

Molecular Rectification by a Bimetallic Ru–Os Compound Anchored to Nanocrystalline TiO<sub>2</sub>

Cornelius Kleverlaan, Monica Alebbi, Roberto Argazzi, and Carlo A. Bignozzi\*

Dipartimento di Chimica dell' Università, Centro di Studio su Fotoreattività e Catalisi CNR, 44100 Ferrara, Italy

Georg M. Hasselmann and Gerald J. Meyer\*

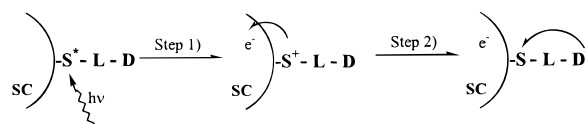
Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218

Received November 9, 1999

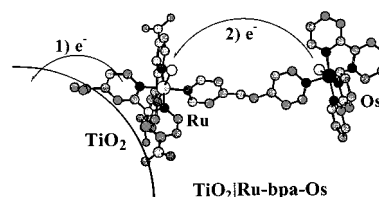
Supramolecular coordination compounds represent a new class of chromophores for sensitization of wide band gap semiconductors to visible light.<sup>1–7</sup> An important strategy for this application is shown in Scheme 1, where a sensitizer, S, is anchored to a semiconductor surface, SC, with an electron donor, D, covalently bound through a bridging ligand, L.<sup>6,7</sup> Light excitation of the sensitizer forms an excited state, S\*, that rapidly injects an electron into the semiconductor, step 1. Intramolecular electron transfer translates the “hole” from the oxidized sensitizer to the covalently bound donor, step 2. This sequence of electron transfer can result in an enhanced lifetime of the interfacial charge separated state, improved power output in regenerative solar cells, and photochromic materials.<sup>6,7</sup> Inorganic donors provide a high degree of molecular flexibility as systematic changes in the ancillary ligands can be used to finely tune the driving force for intramolecular electron transfer, step 2, and the spectral properties of the materials. Here we report the first proof-of-concept example with semiconductor-bound bimetallic coordination compounds that behave like molecular photodiodes: light promotes rapid electron transfer into and hole transfer away from the solid.

The compound of interest is [Ru(dcb)<sub>2</sub>(Cl)-bpa-Os(bpy)<sub>2</sub>(Cl)]-(PF<sub>6</sub>)<sub>2</sub>, abbreviated Ru-bpa-Os where dcb is 4,4'-(COOH)<sub>2</sub>-2,2'-bipyridine and bpa is 1,2-bis(4-pyridyl)ethane. An idealized structure of this coordination compound bound to TiO<sub>2</sub>, abbreviated TiO<sub>2</sub>|Ru-bpa-Os, is shown in Scheme 2. The synthesis, purification, and characterization are given in the Supporting Information, as well as that for Ru(dcb)<sub>2</sub>(py)Cl, where py is pyridine, which serves as a model. The bpa bridge provides weak electronic coupling between Ru(II) and Os(II) as shown by the lack of a measurable intervalence charge transfer band in the one-electron-oxidized form.<sup>8</sup> The visible absorption spectrum is well represented as a sum of the individual Ru(dcb)<sub>2</sub>(py)Cl and Os(bpy)<sub>2</sub>(bpa)Cl<sup>+</sup> spectra with overlapping Ru → dcb and Os → bpy charge transfer band centers ~450 nm and a spin-forbidden <sup>3</sup>MLCT, Os → bpy, charge transfer band centered around 720 nm. The bimetallic and model compounds are nonemissive in

## Scheme 1

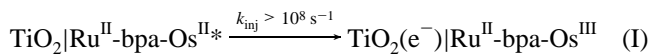


## Scheme 2



acetonitrile or methanol solutions at room temperature. Cyclic voltammetry of the bimetallic compound in 1.0 M LiClO<sub>4</sub> yields  $E_{1/2}(\text{Ru(III/II)}) = +0.98 \text{ V}$  and  $E_{1/2}(\text{Os(III/II)}) = +0.36 \text{ V}$  vs SCE. The model compound gives a single wave with  $E_{1/2}(\text{Ru(III/II)}) = +0.9 \text{ V}$  vs SCE in a methanol electrolyte solution. The coordination compounds anchor to nanocrystalline TiO<sub>2</sub> films in high surface coverages as previously described.<sup>9</sup> The methods for measuring interfacial electron transfer rates have been published.<sup>9</sup>

Pulsed blue (417 nm), green (532.5 nm), or red (683 nm) light excitation of TiO<sub>2</sub>|Ru-bpa-Os results in indistinguishable absorption difference spectra, Figure 1. Comparison of these spectra with one generated by stoichiometric oxidation of Os(II) with Ce(IV) shows that the transient is reasonably assigned to an interfacial charge-separated state with an electron in TiO<sub>2</sub> and an Os(III) center, abbreviated TiO<sub>2</sub>(e<sup>-</sup>)|Ru-bpa-Os(III). Red light (683 nm) selectively forms the Os → bpy metal-to-ligand charge transfer (MLCT) excited state, that rapidly injects an electron into TiO<sub>2</sub> with an injection rate constant,  $k_{\text{inj}}$ , faster than our instrument response, eq 1. Remote injection of this type probably results from



the flexible bpa bridge that allows alternative surface orientations, not shown in the idealized Scheme 2, which park the Os(II) centers proximate to the semiconductor surface.<sup>5</sup>

Blue (417 nm) or green (532 nm) light excitation produces both the Ru and Os MLCT excited states in relative concentrations proportional to their ground state absorption at these wavelengths. We have demonstrated that light absorbed by the Ru(II) chromophore is converted into charge-separated states by comparative actinometry studies of TiO<sub>2</sub>|Ru(dcb)<sub>2</sub>(py)Cl and TiO<sub>2</sub>|Ru-bpa-

(1) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Harwood: Chichester, U.K., 1990.

(2) Bignozzi, C. A.; Schoonover, J. R.; Scandola, F. *Prog. Inorg. Chem.* **1997**, *44*, 1.

(3) Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. *J. Am. Chem. Soc.* **1990**, *112*, 7099.

(4) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

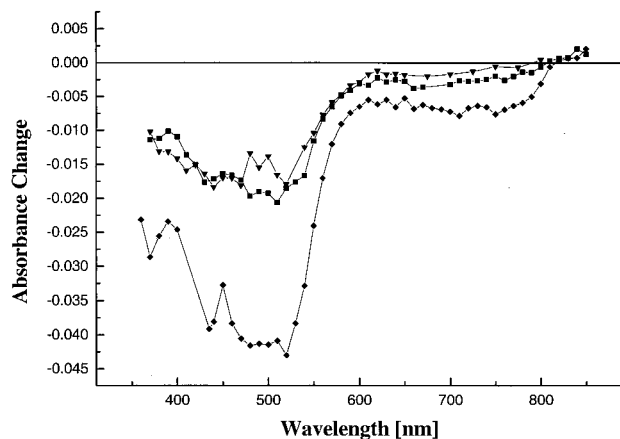
(5) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Meyer, G. J. *Inorg. Chem.* **1997**, *36*, 2.

(6) (a) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *J. Phys. Chem. B* **1997**, *101*, 2591. (b) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *J. Am. Chem. Soc.* **1995**, *117*, 11815.

(7) Bonhote, P.; Moser, J.-E.; Humphry-Baker, R.; Vlachopoulos, N.; Zakeeruddin, S. M.; Walder, L.; Grätzel, M. *J. Am. Chem. Soc.* **1999**, *121*, 1324.

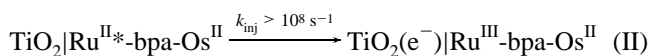
(8) (a) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289. (b) Goldsby, K. A.; Meyer, T. J. *Inorg. Chem.* **1973**, *12*, 2371.

(9) Heimer, T. A.; D'Arcangelis, S. T.; Farzad, F.; Stipkala, J. M.; Meyer, G. J. *Inorg. Chem.* **1996**, *35*, 5319.

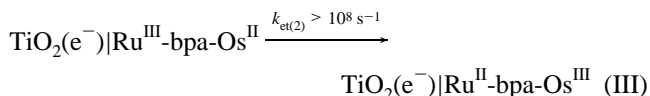


**Figure 1.** Visible absorption difference spectrum of a  $\text{TiO}_2/\text{Ru-bpa-Os}$  material immersed in a 1.0 M  $\text{LiClO}_4$  acetonitrile solution at 25 °C recorded 100 ns after pulsed (8–10 ns fwhm,  $\sim 5 \text{ mJ/cm}^2$ ) light excitation at 417 (◆), 532.5 (■), and 683 nm (▼). The normalized spectra (not shown) are within experimental error the same and assigned to an interfacial charge-separated state with an electron in  $\text{TiO}_2$  and an Os(III) center, abbreviated  $\text{TiO}_2(e^-)|\text{Ru-bpa-Os(III)}$ .

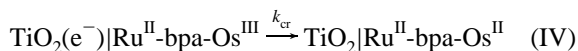
Os. The injection yields in 1.0 M  $\text{LiClO}_4$  in acetonitrile with 532 nm excitation were the same for these two sensitized materials within experimental error,  $\pm 10\%$ . Therefore,  $\text{Ru(II)}^*$  excited states lead to charge separation most probably by direct injection into  $\text{TiO}_2$ , eq II.<sup>10</sup>



The product of eq II,  $\text{TiO}_2(e^-)|\text{Ru}^{\text{III}}\text{-bpa-Os}^{\text{II}}$ , is not observed spectroscopically under any conditions due to rapid intramolecular hole transfer from Ru(III) to Os(II), eq III. The driving force for intramolecular hole transfer is 0.6 V and  $k_{\text{et}(2)} > 10^8 \text{ s}^{-1}$ .



Interfacial charge recombination of the electron in  $\text{TiO}_2$  with the Os(III) center, eq IV, requires milliseconds for completion.



The interfacial electron transfer rates are independent of whether the  $\text{TiO}_2(e^-)|\text{Ru-bpa-Os(III)}$  state was created by direct injection from Os(II), red light excitation, or the two-step path depicted in eqs III and IV. Typical charge recombination data is given in the Supporting Information.

No significant photocurrent is observed when  $\text{TiO}_2/\text{Ru-bpa-Os}$  is used as a photoanode in a regenerative solar cell with 0.5 M  $\text{LiI}/0.05 \text{ M I}_2$  in acetonitrile. This is expected because the Os(III) center is a weak oxidant and charge recombination is faster than iodide oxidation.<sup>13</sup> The lack of a photocurrent indicates that

iodide oxidation by Ru(III) formed after blue or green light excitation does not compete kinetically with intramolecular electron transfer from Os(II).

In summary, the first bimetallic sensitizer designed to display diode-like behavior at semiconductor surfaces is reported. This interface clearly rectifies charge with forward electron transfer rates at least 5 orders of magnitude faster than charge recombination. We note that the design of this compound was largely inspired by the electropolymerized, spatially segregated, two-layer films of Ru(II) and Os(II) reported by Meyer and Murray several years ago.<sup>14</sup> In this work, a Ru(II) polymer layer insulates an outer Os(II) layer from the electrode and charge could be trapped as Os(III) for hours compared to the milliseconds for the molecular analogue reported here. The flexible bpa ligand employed and the geometry about Ru(II) allow direct  $\text{Os(II)}^* \rightarrow$  semiconductor electron transfer and probably provide a direct pathway for charge recombination as well. Future studies will focus on control of the surface orientation and systematic tuning of the thermodynamic driving forces for the light-driven electron transfer processes that control the optoelectronic properties of these fascinating molecular materials.

**Acknowledgment.** This work was supported by EU under the Joule III program, Contract JOR3-CT98-7040. The Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, is gratefully acknowledged for research support. G.M.H. thanks the Link Foundation for an Energy fellowship, and C.K. acknowledges financial assistance from EU under the TMR program FMRX-CT96-0076.

**Supporting Information Available:** The synthesis and characterization of the sensitizers, the injection yields, and recombination kinetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC991311H

- (10) In comparative actinometry experiments the relative injection yields of the model and bimetallic sensitizers were measured under conditions where the ground state absorptions at the 532 nm excitation wavelength were the same. Typical data is given in the Supporting Information. The results demonstrate that  $\text{Ru(II)}^*$  excited states in the model and bimetallic sensitizers lead to charge-separated states with the same efficiency, but do not rule out a  $\text{Ru(II)}^*$  injection mechanism where energy transfer to Os(II) is followed by  $\text{Os(II)}^*$  injection for  $\text{TiO}_2/\text{Ru-bpa-Os}$ . For this pathway to occur, intramolecular energy transfer would have to be kinetically competitive with electron injection. Considering known energy transfer rate constants for related Ru–Os polypyridyl compounds<sup>11</sup> and the ultrafast injection rates recently reported,<sup>12</sup> this pathway seems highly improbable.
- (11) Schlicke, B.; Belsler, P.; DeCola, L.; Sabbioni, E.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 4207.
- (12) (a) Tachibana, Y.; Moser, J. E.; Grätzel, M.; Klug, D. R.; Durrant, J. R. *J. Phys. Chem.* **1996**, *100*, 20056. (b) Hannappel, T.; Burfeindt, B.; Storck, W.; Willig, F. *J. Phys. Chem. B* **1997**, *101*, 6799. (c) Heimer, T. A.; Heilweil, E. J. *J. Phys. Chem. B* **1997**, *101*, 10990. (d) Ellingson, R. J.; Asbury, J. B.; Ferrere, S.; Ghosh, H. N.; Sprague, J. R.; Lian, T.; Nozik, A. J. *J. Phys. Chem. B* **1998**, *102*, 6455.
- (13) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Hasselmann, G. M.; Meyer, G. J. *J. Phys. Chem. B* **1998**, *102*, 7577.
- (14) Abruna, H. D.; Denisevich, P.; Umama, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1.