Subpicosecond Photoinduced Charge Injection from "Molecular Tripods" into Mesoporous TiO$_2$ Over the Distance of 24 Angstroms

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Sensitization processes resulting from the photoexcitation of chromophores (sensitizers) bound to semiconductor nanoparticles are of great importance for solar energy conversion.[1] Examples are TiO$_2$ solar cells, where the sensitizer is usually a Ru^{II}−polypyridyl complex substituted with COOR binding groups, such as Ru(bpy)$_2$-(dme)$^{2+}$ (**1**).[2]

To study the dynamics of long-range interfacial charge-transfer processes in sensitizer/semiconductor nanoparticle systems,[3] we prepared a series of rigid sensitizers made of a tripod-shaped base terminated with a Ru^{II} complex and attached them to the surface of mesoporous nanocrystalline (anatase) TiO$_2$ thin films through three COOR groups.[4] The three-point attachment and the rigidity of these molecules allow the control of the distance and orientation of the sensitizer with respect to the nanoparticle surface. Earlier nanosecond experiments with the tripod/TiO$_2$ systems demonstrated that the excited-state electron injection is quantitative and occurs well within the duration of the laser pulse.[4a,b] In this communication, we report the observation of ultrafast charge injection from the longest tripods prepared in these laboratories, **2** and **3** shown in Figure 1,[5] in which the Ru-to-footprint distance is 24 Å.[6] To our knowledge, this is the first example of subpicosecond photoinduced ET in sensitized TiO$_2$ occurring over such extended distances.

Interfacial charge injection was investigated in **2** and **3** (Figure 1) bound to TiO$_2$ mesoporous films, with **1** serving as the reference. The structures of **2** and **3** are identical except for the ligand connecting the Ru^{II} center to the tripod (phenanthroline in **2** and bipyridine in **3**). The thin films were cast on microscope cover glasses and treated with solutions of **1**, **2**, or **3**, following previously described procedures.[4a] The resulting **1**/TiO$_2$, **2**/TiO$_2$, and **3**/TiO$_2$ systems were excited at 405 nm (SH) and probed with the white light continuum generated by the fundamental output of a home-built 1 kHz multipass Ti:sapphire amplifier.[7] The typical pulse length was 110 fs, and the beams were mildly focused to ∼0.5−1.0 mm diameter at the sample. The injection dynamics was probed over a broad range of wavelengths. The analysis focused on the 750−1100 nm spectral region, where only the MLCT excited state of the Ru^{II} chromophore and the electron injected into the conduction band of TiO$_2$, $e^-_{TiO_2}$, exhibit appreciable absorption[8,9] and no stimulated emission is observed.

For the reference system **1**/TiO$_2$ the electron injection occurred within the response time of our instrument, $k_{inj} > 1 \times 10^{13}$ s^{-1},
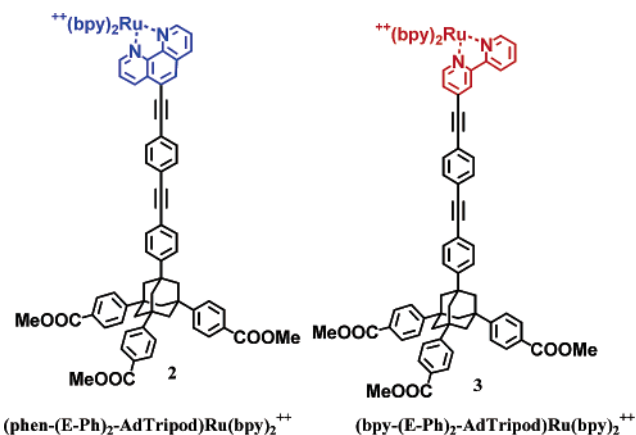

Figure 1. Tripodal semiconductor sensitizers **2** and **3**. Note the *phen* bridging ligand in **2** and *bpy* in **3**.
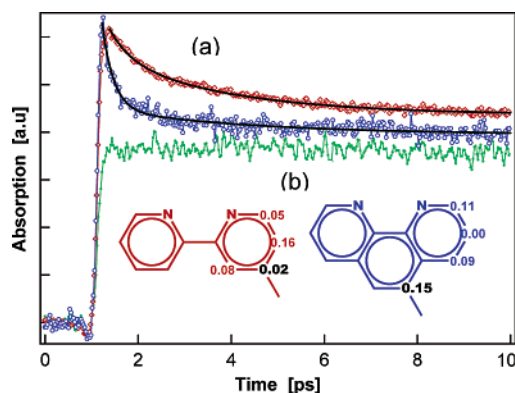

Figure 2. (a) Long-range interfacial charge injection in **3**/TiO$_2$ (top), **2**/TiO$_2$ (middle), and the reference **1**/TiO$_2$ (bottom), monitored at 900 nm. For better presentation the transients were scaled in accordance with the amplitude of the long-lived component, $e^-_{TiO_2}$. The biexponential fits are shown by the solid lines. (b) LUMO electron densities (AM1) of the *bpy* and *phen* ligands. Note the large difference at the bridging carbon atoms.

and only the long-lived absorption of $e^-_{TiO_2}$ was detected (Figure 2a, lowest trace). This is fully consistent with the reports of other groups, which place the injection rate of directly bound Ru^{II}−polypyridyl sensitizers in the sub-100 fs range.[10] Recent state-of-the-art measurements on related sensitizers show that this rate is ∼20−30 fs,[11] i.e., much faster than the duration of our excitation and probe pulses. Upon excitation of **2**/TiO$_2$ and **3**/TiO$_2$ a very rapid long-range charge injection was observed (Figure 2a). The kinetics can be well reproduced by a biexponential decay: $k_1 = 4.1 \times 10^{12}$ s^{-1} ($\pm 8\%$) and $k_2 = 3.0 \times 10^{11}$ s^{-1} ($\pm 15\%$) for **2**, and $k_1 = 2.2 \times 10^{12}$ s^{-1} ($\pm 11\%$) and $k_2 = 3.8 \times 10^{11}$ s^{-1} ($\pm 4\%$) for **3**.[12] Remarkably, in both cases approximately one-half of the charge injection occurs on subpicosecond time scale, with time constants
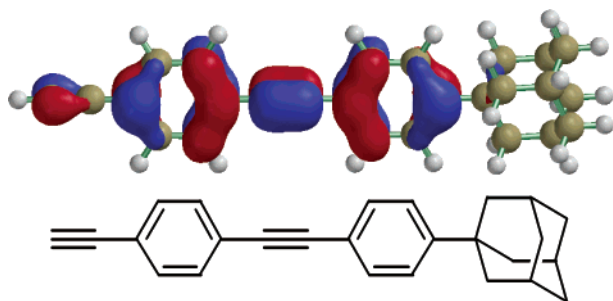
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Figure 3. The delocalized LUMO of the (E−Ph)₂ bridge connecting the phenanthroline or bipyridine ligand to the adamantane core of the tripod (AM1 optimization, Spartan '02, Wavefunction, Inc.).

of 240 fs (67%) and 450 fs (35%), respectively. These very fast rates can be rationalized considering the extensive π-conjugation of the arm that connects the Ru complex to the adamantane base (Figure 3). Similar effects of bridge conjugation ("molecular wire" behavior) have been observed by others,[13] and our own study of shorter tripods has shown considerable delocalization of the MLCT excited state onto the phenylethynyl arm.[4a,d]

The biexponential kinetics of charge injection can occur for a variety of reasons, e.g. inhomogeneity of surface binding, vibrational cooling (IVR), or intersystem crossing (ISC) of the MLCT states.[11b,c,14] Our preliminary experiments have shown no depolarization effects in **1**/TiO₂, **2**/TiO₂, and **3**/TiO₂. The IR spectra of surface-bound **2** and **3** show that within the experimental error all COOR groups participate in the binding. Combined with the trigonal geometry of the tripod, this ensures that the axis of the sensitizer is normal to the local surface of the nanoparticle, and as a result, the distance is well controlled. Consequently, the most likely source of the complex kinetics is the competition between the rapid electron injection on one hand and the combination of IVR and the ISC of the on the other, as it was convincingly demonstrated for several similar sensitizers.[11b,c,15] Thus the subpicosecond component is assigned to the injection from the unrelaxed MLCT state, while the slower one originates from the fully thermalized state. This leads to the intriguing possibility of "hot injection", i.e., electron injection without the complete loss of excess excitation energy, occurring over a large distance separating the sensitizer from the surface of the semiconductor.[16] This type of remote charge injection proceeding prior to full thermalization of the excited state is of great interest in the field of photovoltaics.[17] Clearly, this important aspect of our systems is not fully understood yet and will be the focus of a detailed investigation in the future.

The considerably faster injection exhibited by the phen-based **2** points to the presence of electronic coupling between the phenanthroline fragment and the conjugated bis-phenylethynyl bridge that is stronger than for the otherwise identical bpy-based **3**. MO calculations support this explanation and show that the LUMO electron density at the C5 bridging atom in phen is much higher that that at the corresponding C4 bridging atom in bpy ($\rho_{LUMO} = 0.15$ vs 0.02, see Figure 2b). The pronounced sensitivity to the details of the electronic structure of the sensitizer suggests that despite the fast injection rates these systems may remain within the limits of weak coupling.

In conclusion, we have shown the presence of a remarkably fast subpicosecond component in the long-range (24 Å) charge injection from molecular tripods into TiO₂. This suggests that "hot injection"

in surface-modified semiconductors can be achieved even over such long distances. The likely role of the electronic delocalization of the bridging unit and bridge-ligand states, as well as the distance dependence of the dye-to-semiconductor electron transfer are presently studied using tripodal compounds analogous to **2** and **3**.

Supporting Information Available: Characterization data for **2** and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) The complete synthesis of **2** and **3** will be reported elsewhere. For the characterization data of **2** and **3** (¹H NMR, HRMS elemental analysis, and IR), see the Supporting Information.
(6) The footprint is the plane defined by the three surface bound O-atoms. The Ruᴵᴵ-to-footprint distance in the earlier tripods (ref 4a) was 15−18 Å.
(7) The setup follows closely the design described in Backus, S.; Peatross, J.; Murnane, M. M.; Kapteyn, H. C. *Opt. Lett.* **1995**, *20*, 2000.
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