4386 *Inorg. Chem.* **1999,** *38,* 4386−4387

Visible Region Photooxidation on TiO_2 with a Chromophore−Catalyst Molecular Assembly

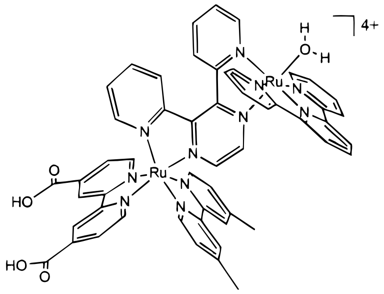
Joseph A. Treadway,[†] **John A. Moss,**[‡] **and Thomas J. Meyer***

Department of Chemistry, The University of North Carolina at Chapel Hill, CB# 3290, Chapel Hill, North Carolina 27599-3290

Received April 30, 1999

Nanocrystalline films of TiO_2 derivatized by adsorption of polypyridyl complexes of Ru^{II} have provided a basis for a family of solution photoelectrochemical devices.[1,2] At the molecular level, a key feature in these devices is irreversible photoinjection into the TiO_2 conduction band following metal-to-ligand charge-transfer (MLCT) excitation giving Ru^{III}. Reduction of Ru^{III} by I^- followed by I_3^- reduction at the anode completes the cell. It should be possible to exploit this basic scheme for the photoproduction of high-energy chemicals, and we report preliminary results on such an example based on an adsorbed chromophore−oxidant molecular assembly.

The work was based on the dpp-bridged molecular assembly $[(4,4'\text{-}(CO_2H)_2bpy)(4,4'\text{-}Me_2bpy)Ru_a^{II}(dpp)Ru_b^{II}(tpy)(OH_2)]^{4+}$ (**1**) ($4,4'\text{-}Me_2bpy$ is 4,4′-dimethyl-2,2′-bipyridine, $4,4'\text{-}(CO_2H)_2bpy$ is 2,2′-bipyridine-4,4′-dicarboxylic acid, dpp is 2,3-bis(2-pyridyl)-pyrazine, and tpy is 2,2′:6′,2″-terpyridine). The tpy side of the assembly is structurally analogous to $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ (bpy = 2,2′-bipyridine), which has an extensive and well-defined catalytic oxidation chemistry following two-electron oxidation to $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$.[3] The tris(heteroleptic) chromophore was prepared by a recently devised strategy[4] for preparing black absorbers which absorb light broadly throughout the visible.[5] In this case, the MLCT absorption of the complex is spread across the visible by utilizing the relatively electron rich $4,4'\text{-}Me_2bpy$ ligand to stabilize the MLCT excited-state hole at *Ru^{III} while the dpp bridge provides a low-lying π^* acceptor level. Additional MLCT transitions to tpy, $4,4'\text{-}Me_2bpy$, and $4,4'\text{-}(CO_2H)_2bpy$ fill in the mid-visible. As shown in Figure 1, the assembly absorbs broadly through much of the visible region.



1

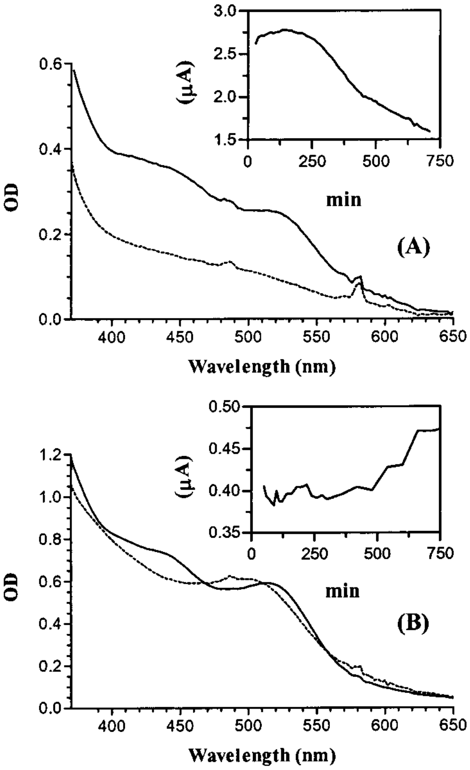


Figure 1. (A) UV−visible spectrum of **1** adsorbed onto optically transparent TiO_2 before (−) and after (···) overnight photolysis while immersed in propylene carbonate 0.1 M in $NaClO_4$. (B) As in A before (−) and after (···) photolysis while immersed in 2-propanol. The insets show the measured photocurrents during the same periods.

Synthetic details are given in the Supporting Information. For the intermediate $[(4,4'\text{-}Me_2bpy)(4,4'\text{-}(CO_2Et)_2bpy)Ru(dpp)Ru(tpy)Cl]^{3+}$ (λ_{max} = 626 nm), cyclic voltammetry in acetonitrile 0.1 M in tetrabutylammonium hexafluorophosphate revealed metal-based oxidations at $E_{1/2} = +0.88$ and $E_{p,a} = +1.56$ V and a ligand-based reduction at −0.82 V versus SSCE. For **1** (λ_{max} = 518 nm), at a glassy carbon electrode, a wave appears at $E_{1/2} = +0.69$ V (0.1 M $HClO_4$) corresponding to overlapping $-(dpp)(tpy)Ru^{II}(OH_2)^{2+} \rightarrow -(dpp)(tpy)Ru^{III}(OH)^{2+}$ and $-(dpp)(tpy)Ru^{III}(OH)^{2+} \rightarrow -(dpp)(tpy)Ru^{IV}(O)^{2+}$ waves as expected from related complexes.[6] In water, oxidation of the chromophoric side was not observed to the solvent limit of ~1.3 V, as expected from the acetonitrile results.

The carboxylate groups in **1** serve as attachment points to nanocrystalline TiO_2 particles annealed onto an optically transparent Sn-doped indium oxide (ITO) electrode by using a modification (Supporting Information) of the method of O'Regan et al.[1]

[†] Present address: Quantum Dot Corporation, 4030 Fabian Way, Palo Alto, CA 94303.

[‡] Present address: Department of Environmental Engineering Science, California Institute of Technology, Pasadena, CA 91125.

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

(2) (a) Grätzel, M.; Kalyanasundaram, K. *Metal Complexes as Photosensitizers in Photoelectrochemical Cells*; Grätzel, M., Kalyanasundaram, K., Eds.; Kluwer: Amsterdam, 1993; pp 247−271. (b) Meyer, G. J. *Molecular Level Artificial Photosynthetic Materials*; John Wiley and Sons: New York, 1997; Vol. 44, p 421. (c) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49.

(3) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845.

(4) Treadway, J. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 2267.

(5) Anderson, P. A.; Strouse, G. F.; Treadway, J. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 3863.

(6) (a) Gerli, A.; Reedijk, J.; Lakin, M. T.; Speck, A. L. *Inorg. Chem.* **1995**, *34*, 1836. (b) Catalano, J. J.; Heck, R. A.; Immoos, C. E.; Ohman, A.; Hill, M. G. *Inorg. Chem.* **1998**, *37*, 2150. (c) Hartshorn, C. M.; Meyer, T. J. Unpublished results.

10.1021/ic990466m CCC: $18.00

Scheme 1

$$\text{i)}\ \mathrm{TiO_2|\text{-}[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+} + H^+(Pt)} \xrightarrow{h\nu} \longrightarrow \mathrm{TiO_2|[\text{-}Ru_a^{II}\text{-}Ru_b^{III}\text{-}OH]^{4+} + H^+ + \tfrac{1}{2}H_2(Pt)}$$

$$\text{ii)}\ \mathrm{TiO_2|\text{-}[Ru_a^{II}\text{-}Ru_b^{III}\text{-}OH]^{4+} + H^+(Pt)} \xrightarrow{h\nu} \longrightarrow \mathrm{TiO_2|\text{-}[Ru_a^{III}\text{-}Ru_b^{III}\text{-}OH]^{5+} + \tfrac{1}{2}H_2(Pt)}$$

$$\text{iii)}\ \mathrm{TiO_2|\text{-}[Ru_a^{III}\text{-}Ru_b^{III}\text{-}OH]^{5+}} \longrightarrow \mathrm{TiO_2|\text{-}[Ru_a^{II}\text{-}Ru_b^{IV}{=}O]^{4+} + H^+}$$

$$\text{iv)}\ \mathrm{TiO_2|\text{-}[Ru_a^{II}\text{-}Ru_b^{IV}{=}O]^{4+} + H^+(Pt)} \xrightarrow{h\nu} \longrightarrow \mathrm{TiO_2|\text{-}[Ru_a^{III}\text{-}Ru_b^{IV}{=}O]^{5+} + \tfrac{1}{2}H_2(Pt)}$$

The molecular assembly was added to the annealed electrode by immersion of the electrode into a saturated ethanolic solution overnight.

The goal of the present study was to devise a *photoelectrosynthetic* cell based on adsorption of **1** onto TiO_2. A two-compartment cell was utilized with the dye-derivatized TiO_2 electrode in one compartment and a platinized Pt electrode immersed in 1 M aqueous $HClO_4$ in the second. In this configuration, the photoinjected electrons are delivered through the circuit to the platinized Pt electrode for reduction of protons to dihydrogen although we have made no attempt to measure its production.

When the TiO_2 electrode was irradiated (250 W Bausch and Lomb mercury lamp with a 460 nm UV cutoff filter to prevent direct semiconductor band-gap excitation), photocurrents were measured in the external circuit. As shown in the inset in Figure 1A, with the assembly-derivatized electrode immersed in propylene carbonate 0.1 M in $NaClO_4$, the photocurrent decreased with time as the dye was oxidized on the surface. Photooxidation of **1** on the surface (TiO_2|**1**) occurs to give $TiO_2|[(4,4'\text{-}(CO_2H)_2bpy)(4,4'\text{-}Me_2bpy)Ru_a^{III}(dpp)Ru_b^{IV}(tpy)(O)]^{5+}$ which is only weakly absorbing in the visible. Because of the high $Ru^{III/II}$ potential for Ru_a in **1** relative to the $Ru_b^{III/II}$ and $Ru_b^{IV/III}$ potentials, the total loss of Ru^{II} MLCT absorption in the visible shows that the initial $Ru^{II}{-}OH_2^{2+}$ site is fully oxidized to $Ru^{IV}{=}O^{2+}$.

We envision that three-electron oxidation of TiO_2|**1** occurs by the series of stepwise reactions in Scheme 1.[7,8] In the scheme, photooxidation of the complex occurs at TiO_2 and H_2 production at platinum. We have no information about the absolute incident photocurrent efficiency (IPCE), but there is a good match between the absorption spectrum of the adsorbed assembly and the photocurrent action spectrum. After formation of $[(4,4'\text{-}(CO_2H)_2bpy)(4,4'\text{-}Me_2bpy)Ru_a^{II}(dpp)Ru_b^{III}(tpy)(OH)]^{4+}$ in the first step, absorption of an additional photon at Ru_a^{II} is followed by a competition between injection and excited-state quenching by Ru_b^{III} which may contribute to a decrease in IPCE. Additional factors that may contribute to the IPCE are the directional character of the lowest MLCT excited state which lies along the ligand bridge rather than toward the electrode and a contribution to the low energy absorption manifold from a $Ru_a^{II} \rightarrow Ru_b^{III}$ mixed-valence transition.

The sequential loss of absorbance at Ru_b^{II} followed by Ru_a^{II} illustrates the value of placing the high potential antenna chromophore on the electrode surface. Adsorption of a $Ru^{II}{-}OH_2^{2+}$ complex alone followed by photoinjection would result in $Ru^{III}{-}OH^{2+}$, which does not absorb in the visible to an appreciable degree. In **1**, oxidation to $-Ru^{II}(dpp)Ru^{III}(OH)-$ causes loss of the $Ru_b^{II} \rightarrow$ tpy MLCT absorption in the visible, but this also lowers the energy of the remaining Ru_a^{II} MLCT transition to the dpp bridge.

When propylene carbonate was replaced with 2-propanol as solvent, a different behavior was observed. The $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ analogue has been shown to oxidize 2-propanol to acetone by a hydride transfer mechanism.[9] Oxidation of 2-propanol apparently also occurs on the surface. As shown in Figure 1B, photocurrents actually *increase* with time although they are of lower magnitude.[10,11] Over the photolysis period, the absorption spectrum blue-shifts slightly with negligible loss of absorbance, perhaps due to the presence of some isolated sites which are slow to rereduce.[12] GC−MS analysis of the 2-propanol solution showed an ~10-fold increase in the concentration of acetone relative to the solution from an underivatized TiO_2 blank. The conclusion that the acetone produced in this cell was formed by the reaction of 2-propanol with the $Ru^{IV}{=}O$ site in Scheme 1 is reasonable. Compared to $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ in solution, oxidation of 2-propanol by $[Ru^{III}(tpy)(bpy)(OH)]^{2+}$ is slower by a factor of 400.[13]

The net reaction in the cell appears to be the visible light driven dehydrogenation of 2-propanol,

$$(CH_3)_2CHOH \xrightarrow{h\nu} (CH_3)_2C{=}O + H_2$$

a reaction which is nonspontaneous by 0.64 eV.

This is very preliminary work, and important studies remain. Nevertheless, the results presented demonstrate that a molecular assembly consisting of a broadly absorbing visible chromophore, a redox center capable of multiple oxidation to an oxo form, and attachment points for surface adsorption can be constructed and utilized to effect net chemical conversion by utilizing long-wavelength light.

Acknowledgment. Support of this work by the U.S. Army Research Office under Grant No. DAAH04-95-0144 and the National Science Foundation under Grant No. CHE-9705724 is gratefully acknowledged.

Supporting Information Available: Synthetic details. Electrode preparation method. Photoelectrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990466M

---

(7) Both halves of **1** contribute to the visible absorption spectrum. The photoaction spectrum closely mirrors the absorption spectrum, indicating that photoinjection occurs from the remote half of the dimer either directly or via electron transfer to the surface-attached half.

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

(9) Thompson, M. S.; Meyer, T. J *J. Am. Chem. Soc.* **1982**, *104*, 4106.

(10) Typically, the photocurrents were found to be lower overall in 2-propanol than in propylene carbonate. They have been shown to be solvent dependent in related systems as well (ref 11). The difference here may also arise from differences in water content between the two solvent systems.

(11) (a) Bahdur, L.; Rao, T. N. *J. Photochem. Photobiol., A* **1995**, *91*, 233. (b) Kavan, L.; Kratochvilova, K.; Grätzel, M. *J. Electroanal. Chem.* **1995**, *394*, 93. (c) Enright, B.; Redmond, G.; Fitzmaurice, D. *J. Phys. Chem.* **1994**, *98*, 6195. (d) Mills, A.; Le Hunte, S. *J. Photochem. Photobiol., A* **1997**, *108*, 1.

(12) The resulting two- or three-component spectrum is blue-shifted as expected since spectra of the oxidized forms of the assembly are also blue-shifted.

(13) Thompson, M. S.; De Giovanni, W. F.; Moyer, B. A.; Meyer, T. J. *J. Org. Chem.* **1984**, *49*, 4972.