

Charge Injection Through Rigid Bridges At Molecule-Semiconductor Nanoparticle Interfaces

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Sensitization processes resulting from the photoexcitation of chromophores (sensitizers) bound to semiconductor nanoparticles are the basis of numerous molecular devices, including TiO_2 solar cells, where the sensitizer is frequently a Ru^{II} -polypyridyl complex. In a solar cell, the net process generates an electrical current with light of lower photon energy than the semiconductor band gap. A simplified illustration of the sensitization process is shown in **Fig. 1**.

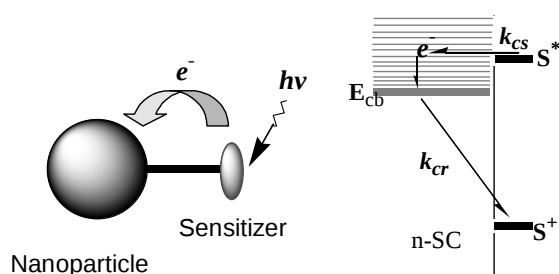


Fig. 1. Upon photoexcitation (S^*) of a sensitizer bound to a semiconductor nanoparticle, an electron is injected (k_{cs}) in the conduction band. Recombination (k_{cr}) to the oxidized sensitizer (S^+) is a competing process.

In order to study key aspects of electron transfer processes at sensitizer-nanoparticles interfaces, including charge injection, charge recombination and distance dependence, we have prepared a series of rigid sensitizers made of tripodal (**I**)¹ and rigid-rod (**II**)² bridges substituted with Ru^{II} -polypyridyl complexes and other chromophores. (**Fig. 2**).

These molecules bind covalently to TiO_2 nanoparticle thin films through COOR groups, and, since are rigid, provide a high degree of control over the position of chromophoric groups on nanoparticle surfaces.

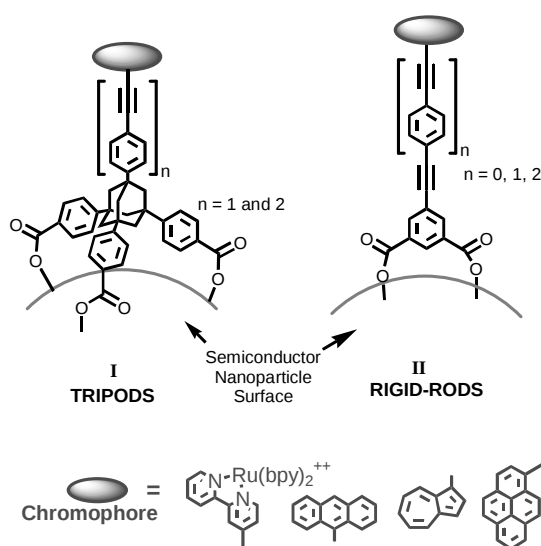


Fig. 2. Examples of rigid-rods and tripods substituted with organic and inorganic chromophores

The excited state and redox properties of sensitizers **I** and **II** were studied in fluid solutions, as well

as on nanocrystalline TiO_2 or ZrO_2 mesoporous thin films to which **I** and **II** were bound. It was found that all tripods bind strongly ($K \sim 10^5 \text{ M}^{-1}$) to the mesoporous thin films and that the surface coverage on the nanoparticles (measured spectroscopically and electrochemically) is very high. For the tripods, IR data are consistent with the formation of three surface ester linkages in a three-point attachment geometry, as illustrated in **Fig. 2**. Pulsed 532 nm light excitation of the tripods substituted with Ru^{II} -complexes and bound to TiO_2 films, resulted in the immediate appearance of the absorption difference spectra of the interfacial charge separated state comprised of an electron in TiO_2 and the oxidized sensitizer (Ru^{III}).¹

More recently, we have performed ultrafast spectroscopy studies to quantify the rate constant for excited state electron injection for tripods bound to TiO_2 . We observed remarkably fast excited state electron transfer ($\sim 500 \text{ fs}$) while the recombination of the injected electron with the oxidized $\text{Ru}(\text{III})$ follows second-order kinetics and requires milliseconds for completion. A comparison of the kinetic traces of two tripods and $(\text{dcb})\text{Ru}(\text{bpy})_2^{2+}$ as the reference (**Fig. 3**) shows that the charge injection rates slow down as the tripod's length increases from 1.5 nm to 2.2 nm.

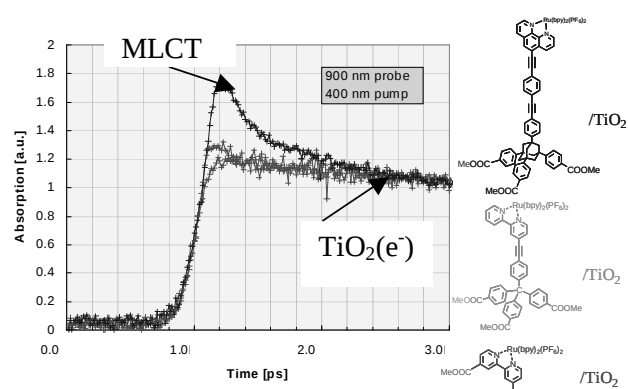


Fig. 3. Ultrafast photoinduced electron injection of chromophores varying in length and bound to TiO_2 films.

Finally, we will discuss preliminary results for the preparation of solar cells from **I** and **II**, and how the molecule-nanoparticle electronic interaction are affected by the presence of conjugated or saturated bridges.

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