

pH Dependent Interfacial Electron Transfer Yields from the Excited States of Ruthenium and Osmium Polypyridyl Compounds to Nanocrystalline TiO₂

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Regenerative solar cells based on dye-sensitized nanocrystalline TiO₂ have achieved efficiencies of 10-11% under simulated sunlight. Maximum photocurrent conditions have perhaps been established using black dyes that contain appropriate excited state energies in conjunction with an I⁻/I₃⁻ regenerative couple. We have initiated studies to elucidate the factors that control the photovoltage in these solar cells, with the goal of optimizing photovoltages while maintaining efficient photocurrent production. In this particular study, we have manipulated the TiO₂ conduction band energy by pre-equilibration of the semiconductor in aqueous pH solutions. Proton adsorption/desorption equilibria shift the band edges by 59 mV/pH unit, Figure 1. The influence of this band edge movement on solar conversion efficiencies and on the excited state and electron transfer properties of covalently bound dyes has been quantified.¹

In recent work, the excited state and redox properties of Ru(deeb)(bpy)₂(PF₆)₂, Ru(dcb-H₂)(bpy)₂(PF₆)₂, Ru(bpy)₂(ina)₂(PF₆)₂, and Ru(dpbb)(bpy)₂(PF₆)₂, where bpy is 2,2'-bipyridine, deeb is 4,4'-(CO₂Et)₂-bpy, dcb-H₂ is 4,4'-(CO₂H)₂-bpy, dpbb is 4,4'-(PO(OEt)₂)₂-bpy, and ina is isonicotinic acid, bound to nanocrystalline TiO₂ and colloidal ZrO₂ films were studied in acetonitrile at room temperature.² It was found that pre-equilibration of the TiO₂ surface with aqueous solutions of known pH had a profound influence on the kinetics for dye binding, the chemical nature of the dye-semiconductor linkage, the dye excited state reduction potential, the interfacial electron injection yield, and the rate constants for intermolecular Ru^{III/II} electron "hopping", while it had no significant effect on the interfacial charge recombination kinetic rate constants.²

Here we extend these studies to the sensitizers Ru(bpy)₂(L)(PF₆)₂ and Os(bpy)₂(L)(PF₆)₂ (where L is a tripodal ligand like that shown in Figure 2). These compounds were strategically chosen since the absorption and emission spectra as well as their redox potentials are independent of the surface pH allowing for a more straightforward application of Gerischer theory. Furthermore, the tripodal ligand L allows for better control of the semiconductor-sensitizer orientation and a well-defined electron transfer distance. With the same excitation wavelength, the Franck-Condon excited state of the Ru sensitizer is a stronger reductant than the Os analogue by ~350 meV. Interestingly, the thermally equilibrated excited states of the osmium and ruthenium compounds are nearly identical in energy. Therefore, the pH dependent injection data provides insights into the nature of the excited state(s) that transfers electrons to the semiconductor.

1. (a) Clark, W.D.K.; Sutin, N.I. *J. Am. Chem. Soc.* **1977**, *99*, 4676-4682. (b) Sonntag, L.P.; Spittler, M.T. *J. Phys. Chem.* **1985**, *89*, 1453-1457.

2. Qu, P.; Meyer, G.J. *Langmuir* **2001**, *17*, 6720-6728.

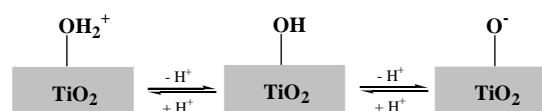


Fig. 1. The proton adsorption/desorption equilibrium on titanium dioxide that is thought to underlie the Nernstian 59 mV/pH shift in the band edge positions.

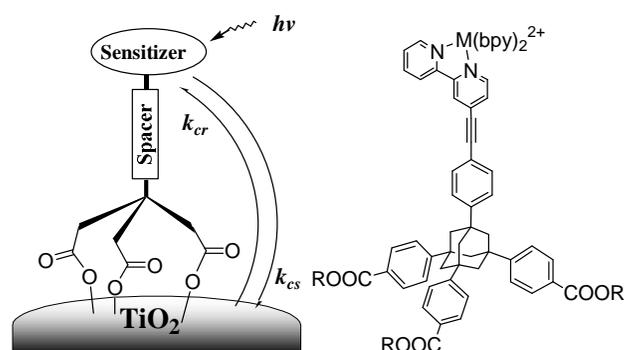


Fig. 2. Schematic representation of the idealized sensitizer-semiconductor orientation for interfacial electron transfer studies and a chem-draw picture a sensitizer used in this study, where M = ruthenium or osmium.