Competitive Intermolecular Energy Transfer and Electron Injection at Sensitized Semiconductor Interfaces

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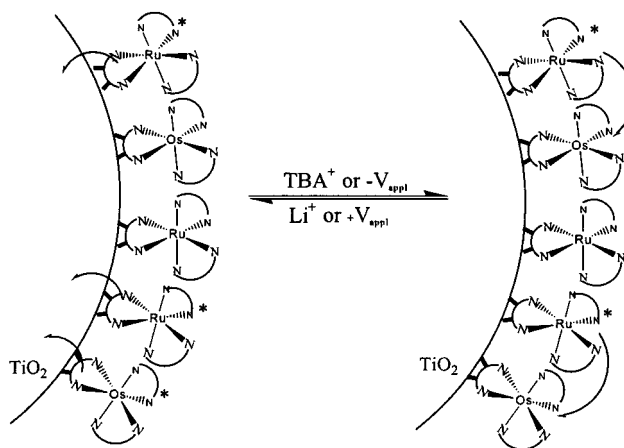
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Sensitization of nanocrystalline TiO$_2$ electrodes with molecular chromophores forms the basis for efficient solar energy conversion in regenerative photoelectrochemical cells.[1] The study of interfacial electron-transfer dynamics in these solar cells is an area of intense and active investigation.[2−14] The nanocrystalline materials also have the potential to act as supports for molecular reagents and could increase the efficiency of reactions that are otherwise limited by diffusive encounters in fluid solution. The ability to photoinduce interfacial electron transfer coupled with exploitation of lateral reaction chemistry will produce materials that have applications that extend beyond solar energy conversion. Here we report an unprecedented example of molecular excited states that can be switched from lateral energy transfer across a nanocrystalline TiO$_2$ surface to orthogonal interfacial electron injection by electrolyte modification or with an externally applied potential. Significantly, the process is reversible and serves as a molecular charge−energy transfer switch, Scheme 1.

Nanocrystalline TiO$_2$ electrodes were prepared through a previously described sol−gel route that yields ∼20 nm anatase particles interconnected in a mesoporous ∼10 μm thick film.[6c] Ru(dcb)(bpy)$_2$(PF$_6$)$_2$ and Os(dcb)(bpy)$_2$(PF$_6$)$_2$, where dcb is 4,4′-(COOH)$_2$-2,2′-bipyridine, have previously been described in the literature.[15,16] The diethyl ester derivatives, deeb, were also prepared and anchored to TiO$_2$. The photoluminescence (PL) properties were characterized in argon saturated acetonitrile: for Ru(deeb)(bpy)$_2$(PF$_6$)$_2$ τ = 930 ns, λ_{max} = 690 nm, ϕ_{PL} = 4.4 × 10^{-2}, and for Os(deeb)(bpy)$_2$(PF$_6$)$_2$ τ = 40 ns, λ_{max} = 840 nm,

(1) O'Regan, B.; Grätzel, M. *Nature* **1991,** *353,* 737.
(2) (a) Bach, U.; Lupo, D.; Comte, R.; Moser, J. E.; Weissortel, F.; Salbeck, J.; Spreitzer, H.; Grätzel, M. *Nature* **1998,** *342,* 583. (b) Haque, S. A.; Tachibana, Y.; Klug, D. R.; Durrant, J. R. *J. Phys. Chem. B* **1998,** *102,* 1745. (c) Bonhôte, P.; Gogniat, E.; Tingry, S.; Barbé, C.; Vlachopoulos, N.; Lenzmann, F.; Comte, P.; Grätzel, M. *J. Phys. Chem. B* **1998,** *102,* 1498.
(3) Hannappel, T.; Burfeindt, B.; Storck, W.; Willig, F. *J. Phys. Chem. B* **1997,** *101,* 6799.
(4) Heimer, T. A.; Heilweil, E. J. *J. Phys. Chem. B* **1997,** *101,* 10990.
(5) 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.
(6) (a) Thompson, D. W.; Kelly, C. A.; Farzad, F.; Meyer, G. J. *Langmuir* **1999,** *15,* 650. (b) Argazzi, R.; Bignozzi, C. A.; Hasselmann, G. M.; Meyer, G. J. *Inorg. Chem.* **1998,** *37,* 4533. (c) Heimer, T. A.; D'Arcangelis, S. T.; Farzad, F.; Stipkala, J. M.; Meyer, G. J. *Inorg. Chem.* **1996,** *35,* 5319.
(7) (a) Lu, H.; Prieskorn, J. N.; Hupp, J. T. *J. Am. Chem. Soc.* **1993,** *115,* 4927. (b) Yan, S. G.; Hupp, J. T. *J. Phys. Chem.* **1996,** *100,* 6867.
(8) (a) Nasr, C.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem. B* **1998,** *102,* 4944. (b) Bedja, I.; Hotchandani, S.; Kamat, P. V. *Ber. Bunsen-Ges Phys. Chem.* **1998,** *3122.*
(9) Hilgendorff, M.; Sundstrom, V. *J. Phys. Chem. B* **1998,** *102,* 10505.
(10) Will, G.; Boschloo, G.; Hoyle, R.; Rao, S. N.; Fitzmaurice, D. *J. Phys. Chem. B* **1998,** *102,* 10272.
(11) Solbrand, A.; Lindstrom, H.; Rensmo, H.; Hagfeldt, A.; Lindquist, S.-E. *J. Phys. Chem B* **1997,** *101,* 2514.
(12) Ghosh, H. N.; Asbury, J. B.; Weng, Y.; Lian, T. *J. Phys. Chem. B* **1998,** *102,* 10208.
(13) (a) Martini, I.; Hodak, J. H.; Hartland, G. V. *J. Phys. Chem. B* **1998,** *102,* 607. (b) Martini, I.; Hodak, J. H.; Hartland, G. V. *J. Phys. Chem. B* **1998,** *102,* 9508.
(14) (a) Ferrere, S.; Gregg, B. A. *J. Am. Chem. Soc.* **1998,** *120,* 843. (b) Zaban, A.; Ferrere, S.; Sprague, J.; Gregg, B. A. *J. Phys. Chem B* **1998,** *101,* 55.
(15) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977,** *99,* 4947.
(16) Meyer, T. J.; Meyer, G. J.; Pfenning, B.; Schoonover, J. R.; Timpson, C.; Wall, J. F.; Kobusch, C.; Chen, X. Peek, B. M.; Wall, C. G.; Ou, Wei; Erickson, B. W.; Bignozzi, C. A. *Inorg. Chem.* **1994,** *33,* 3952.
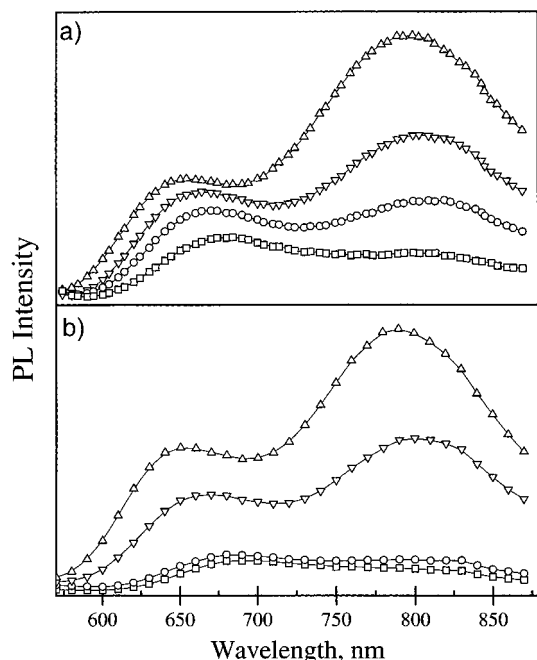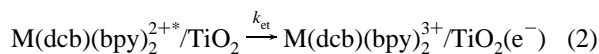
Scheme 1

ϕ_{PL} = 5.6 × 10^{-4}. The ethyl ester and carboxylic acid compounds can bind to TiO$_2$ to give indistinguishable materials, abbreviated Ru(dcb)(bpy)$_2$$^{2+}$/TiO$_2$ and Os(dcb)(bpy)$_2$$^{2+}$/TiO$_2$ throughout the text. Typical surface coverages were 7 (±2) × 10^{-8} mol/cm^2. Cyclic voltammetry of the derivatized TiO$_2$ materials in 0.1 M LiClO$_4$ acetonitrile reveal stable voltammograms assigned to the M(III/II) couple, $E_{1/2}$ = 1.34 V for Ru(dcb)(bpy)$_2$$^{2+}$/TiO$_2$ and $E_{1/2}$ = 0.88 V for Os(dcb)(bpy)$_2$$^{2+}$/TiO$_2$ vs SCE.[6c]

Both inter- and intramolecular energy transfer from Ru(II) polypyridyl excited states to Os(II) are well-known in fluid solution.[17−19] Placing a nanocrystalline TiO$_2$ film in an acetonitrile solution that contains equal concentrations of Ru(dcb)(bpy)$_2$(PF$_6$)$_2$ and Os(dcb)(bpy)$_2$(PF$_6$)$_2$ yields sensitized materials whose MLCT absorption band envelopes are linear combinations of the component chromophores expected for a 1:1 mixture of surface-bound complexes. Selective light excitation of Os(dcb)(bpy)$_2$$^{2+}$/TiO$_2$ at 580 nm in neat acetonitrile, results in the characteristic Os(dcb)-(bpy)$_2$$^{2+*}$ photoluminescence spectrum. Light excitation at 460 nm, where the two chromophores absorb approximately equally, yields the PL spectrum shown in Figure 1a. If the molecular sensitizers were behaving independently, one would expect the PL intensity from Ru(dcb)(bpy)$_2$$^{2+*}$/TiO$_2$ to be ∼80 times more intense than the Os(dcb)(bpy)$_2$$^{2+*}$/TiO$_2$. The observed ratio of 0.3, estimated by Gaussian deconvolution, provides compelling evidence for efficient energy transfer, $\phi_{en} \approx$ 1, eq 1

$$\text{Ru(dcb)(bpy)}_2^{2+*}/\text{TiO}_2 + \text{Os(dcb)(bpy)}_2^{2+}/\text{TiO}_2 \xrightarrow{k_{en}}$$
$$\text{Ru(dcb)(bpy)}_2^{2+}/\text{TiO}_2 + \text{Os(dcb)(bpy)}_2^{2+*}/\text{TiO}_2 \quad (1)$$
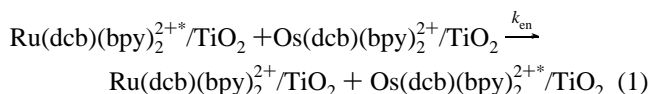
The rate constant for energy transfer across the nanocrystalline surface could not be time-resolved by the appearance of Os(dcb)-(bpy)$_2$$^{2+*}$ luminescence or absorption under our conditions indicating that k_{en} > 10^8 s^{-1}.

Addition of LiClO$_4$ to the external acetonitrile solution lowers the yield of energy transfer products by promoting interfacial electron transfer, eq 2.[20] Significant attenuation of the Os(dcb)-(bpy)$_2$$^{2+*}$-based emission was observed demonstrating that energy

(17) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980,** *102,* 1309.
(18) (a) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996,** *96,* 759. (b) Sauvage, J.-P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; DeCola, L.; Flamigni, L. *Chem. Rev.* **1994,** *94,* 993.
(19) (a) Dupray, L. M.; Devenney, M.; Striplin, D. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1997,** *119,* 10243. (b) Jones, W. E., Jr.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993,** *115,* 7363. (c) Strouse, G. F.; Worl, L. A.; Yonathan, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1990,** *112,* 7571.

Figure 1. (a) Corrected photoluminescence spectra of a 1:1 mixture of Ru(dcb)(bpy)$_2^{2+}$ and Os(dcb)(bpy)$_2^{2+}$ anchored to a nanocrystalline TiO$_2$ film immersed in argon-saturated acetonitrile solutions that contain 0.0 ($\triangle$), 0.3 mM ($\triangledown$), 5 mM ($\bigcirc$), 1 M ($\square$) LiClO$_4$. (b) Corrected photoluminescence spectra of a 1:1 mixture of Ru(dcb)(bpy)$_2^{2+}$ and Os(dcb)-(bpy)$_2^{2+}$ anchored to a nanocrystalline TiO$_2$ film immersed in argon saturated 0.1 M LiClO$_4$ acetonitrile electrolyte at the following applied potential vs SCE, 0.0 V ($\square$), -0.4 V ($\bigcirc$), -0.6 V ($\triangledown$), -0.7 V ($\triangle$).

$$M(dcb)(bpy)_2^{2+*}/TiO_2 \xrightarrow{k_{et}} M(dcb)(bpy)_2^{3+}/TiO_2(e^-) \quad (2)$$

transfer is less efficient at high Li$^+$ concentrations. In addition, Li$^+$ exposure stabilizes the MLCT excited state, and a bathochromic shift is observed in both the PL and absorption spectra. Significantly, energy transfer can be reversibly turned on and off over 10 times by alternating between neat acetonitrile and 1.0 M LiClO$_4$.

Energy transfer can also be controlled with applied potential. When the Fermi level in the nanocrystalline TiO$_2$ film is shifted to more negative electrochemical potentials with an external bias, the sensitizers anchored to TiO$_2$ photoluminesce efficiently.[21] PL spectra of a 1:1 mixed surface at open circuit and -0.7 V vs SCE are shown in Figure 1b. At -0.7 V the energy transfer efficiency is approximately unity. Stepping the potential further negative, <-0.8 V vs SCE, results in desorption of the sensitizers from the surface. However, at moderate potentials the optical changes are reversible and can be switched over 10 times without significant loss, Scheme 1.

The photoelectrochemical properties of two sensitizers anchored to the same nanostructured semiconductor surface have never, to our knowledge, been reported. For applications in regenerative solar cells, combinations of sensitizers can be used to tune the sensitivity of the semiconductor material to different wavelengths of light. A potential complication is that intermolecular energy and/or electron-transfer processes might compete with interfacial electron transfer. The photoelectrochemical properties of the sensitized TiO$_2$ materials were explored in 0.5 M LiI, 0.05 M I$_2$ acetonitrile electrolyte in a two-electrode arrangement. The monochromatic incident photon-to-current efficiency (IPCE) observed for Ru(dcb)(bpy)$_2^{2+}$/TiO$_2$ was 0.36 $\pm$ 0.01 and 0.15 $\pm$ 0.02 for Os(dcb)(bpy)$_2^{2+}$/TiO$_2$ at 460 nm. Typical data is shown in Figure 2a. The photoaction spectrum of the 1:1 mixed surface and a hypothetical spectrum based on an IPCE that is a linear sum of the individual sensitizers is shown in Figure 2b. The results presented demonstrate a small, but significant, decrease in the
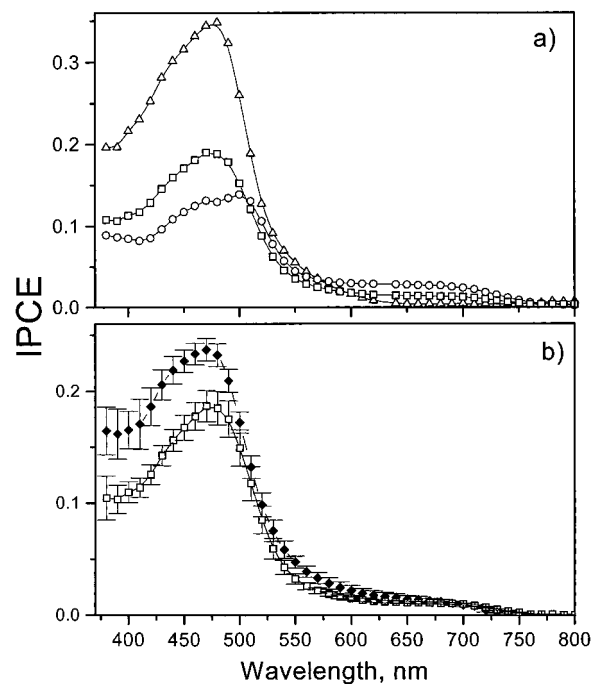

Figure 2. (a) Incident-photon-to-current efficiency (IPCE) of nanocrystalline TiO$_2$ films sensitized to visible light with Ru(dcb)(bpy)$_2^{2+}$ ($\triangle$), Os(dcb)(bpy)$_2^{2+}$ ($\bigcirc$), and a 1:1 mixture of Ru(dcb)(bpy)$_2^{2+}$ and Os(dcb)-(bpy)$_2^{2+}$ ($\square$), anchored to a nanocrystalline TiO$_2$ film in 0.5 M LiI and 0.05 M I$_2$ in acetonitrile. (b) Photoaction spectrum of the 1:1 mixed surface given in 2a ($\square$), and a calculated spectrum ($\blacklozenge$) based on an IPCE that is a weighted sum of the individual sensitizers.

photocurrent efficiency over what would be expected if the sensitizers were acting independently.

In conclusion, the photophysical and photoelectrochemical properties of TiO$_2$ materials derivatized with two sensitizers reveal a unique interplay between intermolecular energy transfer and interfacial electron transfer. We have reported the first direct demonstration of intermolecular energy transfer across a semiconductor surface.[22] Efficient energy migration observed in neat acetonitrile, or with negative applied potentials, and fast interfacial electron transfer is observed in the presence of Li$^+$ at open circuit or positive applied potentials. Energy transfer may be exploited in photocatalysis for long-range sensitization of remote reactive sites. Arrays of sensitizers with complimentary absorption bands can be used to tune the spectral response of solar cells. More fundamentally, with better defined donors and acceptors,[23] energy-transfer dynamics can provide orientation and distance information on chromophores bound in the unique restricted geometry of these mesoporous nanocrystalline semiconductor materials.

(20) Lithium cation is a potential determining ion for TiO$_2$. In the absence of Li$^+$ the quantum yield for injection is very low but increases approximately linearly with the log of the Li$^+$ concentration. See: Kelly, C. A.; Thompson, D. W.; Farzad, F.; Stipkala, J. M.; Meyer, G. J., submitted for publication and references therein.

(21) (a) O'Regan, B.; Moser, J.; Anderson, M.; Gratzel, M. *J. Phys. Chem.* **1990**, *94*, 8720. (b) Kamat, P. V.; Bedja, I.; Hotchandani, S.; Patterson, L. K. *J. Phys. Chem.* **1996**, *100*, 4900.

(22) To our knowledge, this is the first demonstration by direct identification of the energy-transfer products. Indirect evidence for energy transfer has been put forth with kinetic data. See, for example: (a) Khairdutdinov, R. F.; Levin, P. P.; Costa, S. M. B. *Langmuir* **1996**, *12*, 714. (b) Kelly, C. A.; Thompson, D. W.; Farzad, F.; Meyer, G. J. *Langmuir* **1999**, *15*, 731.

(23) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy;* Plenum Press: New York, 1983.