms within the 10 ns instrument response function, demonstrating the occurrence of rapid interfacial electron transfer, $k_{cs} > 10^8\ s^{-1}$, over a large distance. Charge recombination of the injected electron with the Ru(III) center is complete within about 200 $\mu$s, and the recombination kinetics are well described by a sum of two second-order kinetic rate constants, Figure 2, inset. Uncertainties in the extinction coefficient and optical path length preclude meaningful reports of the true second-order rate constants. Second-order equal concentration kinetics were expected as have been previously observed for $TiO_2(e^-) \rightarrow$ Ru(III) charge recombination.[18] Remarkably, however, we found that charge recombination for **1**/$TiO_2$ is much *faster* than that previously reported for Ru(II) compounds bound to anatase $TiO_2$ through dcb ligands.[22] An interesting comparison is with $Ru(deeb)(bpy)_2^{2+}$ which has a similar Ru(III/II) potential (1.30 V vs Ag/AgCl) yet charge recombination is about 3 orders of magnitude slower (200 ms) under identical conditions of irradiance, electrolyte, and temperature, Figure 2, inset.

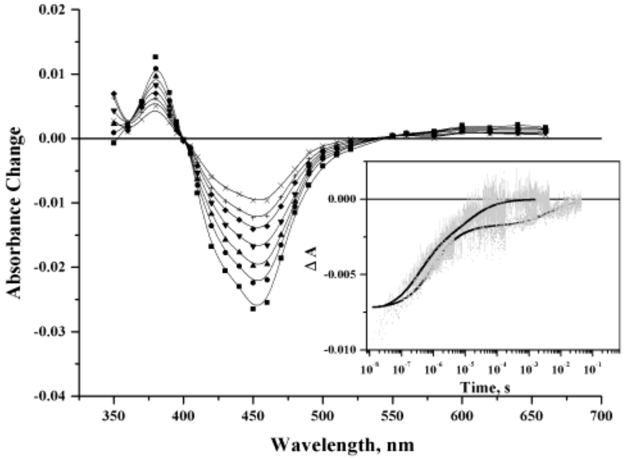

**Figure 2.** Time-resolved absorption difference spectra obtained after pulsed 532.5 nm light (5 mJ/$cm^2$, fwhm 8 ns) excitation of **1**/$TiO_2$ in $CH_3CN$ at r.t. The spectra are shown at delay times of (■) 0 ns, (●) 50 ns, (▲) 100 ns, (▼) 200 ns, (◆) 500 ns (+) 1 $\mu$s, and (×) 2 $\mu$s. (Inset) Single wavelength transients monitored at ground/excited-state isosbestic points for **1**/$TiO_2$ and $Ru(deeb)(bpy)_2^{2+}/TiO_2$. The fit to a second-order kinetic model is overlaid as a solid line on the data.

The faster charge recombination observed for **1** was not expected, considering the 18 Å distance of the Ru center from the surface. Our working hypothesis is that the phenylethynyl spacer and the large footprint[14] of **1** are responsible for the fast recombination. Further studies will test this hypothesis by tuning the $\pi^*$ levels of the spacer and systematically controlling the footprint size.

A specific application of these materials is as photoanodes in regenerative solar cells.[22] Photoelectrochemical studies demonstrate that **1**/$TiO_2$ does convert light into electricity as efficiently as other Ru(II) complexes at individual wavelengths of light. A potential advantage of positioning a chromophore at some distance from the semiconductor surface is that recombination to the oxidized donors (typically iodide) will be inhibited. This will not significantly increase the photocurrent, but it is expected to have a significant effect on the open circuit photovoltage and hence increase the power output.[22] Studies designed to quantify this behavior are underway.

In summary, we have reported a new approach for studying fixed distance electron transfer at molecule−nanoparticle interfaces and the first experiments with $TiO_2$ nanocrystallites. This approach can easily be extended to other nanoparticles, for instance colloidal metals, simply by changing the functional groups responsible for surface binding. Furthermore, the size of the footprint and the length of the spacer can be independently varied for specific applications.

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**Supporting Information Available:** The experimental procedure and characterization data for **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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