Ligand Localized Trapping of Conduction Band Electrons in Ruthenium(II) and Osmium(II) Sensitized Titanium Dioxide Films.

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Herein, we report the first evidence that electrons injected into TiO_2 by sensitizer excited states can be subsequently trapped by low-lying ligands of other ground state sensitizers forming a long-lived charge-separated state. The dye molecules employed in this study are $[Ru(bpy)_2(deebq)](PF_6)_2$ (**1**) and $[Os(bpy)_2(deebq)](PF_6)_2$ (**2**), where bpy is 2,2'-bipyridine and deebq is 4,4'-diethylester-2,2'-biquinoline. The ethyl ester moieties on deebq allow for attachment of the dye molecules to nanocrystalline, mesoporous TiO_2 substrates. Upon surface attachment, the deebq ligands are adjacent to the surface while the bpy ligands are remote. Photophysical and electrochemical properties of the two compounds have been measured and are listed in Table I. Upon pulsed (10 Hz) 417 nm laser (Nd:YAG) excitation of $[Ru(bpy)_2(deebq)](PF_6)_2/TiO_2$ or $[Os(bpy)_2(deebq)](PF_6)_2/TiO_2$ films submersed in an acetonitrile bath under Argon, long-lived UV-Vis spectral changes are observed (Figure 1). Over time, the original ground state absorbance spectra returns ($k_{obs} \sim 10^{-3}$ s^{-1}). No long-lived (>1 s) absorbance changes are observed when the same films are irradiated with 532 nm pulsed laser excitation or when the sensitizers are attached to ZrO_2 and irradiated in a similar fashion. It is proposed that the absorbance changes arise from the formation of a $(Ru/Os)^{III}/(Ru/Os)^{I}$ charge separated state, where $(Ru/Os)^{I}$ is $[(Ru/Os)^{II}(bpy)_2(deebq^{\cdot-})]^+$ in which the deebq ligand has been reduced. The proposed mechanism involves the following elementary steps: 1) Ultrafast injection ($k_{inj} > 10^8$ s^{-1}) into TiO_2 from a remote bpy ligand, 2) Diffusion of injected electrons away from the oxidized $Ru(Os)^{III}$ molecule, 3) Trapping of the injected electrons by low-lying deebq ligands of ground state dye molecules, 4) Self-exchange between neighboring $(Ru/Os)^{II}/(Ru/Os)^{I}$ sensitizers, 5) Recombination between $(Ru/Os)^{III}/(Ru/Os)^{I}$ (Figure 2). The electron trapping step is assumed to be statistically favorable due to the ratio (~99:1) of ground state sensitizers per TiO_2 particle to oxidized sensitizers per TiO_2 particle following photo-induced injection.

In support of such a mechanism, spectroelectrochemistry shows that the deebq ligand is reduced prior to acceptor states in TiO_2 in both the Ru and Os sensitizers (Figure 3); as expected, the electron trapping step is thermodynamically downhill. From spectroelectrochemical experiments, simulated spectra for $(Ru^{III} + Ru^{I})/TiO_2$ and $(Os^{III} + Os^{I})/TiO_2$ were obtained. The difference spectra from UV-Vis "flashing" experiments agree well with the simulated spectra. Likewise, transient absorbance spectra after 5 μs also agree well with the simulation. Finally, long-lived charge separation is apparently dependent upon the conduction band edge energy as is surmised from experiments involving Li^+ or H^+; the electron trapping step is unfavorable in the presence of $LiClO_4$ or when the TiO_2 film is pretreated with pH=1 H_2SO_4 (aq) prior to sensitization.

The above results could find applications in electrochromic or photochromic devices. In addition, the technology can be used in novel write-erase devices.
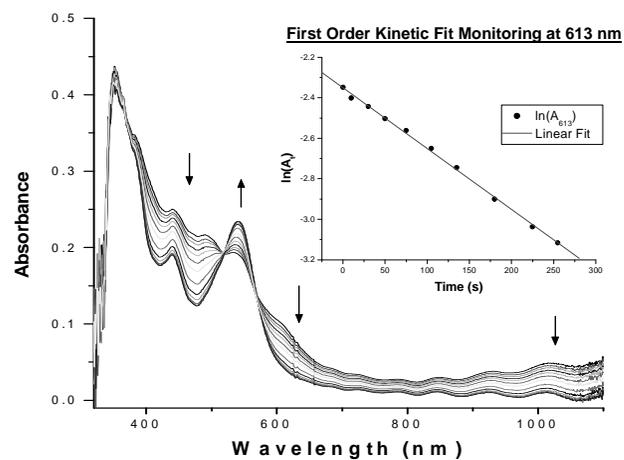

Figure 1. UV-Vis spectral changes with time for $[Ru(bpy)_2(deebq)](PF_6)_2/TiO_2$ following 417 nm excitation. Inset: First Order kinetic fit
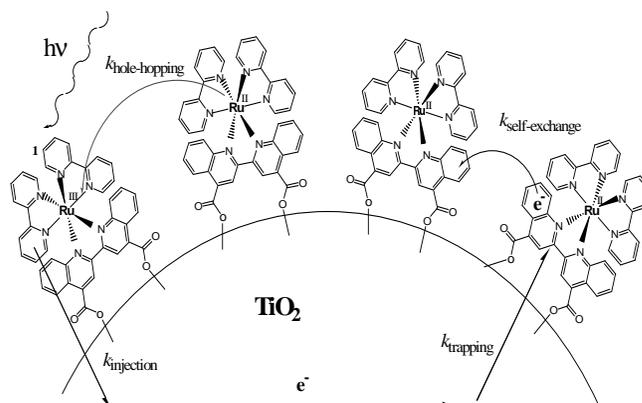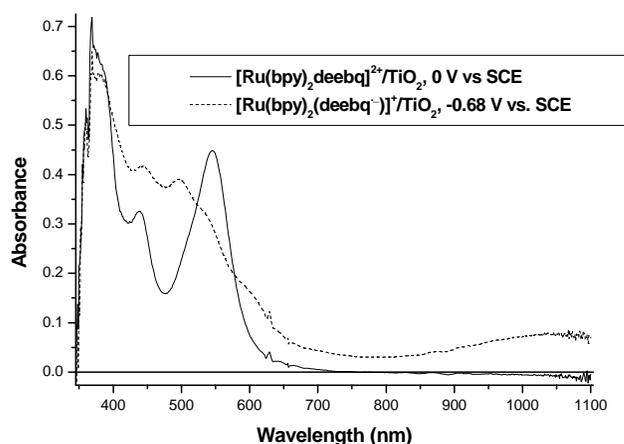

Figure 2. Schematic of Proposed Mechanism.

Figure 3. Absorbance changes arising from the electrochemical reduction of $[Ru(bpy)_2(deebq)](PF_6)_2/TiO_2$.

Table I. Photophysical and Electrochemical Properties of Sensitizers in Acetonitrile

S	λ_{abs} (nm)	τ (ns)	λ_{PL} (nm)	$E_{1/2}$, V		
				$M^{III/II}$	$(deebq)^{0/-}$	$M^{III/II*}$
1	427 555	90	835	1.49	-0.56	-0.15
2	442 579	11	[a]	1.10	-0.60	[a]

[a] If compound is emissive, it occurs at wavelengths greater than 900 nm, which is beyond our instrument's ability to detect.