Subpicosecond Photoinduced Charge Injection from “Molecular Tripods” into Mesoporous TiO₂ 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. Examples are TiO₂ solar cells, where the sensitizer is usually a RuII—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, we prepared a series of rigid sensitizers made of a tripod-shaped base terminated with a RuII complex and attached them to the surface of mesoporous nanocrystalline (anatase) TiO₂ thin films through three COOR groups.³ 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/TiO₂ systems demonstrated that the excited-state electron injection is quantitative and occurs well within the duration of the laser pulse.⁴ 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, 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 TiO₂ occurring over such extended distances.

Interfacial charge injection was investigated in 2 and 3 (Figure 1) bound to TiO₂ mesoporous films, with 1 serving as the reference. The structures of 2 and 3 are identical except for the ligand connecting the RuII 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.⁶ The resulting 1/TiO₂, 2/TiO₂, and 3/TiO₂ 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 RuII chromophore and the electron injected into the conduction band of TiO₂, e⁻/TiO₂, exhibit appreciable absorption⁸ and no stimulated emission is observed.

For the reference system 1/TiO₂ the electron injection occurred within the response time of our instrument, k⁰_{inj} > 1 × 10¹³ s⁻¹.

and only the long-lived absorption of e⁻/TiO₂ was detected (Figure 2a, lowest trace). This is fully consistent with the reports of other groups, which place the injection rate of directly bound RuII—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, i.e., much faster than the duration of our excitation and probe pulses. Upon excitation of 2/TiO₂ and 3/TiO₂ a very rapid long-range charge injection was observed (Figure 2a). The kinetics can be well reproduced by a biexponential decay: k₁ = 4.1 × 10¹² s⁻¹ (±8%) and k₂ = 3.0 × 10¹¹ s⁻¹ (±15%) for 2, and k₁ = 2.2 × 10¹² s⁻¹ (±11%) and k₂ = 3.8 × 10¹¹ s⁻¹ (±4%) for 3.¹² Remarkably, in both cases approximately one-half of the charge injection occurs on subpicosecond time scale, with time constants...
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 the arm that connects the Ru complex to the adamantane base shows no depolarization (IVR), or intersystem crossing (ISC) of the MLCT excited state onto the phenylethynyl arm.4a,d

The delocalized LUMO of the (E-Ph)3 bridge connecting the phenanthroline or bipyridine ligand to the adamantane core of the tripod (AM1 optimization, Spartan ’02, Wavefunction, Inc.) has been observed by others,13 and our own study of 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 the arm that connects the Ru complex to the adamantane base shows no depolarization (IVR), or intersystem crossing (ISC) of the MLCT excited state onto the phenylethynyl arm.4a,d

Figure 3. The delocalized LUMO of the (E-Ph)3 bridge connecting the phenanthroline or bipyridine ligand to the adamantane core of the tripod (AM1 optimization, Spartan ’02, Wavefunction, Inc.).

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 triposial compounds analogous to 2 and 3.

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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.

References

(3) Injection from dyes bound to TiO2 via methylene spacers was reported by others: (a) Ashby, J. B.; Hao, E.; Wang, Y.; Lian, T. J. Phys. Chem. B 2001, 104, 1957. (b) Heimer, T. A.; D’Arcangelis, S. F.; Faragg, P.; Stolbukaj, M. J.; Meyer, G. J. Inorg. Chem. 1996, 35, 5319. However, the flexible (–CH2–)4 spacers are likely to generate a broad distribution of distances and orientations between the chromophore and the surface.
(5) The complete synthesis of 2 and 3 will be reported elsewhere. For the characterization data of 2 and 3 (H 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 Ru4+-to-footprint distance in the earlier tripods (ref 4a) was 15–18 Å.

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