

High Quantum Yield Sensitization of Nanocrystalline Titanium Dioxide Photoelectrodes with *cis*-Dicyanobis(4,4'-dicarboxy-2,2'-bipyridine)osmium(II) or Tris(4,4'-dicarboxy-2,2'-bipyridine)osmium(II) Complexes

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Received: April 30, 1999; In Final Form: January 7, 2000

Osmium polypyridyl complexes were used as sensitizers in solar cells that utilize nanocrystalline titanium dioxide photoelectrodes. Exposure of TiO₂ electrodes to sources of Os^{II}(H₂L')₂(CN)₂ (where L' is 4,4'-dicarboxylato-2,2'-bipyridine) or Os^{II}(H₂L')₃²⁺ extended the light absorption and spectral response of the cell to longer wavelengths than did exposure of TiO₂ to Ru(H₂L')₂(NCS)₂. The Os complexes also provided very high external quantum yields for photocurrent flow and produced open-circuit voltages similar to those of the Ru complex. The Os-based systems therefore offer promise in developing efficient dye-sensitized nanocrystalline TiO₂-based photoelectrochemical cells.

Dye-sensitized nanocrystalline titanium dioxide photoelectrochemical cells present a promising strategy for solar energy conversion, with energy conversion efficiencies as high as 10% reported using the transition-metal sensitizer Ru^{II}(H₂L')₂(NCS)₂ (where H₂L' is 4,4'-dicarboxylic acid 2,2' bipyridine).^{1,2} Further improvements in efficiency should be possible because this sensitizer does not effectively absorb light below 1.77 eV³ and because ≈0.4 V is wasted in the reaction of Ru^{III}(H₂L')₂(NCS)₂⁺ with I[−] in order to sustain faradaic current flow in the cell.⁴ Replacing Ru(II) with Os(II), to obtain a lower-energy absorption band and also to obtain a more negative M(III)/M(II) redox potential,⁵ might provide improved performance in photoelectrochemical energy conversion. However, this approach has had limited success to date.^{6,7} We report herein that the adsorption onto TiO₂ of complexes derived from Os^{II}(H₂L')₂(CN)₂ or Os^{II}-(H₂L')₃²⁺ extends the light absorption and spectral response of the cell to longer wavelengths, while also providing high photocurrents and high external quantum yields for photocurrent flow.

Experimental Section

Ru(H₂L')₂(NCS)₂ was synthesized by refluxing Ru(H₂L')₂-Cl₂^{8,9} under N₂ with an excess of NaNCS in basic water for 22 h. The protonated form of the complex was precipitated by addition of acid, and the solid was filtered and then purified by column chromatography using Sephadex LH-20 as the column support and methanol as the eluent. For comparison, Ru(H₂L')₂-(NCS)₂ was also purchased as sold under the name "Ru 535" by Solaronix Inc. A source of Os(H₂L')₂(CN)₂ was synthesized by refluxing Os^{II}(H₂L')₂Cl₂^{6,10} under N₂ with excess KCN. In this procedure, Os(H₂L')₂Cl₂ (0.084 g, 1.1 × 10^{−4} moles) was dissolved with KCN (0.27 g, 4.1 × 10^{−3} mol) in 7 mL of water and the solution was refluxed for 12 h with stirring under a

nitrogen atmosphere. The cooled reaction mixture was poured into 100 mL of DMF to precipitate K₄[OsL'₂(CN)₂]. The brown precipitate was isolated by filtration, washed with DMF and acetone, and dried under vacuum overnight. The crude product was dissolved in water and purified by column chromatography using Sephadex DEAE A-25 as the column support and 0.5 M KNO₃(aq) as the eluent. The green-brown band was collected. The mixture was evaporated to about 100 mL and filtered to remove excess KNO₃. The filtrate was further evaporated to 20 mL and filtered to remove additional KNO₃. A 1 mL aliquot of 0.26 M CF₃SO₃H(aq) was added to the filtrate to precipitate the desired complex. The complex was isolated by filtration, washed with 0.26 M CF₃SO₃H(aq) and ether, and then dried under vacuum overnight. Os^{II}(H₂L')₃²⁺ was synthesized by refluxing Os(H₂L')₂Cl₂ under N₂ with (H₂L') in ethylene glycol for 2 h. The product was precipitated upon addition of acid, filtered, dissolved in 0.2 M KOH and subjected to ion-exchange column chromatography using Sephadex DEAE A-25 resin with 0.4 M KI as the eluent. After evaporating the mixture to dryness, the KI was extracted with ethanol and then with acetone. The deprotonated potassium salt of the complex, K₄[OsL'₃]·6H₂O, was isolated, filtered, and washed with acetone. The chloride salt of the fully protonated complex was obtained by dissolving K₄[OsL'₃] in a few milliliters of water, adding 1 M HCl to precipitate the chloride salt, and filtering with a fine-porosity glass frit. The ¹H NMR (in D₂O–NaOD) and elemental analysis data for all of the complexes supported their metal/ligand formulations as proposed.¹¹

The absorption spectra and emission spectra were obtained in methanol containing 1.0 mM pyridine and 1.0 mM pyridinium triflate. Pyridine and pyridinium were added to control the protonation of the complexes, and this step produced much greater reproducibility of the spectra from trial to trial. The protonation states of the L' ligands in the various complexes are not known under these specific conditions, so although the sources of the materials were prepared as stated above, for convenience the complexes will be represented notationally as being in their fully protonated forms in the remainder of the

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discussion below. Emission spectra were recorded at room temperature using a R406 (Products for Research, Inc.) photo-multiplier tube that was cooled with dry ice. The emission spectra were corrected for instrument response.

Methanol was used as the solvent for both cyclic voltammetry and differential pulse voltammetry because it was the only nonaqueous solvent into which 1 mM of the complexes could be dissolved. Except where noted, the supporting electrolyte was 1.00 M LiClO₄, and 10 mM pyridine and 10 mM pyridinium were added to control the acidity. The protonated chloride form of OsL'₃⁴⁺, [Os(H₂L')₃]Cl₂, was used as the source of this metal complex because the protonated salt was more soluble in methanol than the deprotonated species. For measurements using Os(H₂L')₃²⁺, pyridine was omitted because its presence caused precipitation of the complex even at dye concentrations as low as 0.1 mM. The cyclic voltammograms of Os(H₂L')₂(CN)₂ and Os(H₂L')₃²⁺ were reversible. In the case of Ru(H₂L')₂(NCS)₂, the cyclic voltammogram was irreversible in methanol, and its value is an estimate of the true reversible potential in this solvent.

Transparent nanocrystalline TiO₂ electrodes (Institut fuer Angewandte Photovoltaik) were first treated by depositing a freshly made solution of 0.2 M TiCl₄(aq) onto the TiO₂ overnight.¹ The electrodes were then rinsed with water, dried with flowing nitrogen, and heated to 450 °C in air for 30 min. Once the electrodes were cooled to about 120 °C, they were immersed for 15–24 h into an ethanolic solution containing 5 × 10⁻⁵ to 1 × 10⁻⁴ M of the desired complex, 1.0 mM pyridine, and 1.0 mM pyridinium triflate. In the case of Os(H₂L')₃²⁺, the solution contained 2.0 mM pyridinium triflate. The UV/vis spectra of the electrodes were obtained prior to the photoelectrochemistry. The blank was a TiO₂ electrode that had been treated nominally identically to the other electrodes but which was immersed into an ethanolic solution that contained no dye.

The electrolyte for the photoelectrochemical cell consisted of 0.500 M LiI–0.040 M I₂/0.050 M pyridine–0.020 M pyridinium triflate in dry CH₃CN. Pyridine/pyridinium triflate was added to the solution to ensure a constant proton activity of the electrolyte from run to run, thereby stabilizing the conduction band edges of TiO₂ (which are well-known to be pH sensitive¹²) and to control reproducibly the degree of protonation of the ligands on the dissolved metal complexes. This particular buffer was chosen because the reagents are soluble in acetonitrile and because the pK_a of pyridinium is 5.2 in water, which is near the point of zero charge for TiO₂ in aqueous solutions.^{13–15} The light source was an ELH-type tungsten halogen bulb and light intensities were determined by using a calibrated silicon photodiode (Solarex). A 385 nm cutoff filter was used during measurements (but not during the calibration with the Solarex cell) to avoid direct excitation of electrons in the titanium dioxide. The current density–potential (*J*–*E*) curves and spectral response data were both recorded using a three-electrode potentiostatic setup with a Pt wire reference and Pt gauze counter electrode, with illumination striking the working electrode through the transparent conducting glass. The illuminated surface area was 0.25 cm². All efficiency data are averages of at least three different electrodes. We note that although three-electrode setups have previously been reported to yield much lower external quantum yields than sandwich cells,¹⁶ we did not observe this to be the case in our particular 3-electrode cells, which had small interelectrode gaps and produced relatively efficient mass transport of redox species and electrolyte between the working and counter electrodes.

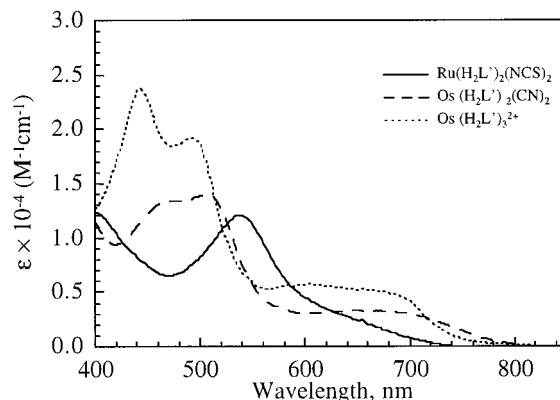


Figure 1. UV/vis absorption spectra in methanol with 1 mM pyridine and 1 mM pyridinium triflate.

Spectral response data were obtained by maintaining the cell at short circuit (no potentiostatic control) and measuring the current with a Keithley 177 μ V DMM multimeter. The system calibration was performed by placing a calibrated Si photodiode (obtained from United Detector Technology, Inc. and calibrated by UDT traceable to a NIST standard) in the same position as the TiO₂ working electrode and measuring the photocurrent at short circuit from each system. The calibrated diode had a mask with the same surface area as the TiO₂ working electrode, and the ratio of the response of the TiO₂ cell to that of the calibration diode yielded the quantum yield for the TiO₂ cell. Any variation in the light intensity between measurements was accounted for by dividing the current obtained from the sample or calibration device by the current produced by the reference beam, which was directed onto a separate silicon photodiode (obtained from UDT). The quantum yields were therefore computed using the following equation:

$$\Phi_{\text{smp}} = \Phi_{\text{cal}} \left(\frac{I_{\text{smp}}/\text{area}}{I_{\text{ref,smp}}} \right) \left(\frac{I_{\text{ref,cal}}}{I_{\text{cal}}/\text{area}} \right) \quad (1)$$

where Φ_{smp} and Φ_{cal} are the quantum yields for the sample and the calibrated photodiode, respectively, I_{smp} and I_{cal} are the photocurrents obtained at the sample and at the calibrated diode, respectively, and I_{ref} is the photocurrent of the reference diode. For the TiO₂ electrodes, the dark current was measured periodically and the photocurrent I_{smp} was obtained by subtracting the dark current from the measured total current. The external quantum yields obtained using this measurement procedure were not corrected for optical scattering or reflection losses nor for incomplete absorption by the dye at certain wavelengths.

Results and Discussion

The absorption spectra of these complexes (Figure 1) all showed intense metal-to-ligand charge transfer (MLCT) bands in the visible region of the spectrum. The osmium complexes all displayed an extra band at longer wavelength that is ascribable to the direct excitation to the triplet state. Table 1 depicts the ground-state potentials and estimated excited-state potentials for these systems. The excited-state redox potentials for the osmium complexes were similar to that of Ru(H₂L')₂(NCS)₂, so the osmium excited states should have sufficient energy to inject an electron into the conduction band of TiO₂.¹⁷ In addition, the ground-state potentials are sufficiently positive to oxidize I⁻ in CH₃CN such that a sustained faradaic current flows in the cell.⁴

TABLE 1: Spectral and Electrochemical Properties of the Complexes in Methanol

complex	abs max (nm)		em max. (nm)	$E^{\circ'}$	$E^{\circ'*}$ ^a
Ru(H ₂ L') ₂ (NCS) ₂	396	534	880	0.68	-1.1
Os(H ₂ L') ₂ (CN) ₂	378	500	~660	0.72	-1.1
Os(H ₂ L') ₃ ²⁺	442	494	~640	1.01	-0.8

^a Calculated by subtracting E_{0-0} from the formal potential, $E^{\circ'}$. E_{0-0} values were estimated from the intersection of the absorption spectra and emission spectra (both in MeOH), when the most intense MLCT absorption band and the emission peak were adjusted to the same height. Values for $E^{\circ'}$ and $E^{\circ'*}$ are quoted vs aqueous SCE.

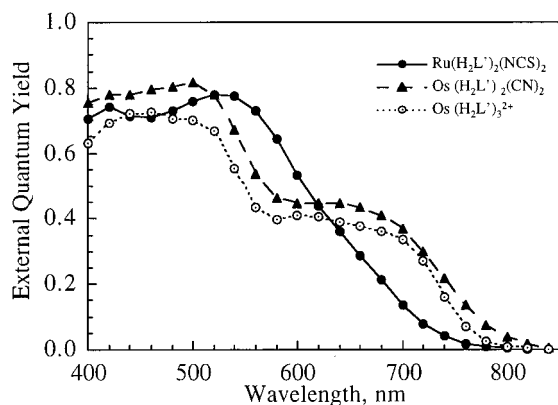


Figure 2. Spectral response data obtained for the complexes coated onto transparent TiO₂ electrodes. The spectral responses are the average of three or more measurements. The standard deviations for the external quantum yields were less than 0.05.

Figure 2 displays the spectral response characteristics, collected under short circuit conditions, of the various TiO₂-coated electrodes studied in this work. The spectral response of the dye-coated TiO₂ electrodes showed a good correlation with the absorption spectrum of each metal complex. Using Ru(H₂L')₂(NCS)₂ produced very high maximum external quantum yields, but the Os(H₂L')₂(CN)₂-exposed TiO₂ electrodes exhibited similar maximum quantum yields with significantly larger responses in the red region of the spectrum. TiO₂ electrodes that had been exposed to the Os(H₂L')₃²⁺ complex showed similar quantum yields and again showed an improved response in the red relative to the Ru system under these loading conditions.

The photoelectrochemical data are reported in Table 2. The photocurrents of TiO₂ electrodes coated with Os(H₂L')₂(CN)₂ or Os(H₂L')₃²⁺ were comparable to the photocurrent obtained with Ru(H₂L')₂(NCS)₂-coated TiO₂. The two osmium-based dyes are therefore very promising photosensitizers. Table 2 also reports the predicted photocurrent under the global AM1.5 spectrum¹⁸ at a total intensity of 100 mW cm⁻². The predicted photocurrents are similar to the experimental photocurrents, indicating that use of the ELH-type tungsten halogen bulb does not seriously overestimate the photocurrents produced by these electrodes under solar illumination conditions.

The other key property of concern is the photovoltage, V_{oc} , of the system. In our work, we have not optimized the performance of the devices. Instead we have chosen relatively uncomplicated standard conditions (of controlled proton activity) to facilitate comparison between the performance of the various metal complex-coated TiO₂ electrodes of interest in our studies. In addition to illumination under constant total light intensity, V_{oc} values for electrodes coated with the various metal complexes were also obtained under a light intensity sufficient

TABLE 2: Photoelectrochemical Data^a

complex	% T ^c	V_{oc}^d (mV)	J_{sc}^e (mA cm ⁻²)	J_{sc} at 1 sun ^f (mA cm ⁻²)	V_{oc}^g (mV)
Ru(H ₂ L') ₂ (NCS) ₂	7.4	520	10.8	10.4	430
Ru 535 ^b	8.5	620	12.0	11.0	540
Os(H ₂ L') ₂ (CN) ₂	14.8	570	11.6	12.0	500
Os(H ₂ L') ₃ ²⁺	5.5	510	10.0	10.3	450

^a The values reported are averages obtained from the data of three to five different electrodes. ^b Ru(H₂L')₂(NCS)₂ from Solaronix, Inc. ^c Percent optical transmittance of a typical electrode at the wavelength of maximum external quantum yield. ^d Measured after an equilibration time of 5 min under illumination at open circuit. The standard deviations were less than 15 mV. ^e Obtained at short circuit from the current-voltage curves. The standard deviations were less than 0.6 mA cm⁻². The values of V_{oc} and J_{sc} were obtained using illumination from an ELH-type tungsten-halogen light source. ^f Predicted J_{sc} value under 1 sun computed from the ratio of the integrated spectral response of the dye-coated TiO₂ electrodes to that of the NREL Global AM 1.5 solar spectral irradiance at a total incident light intensity of 100 mW cm⁻². ^g Value of V_{oc} measured at a light intensity sufficient to provide a constant short circuit photocurrent of 1.0 mA cm⁻² for each photoelectrode.

to produce 1.0 mA cm⁻² of short-circuit photocurrent density (Table 2). The V_{oc} values under these conditions were different for each complex, indicating different contributions of back current for the same overall short circuit photocurrent density.

We found that the photoelectrochemical properties of the cell were sensitive to the preparation methods of the metal complex. For instance, electrodes sensitized with a source of Os(H₂L')₃²⁺ that had been subjected to anion exchange chromatography yielded photocurrents that were twice as large as and V_{oc} values that were 100 mV larger than an electrode sensitized with unchromatographed material even though the unchromatographed complex had a satisfactory elemental analysis and ¹H NMR spectrum. Low quantum yields have been reported previously for TiO₂ electrodes coated with a source of Os(H₂L')₂(CN)₂,⁷ and many variables, including the preparation of the TiO₂, the protonation state of the complexes during adsorption onto the TiO₂, and the composition of the electrolyte during J - E measurements, could be significant factors in producing the high quantum yields that were observed under our experimental conditions. The high quantum yields reported herein are consistent with the plateau in the current-potential properties that is observed at positive bias, where recombination should be minimized and a limiting quantum yield close to unity is expected theoretically in most instances.

The Os complexes have other potential advantages relative to their Ru analogues. Although the excited-state lifetimes for Os complexes are typically shorter than those for the analogous Ru complexes,¹⁹ the Os(II) excited state should be as effective in sensitizing TiO₂ because electron injection into nanocrystalline TiO₂ is thought to occur on a subpicosecond time scale.²⁰⁻²⁴ Perhaps more importantly, the ground-state potential of the Os complexes can be readily tuned to less positive potentials by using stronger donor ligands.¹⁷ By using a sensitizer with a less positive ground state redox potential and a constant excited state redox potential, less energy will be wasted in the reduction of Os(III) to Os(II) by iodide, possibly yielding even further improvements in the efficiency of the overall system. In addition, the reversibility of the Os(III/II) cyclic voltammetry indicates that the Os(H₂L')₂(CN)₂⁺ species is more stable than the Ru(H₂L')₂(SCN)₂⁺ species in CH₃CN, so that a larger turnover number is expected for the Os system if all other factors are constant. It should be noted, however, that the Ru-based systems

have undergone an extensive series of optimization steps through addition of surface passivants, optimization of sensitizer coverage, posttreatments of the electrode and electrolyte, etc., to obtain the highest energy conversion efficiency values reported to date.¹ It is not known whether these procedures will be equally effective on the Os-based photoelectrodes or, if not, whether alternative procedures can be developed that have similar beneficial effects. In this respect, the Os-based systems lag behind the Ru systems, but they nevertheless seem to offer promise from a fundamental viewpoint in developing efficient dye-sensitized nanocrystalline TiO₂-based photoelectrochemical cells.

Acknowledgment. Support for this project was provided by the U.S. Department of Energy, DE-FG07-96ER14725. We thank Kodak for a generous gift in support of photoelectrochemistry at Caltech. We are grateful to Dr. G. Coia of Caltech for assistance with the instruments used to perform the emission measurements and to Dr. G. W. Walker of Caltech for useful discussions. G.S. thanks FCAR (Fonds pour la Formation de Chercheurs et l'Aide à la Recherche, Québec, Canada) for a doctoral scholarship.

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- (9) The reaction was performed in ethylene glycol instead of dimethylformamide, DMF.
- (10) The procedure was modified as follows: we added 200 mL of water and excess sodium dithionite to reduce any Os(III) to Os(II), and then added sufficient 1.0 M HCl to precipitate the product.
- (11) Anal. (C₂₆H₁₆N₆O₈S₂Ru·3H₂O) Calcd (found): C, 41.11 (41.16); H, 2.92 (2.67); N, 11.06 (10.85). Anal. (C₃₆H₁₈N₆O₁₂K₄Os·6H₂O) Calcd (found): C, 36.54 (36.70); H, 2.73 (2.60); N, 7.10 (6.97).
- (12) V_{oc} was unstable when pyridine and pyridinium triflate were not present in the electrolyte. The amines might also have other roles as well such as surface state passivation, etc., but we have no direct evidence to support these other possible functions.
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