

Remote Interfacial Electron Transfer from Supramolecular Sensitizers

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There has been intense research in light-to-electrical energy conversion with ruthenium(II) polypyridyl charge transfer sensitizers anchored to wide bandgap semiconductors such as TiO₂.^{1–3} In an effort to achieve improved molecular control of sensitizer orientation we turned to bimetallic coordination compounds based on rhenium and ruthenium where the facial geometry of the Re center holds a Ru sensitizer proximate to the TiO₂ surface, Scheme 1. In this communication, we report the photophysical and photoelectrochemical properties of two Re–Ru linkage isomers in solution and the same isomers anchored to nanostructured TiO₂ films. The results demonstrate rapid efficient interfacial electron transfer and a remarkably high light-to-electrical energy conversion even though the sensitizer is remote to the semiconductor-bound ligand.

The preparation of [(4,4'-(CO₂H)₂bpy)Re^I(CO)₃–CN–Ru^{II}–(bpy)₂(CN)](PF₆), abbreviated Re–CN–Ru, and [(4,4'-(CO₂H)₂bpy)Re^I(CO)₃–NC–Ru^{II}(bpy)₂(CN)](PF₆), abbreviated Re–NC–Ru, are described in Supporting Information. We note that related compounds have been previously described in the literature.^{4–6} *cis*-Ru(bpy)₂(CN)₂ and *cis*-Ru(4,4'-(CO₂H)₂bpy)₂(CN)₂ were available from previous studies.² TiO₂ electrodes for photoelectrochemical measurements were prepared from commercially available Degussa P25 TiO₂ as has been previously described.^{2b} Nanocrystalline TiO₂ films with high transmission in the visible region were utilized for time-resolved absorbance measurements.^{1a} Photoluminescence (PL) measurements were performed in methanol with apparatus which has been previously described.⁷ Excited state absorption measurements were made in neat propylene carbonate with previously described apparatus.⁸ Photoelectrochemical measurements were performed with an electrometer in a sandwich cell arrangement.^{2b,8} The photoaction spectra were corrected for the small fraction of light absorbed by the tin oxide support.

The electrochemical and spectroscopic properties of the linkage isomers were explored in methanol, Table 1. Both compounds display intense visible metal-to-ligand charge

Scheme 1

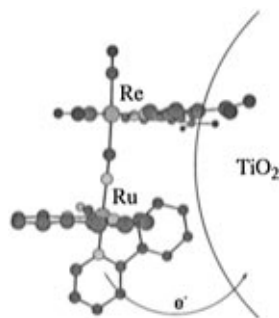


Table 1. Photophysical and Electrochemical Properties of the Sensitizers in Methanol

sensitizer ^a	λ , Abs (nm) ^b	λ , PL (nm) ^c	τ (ns) ^d	ϕ^e	$E_{1/2}$
Re–CN–Ru	460	650	340	0.0138	1.03
Re–NC–Ru	442	620	640	0.0517	1.16

^a Sensitizers where Re–CN–Ru is [(4,4'-(CO₂H)₂bpy)Re^I(CO)₃–CN–Ru^{II}(bpy)₂(CN)](PF₆) and Re–NC–Ru is [(4,4'-(CO₂H)₂bpy)Re^I(CO)₃–NC–Ru^{II}(bpy)₂(CN)](PF₆). ^b The visible absorption maximum, ± 2 nm. ^c The corrected photoluminescence (PL) maximum, ± 4 nm. ^d The excited state lifetime in argon saturated methanol, $\pm 5\%$. ^e The quantum yield for photoluminescence. ^f $E_{1/2}$ for the Ru^{III/II} couple vs SCE.

transfer (MLCT) absorption bands, which extend beyond 450 nm. With 460 nm excitation, room temperature PL is observed. The Re–NC–Ru isomer displays a corrected PL maximum at 620 nm and the Re–CN–Ru isomer at 650 nm. Time-resolved PL kinetics were first order. Cyclic voltammetry reveals a reversible wave assigned to the Ru^{III/II} couple. The Re–CN–Ru isomer is 130 mV easier to oxidize than the Ru–CN–Re isomer. Information on the Re^{III/I} couple could not be obtained due to the onset of methanol oxidation, $E_{1/2} > 1.5$ V vs SCE.

Photoaction spectra shown in Figure 1 very closely resemble the shape of the absorbance band. A remarkably high monochromatic photocurrent efficiency is observed for both bimetallic sensitizers. The photoelectrochemical properties of these dimers at individual wavelengths of light places them among the most efficient sensitizers studies to date.^{1–3} Under white light excitation the performance is not as impressive due to the weak absorbance at long wavelengths. The MLCT absorption maximum of monomeric (4,4'-(COOH)₂bpy)Re^I(CO)₃CN is in the ultraviolet region, $\lambda_{\max} = 386$ in methanol, which indicates that excitation in the range of 450–600 nm produces almost exclusively the MLCT excited state of the ruthenium unit, [(4,4'-(COOH)₂bpy)Re^I(CO)₃–CN–Ru^{III}(bpy^{•+})(bpy)(CN)]^{+*}. To better understand the molecular electron transfer processes that convert this MLCT state to an electrical current, excited state absorption measurements were performed.

The excited state absorption difference spectra of the dimers in methanol solution with 532 nm light excitation show an isosbestic point and kinetics which agree well with the time

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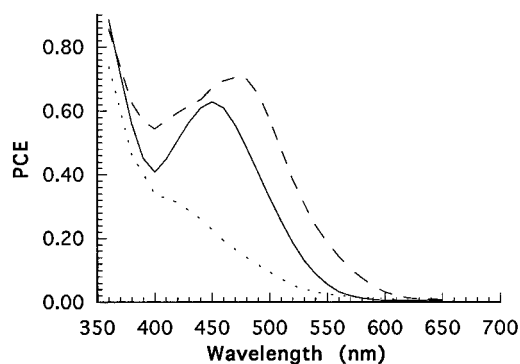


Figure 1. Photoaction spectra of [(4,4'-(CO₂H)₂bpy)Re^I(CO)₃-CN-Ru^{II}(bpy)₂(CN)](PF₆) (---), [(4,4'-(CO₂H)₂bpy)Re^I(CO)₃-NC-Ru^{II}(bpy)₂(CN)](PF₆) (—), and (4,4'-(CO₂H)₂bpy)Re^I(CO)₃(CN) (···) bound to nanocrystalline TiO₂ films. The PCE is the photon-to-current efficiency measured in a 0.5 M NaI, 0.05 M I₂ propylene carbonate electrolyte.

resolved PL data. The spectral features are coincident with *cis*-Ru(bpy)₂(CN)₂ measured under the same conditions. The excited state absorption difference spectra for the sensitizers bound to transparent TiO₂ reveal a broad bleach from 400 to 600 nm. By monitoring at the isosbestic wavelength, the kinetics for the formation and loss of Re^I-NC-Ru^{III} state or the Re^I-NC-Ru^{III} state can be quantified. At this wavelength the bleach is promptly observed after the laser pulse. This indicates that either electron injection into TiO₂ or intraligand hopping, from bpy to 4,4'-(COOH)₂-bpy, occurs within 20 ns ($k > 5 \times 10^7$ s⁻¹). Our inability to time resolve positive absorption bands that might be attributed to the reduced ligands precludes us from distinguishing between these two possibilities.

The recovery of this transient is attributed to electron tunneling from TiO₂ donor state(s) to the oxidized Ru^{III} center which yields ground state products.⁹ This process competes directly with photocurrent production. Assuming a common donor for both sensitizers, the driving force for this process is 130 mV larger for the Re-NC-Ru isomer. The observed kinetics are complex and well described by the Kohlrausch-Williams-Watts function.¹⁰ Average rate constants calculated with this function are the same for the two sensitizers within experimental error, $3.1 \pm 0.4 \times 10^5$ s⁻¹ for Re-NC-Ru/TiO₂ and $2.5 \pm 0.4 \times 10^5$ s⁻¹ for Re-CN-Ru/TiO₂. These rates are approximately a factor of two slower than *cis*-(4,4'-(CO₂H)₂-bpy)₂Ru^{II}(CN)₂/TiO₂, $6.1 \pm 0.4 \times 10^5$ s⁻¹, which has a similar redox potential,² measured under the same conditions. It has recently been shown that a slow recombination process produces a higher power output in a regenerative solar cell.¹¹ The difference in recombination observed here is not sufficient to manifest itself in a larger power output. However, the decreased rate suggests that an as of yet undetermined optimal sensitizer-TiO₂ orientation exists wherein quantitative electron injection still occurs, but the back-reaction to ground state products is further inhibited.

These sensitizers are anchored to TiO₂ through the dehydrative coupling of surface hydroxyl groups with the carboxylic

acid groups on the bipyridine ligand to form ester linkages.¹² Goodenough first proposed that the ester linkage should enhance electronic coupling between the π^* orbitals of the bipyridine ring and the Ti 3d orbital manifold of the semiconductor.¹² In support of this, a comparison of the solution absorption spectrum with the photoaction spectrum on rutile reportedly reveals a significant red shift upon surface attachment.¹³ A similar energy shift was observed for *cis*-Ru(4,4'-(COOH)₂bpy)₂(NCS)₂ anchored to anatase nanocrystalline films,^{1b} which is consistent with stabilization of the MLCT excited states by the TiO₂ surface. Vibrational studies support the presence of surface ester bonds.^{2b} However, whether this linkage increases photocurrent efficiency or promotes electronic coupling between the sensitizer and the surface remains largely unknown.

The data reported here strongly suggest that a direct chemical bond between the chromophoric ligand of Ru(II) sensitizers and the TiO₂ surface is not a requirement for efficient electron injection. While it could be argued that these supramolecular sensitizers represent a special case, this scenario appears unlikely. For example, the photoelectrochemical properties of ruthenium(II) polypyridyl sensitizers that contain a propylene spacer between the bipyridine ligand and the surface anchoring group reveal monochromatic PCE's of 0.3–0.5.⁸ Further, in the original report of sensitization of rutile single crystals by ruthenium(II) polypyridyl sensitizers, Clark and Sutin concluded that the quantum yield for electron injection from Ru(4,7-(CH₃)₂-1,10-phenanthroline)₃^{2+*} is close to unity despite a low photocurrent observed.¹⁴ It therefore appears that efficient electron injection from MLCT excited states to TiO₂ can occur in the absence of *any* semiconductor-to-sensitizer link. An important implication from this conclusion is that sensitizers anchored to TiO₂ through nonchromophoric ligands or without a direct chemical bond may also be efficient for sensitization of wide bandgap nanocrystalline semiconductors.

In summary, rapid and efficient remote injection from two supramolecular sensitizers into TiO₂ nanocrystalline films has been demonstrated. When employed in regenerative solar cells, these sensitizers convert light into electricity with high efficiencies despite the fact that the chromophoric unit, -Ru(bpy)₂, is not directly bound to the semiconductor surface. The photocurrent efficiency is comparable and the charge-separated pair lifetime is slightly longer than the related *cis*-Ru(4,4'-(COOH)₂bpy)₂(CN)₂ sensitizer. Finally, we note that supramolecular sensitizers continue to provide insights into interfacial electron transfer processes and fundamental optoelectronic aspects of these fascinating materials.

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Supporting Information Available: Text giving the synthesis of the supramolecular sensitizers and a figure showing time-resolved absorption data (3 pages). Ordering information is given on any current masthead page.

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