

**Electron Transfer Dynamics in
Nanocrystalline Titanium Dioxide Solar Cells
Sensitized with Ruthenium or Osmium
Polypyridyl Complexes**

Darius Kuciauskas,¹ Michael Freund,¹ Jay Winkler,¹
Harry Gray¹ and Nathan Lewis¹

¹Division of Chemistry and Chemical Engineering,
California Institute of Technology
127-72 Noyes Laboratory
Pasadena, Caltech (MS 127-72) 91125
USA

The electron transfer dynamics in solar cells that utilize sensitized nanocrystalline titanium dioxide photoelectrodes and the iodide/triiodide redox couple have been studied on a nanosecond time scale. The ruthenium and osmium bipyridyl complexes Ru(H2L)2(CN)2, Os(H2L)2(CN)2, Ru(H2L)2(NCS)2, and Os(H2L)2(NCS)2, where H2L is 4,4-dicarboxylic acid 2,2-bipyridine, inject electrons into the semiconductor with a rate constant $k \approx 10^8$ s⁻¹. The effects of excitation intensity, temperature, and applied potential on the recombination reaction were analyzed using a second-order kinetics model. The rates of charge recombination decrease with increasing driving force to the oxidized sensitizer, indicating that charge recombination occurs in the Marcus inverted region. The electronic coupling factors between the oxidized sensitizer and the injected electrons in the TiO2 and the reorganization energies for the recombination reaction vary significantly for the different metal complexes. The charge recombination rates are well-described by semiclassical electron transfer theory, and reorganization energies are 0.55-1.18 eV. Solar cells sensitized with Ru(H2L)2(CN)2, Os(H2L)2(CN)2, and Ru(H2L)2(NCS)2 have favorable photoelectrochemical characteristics and iodide is oxidized efficiently. In contrast, iodide oxidation limits the efficiency of cells based on sensitization of TiO2 with Os(H2L)2(NCS)2. The observation that charge recombination occurs in the Marcus inverted region has important implications for the design of molecular sensitizers in nanocrystalline solar cells operated under our experimental conditions.