

Remote Electron Injection at Dye-Sensitized TiO₂

Feng Liu, Ping Qu, and Gerald J. Meyer
Department of Chemistry, Johns Hopkins University
3400 N. Charles Street, Baltimore, MD 21218

Dye sensitization of nanocrystalline TiO₂ electrodes with transition metal polypyridyl compounds has been intensively investigated for solar energy conversion. In this type of solar cell, the transition metal compounds are generally anchored to the nanoporous TiO₂ electrode via carboxylic acid groups located in the 4 and 4' positions of one or more bipyridine ligand. We recently initiated studies of Ru(II) polypyridyl compounds bound to semiconductor surfaces through isonicotinic acid ligands, Figure 1.¹ The isonicotinic acid ligands profoundly influence: 1) excited state-semiconductor electronic coupling, 2) photochemical stability, 3) excited state interfacial electron injection yields, and 4) the activation energies for metal-to-ligand charge-transfer (MLCT) to ligand field (LF) excited state internal conversion.

In this presentation, we will focus on remote interfacial electron injection from compounds of the type, Ru(LL)₂(ina)₂(PF₆)₂ where LL is a bipyridine, phenanthroline, or a substituted bipyridine or phenanthroline ligand. These compounds have been prepared, characterized, and anchored to colloidal ZrO₂ and TiO₂ thin films for excited state and interfacial electron transfer studies. For these compounds, the Ru → ina MLCT bands occur at high energy and are generally obscured by the fundamental absorption of TiO₂. The thermally equilibrated excited (thexi) states, therefore, are localized on LL ligands that are remote to the semiconductor surface, Figure 2. The behavior is contrasted to adjacent electron injection observed with other sensitizers that have excited states localized on a surface bound ligand.

Results with the unsubstituted bipyridyl compound, Ru(bpy)₂(ina)₂(PF₆)₂, were recently reported.¹ In neat acetonitrile at 22 ± 2 C, Ru(bpy)₂(ina)₂(PF₆)₂ is photochemically unstable and non-emissive with a short excited state lifetime, τ < 10 ns. When anchored to ZrO₂, the lifetime of Ru(bpy)₂(ina)₂(PF₆)₂ increases to 60 ns at 22 ± 2 C and is highly temperature dependent due to the population of a low-lying state(s) that are proposed to be LF state(s). The LF state(s) can be populated directly from hot vibrational excited states (¹MLCT) and from the thermally equilibrated metal-to-ligand charge transfer excited (thexi) state. On TiO₂ the excited state behavior of Ru(bpy)₂(ina)₂(PF₆)₂ is very similar to that on ZrO₂, except that fast remote interfacial electron injection occurs, $k_{inj} > 10^8 \text{ s}^{-1}$. Ru(bpy)₂(ina)₂/TiO₂ displays temperature dependent electron injection, intersystem crossing, and emission quantum yields. The Jablonski-type diagram shown in Figure 3 was proposed to account for the observed behavior wherein the population of LF states from hot vibrational excited states competes kinetically with electron injection.

In this presentation, new details of the temperature dependent processes will be reported for a family of Ru(LL)₂(ina)₂(PF₆)₂ sensitizers. The data provide insights into how molecular photonic materials with desired temperature dependent electronic and optical properties can be rationally designed.

¹ Qu, P.; Thompson, D.W.; Meyer, G.J. *Langmuir* **2000**, *16*, 4662-4671.

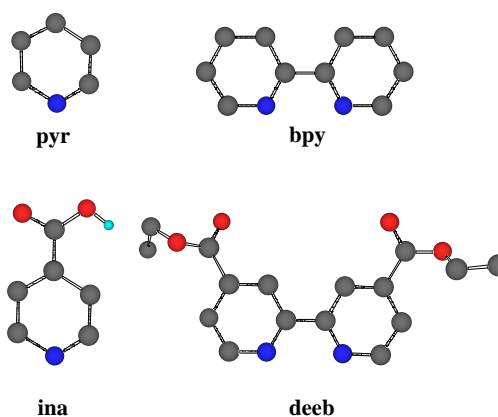


Fig. 1. Ligands used for sensitization studies where pyr is pyridine, bpy is 2,2'-bipyridine, ina is isonicotinic acid, and deeb is 4,4'-(CO₂Et)₂-bpy.

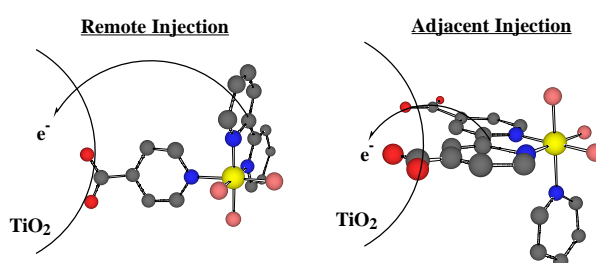


Fig. 2. Schematic representation of 'remote injection' from a Ru(II) coordination compound bound to TiO₂ through an ina ligand and of 'adjacent injection' from a deeb ligand.

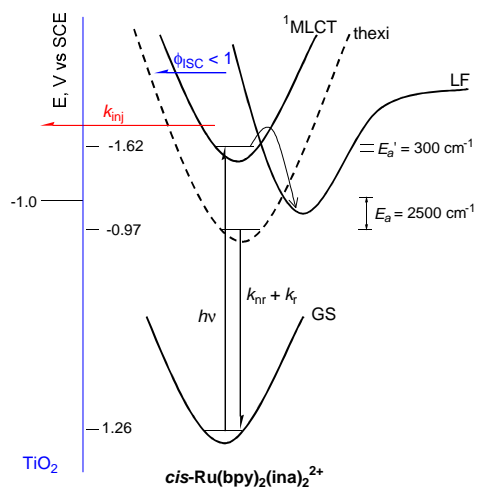


Fig. 3. Jablonski-type diagram abstracted from the photophysical and electrochemical properties of Ru(bpy)₂(ina)₂/TiO₂, where GS is the ground state, ¹MLCT is the initially formed excited state, thexi is the thermally equilibrated excited state, LF is the ligand field excited state, φ_{isc} is the intersystem crossing yield.