Ru(II)-Bpy Complexes Bound to Nanocrystalline TiO$_2$ Films through Phenyleneethynylene (OPE) Linkers: Effect of the Linkers Length on Electron Injection Rates

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Three rigid-rod Ru-bpy sensitizers with linkers made of an oligo(phenyleneethynylene) (OPE) bridge varying in length (9.6–23.3 Å) and ending with an isophthalic acid anchoring unit were bound to TiO$_2$ (anatase) nanoparticle films, and the photoinduced electron injection rates for all three compounds were studied by femtosecond laser spectroscopy. The sensitized films were excited at 530 nm, in the MLCT region, and the injection dynamics was probed in the 600-1000 nm range. The excited state for all three compounds ($\tau \sim 2 \mu$s in acetonitrile solution) was readily quenched upon binding to TiO$_2$. All injection traces could be fitted with bi-exponential decays on a measured timescale of 130 ps. Plots of the fast or slow component of the electron injection time constants probed at 670 nm vs the spacer length yielded a very low value for the attenuation factor ($\beta \sim 0.04$ Å$^{-1}$). Although the dependence was weak, the length of the linker clearly resulted in slower injection rates. The weak and monotonic linker length dependence had not been observed with other rigid-rod models, demonstrating the importance of anchoring groups in the design of model compounds for electron transfer studies at the semiconductor interfaces.

Ru(II)–polypyridine complexes are among the most efficient photosensitizing dyes that have been employed in nanocrystalline TiO$_2$ solar cells (Grätzel cells or DSSCs). Photoexcitation of the Ru dyes, which are covalently bound to the TiO$_2$ nanoparticles surface through anchoring groups, is followed by electron injection into the conduction band of the semiconductor. The electron injection is usually an ultrafast process, complete within a few tenths of femtoseconds. Because of the potential applications in the field of solar energy conversion and the fundamental interest in interfacial electron-transfer processes, the charge injection step is investigated by many groups worldwide. To date, however, there are only a few experimental studies addressing the influence of the spacer length on the rates of electron transfer at dy-semiconductor nanoparticle interfaces. Here we report the femtosecond laser spectroscopy study of electron injection for three rigid-rod Ru sensitizers with linkers varying in length, 1, 2, and 3 in Figure 1, bound to TiO$_2$ thin films. Each linker is made of an oligo(phenyleneethynylene) (OPE) bridge that ends with an isophthalic acid (Ipa) unit. The two anchoring COOH groups on the Ipa unit ensure fewer degrees of freedom and surface orientations, when compared to structurally similar model dyes with one COOH group that have been described by others. However, the angle at which 1–3 bind to the surface is not known, and for this reason in this study, we refer to the length of the linker (C to N) rather than to a dye-to-surface distance. The FTIR-ATR spectra of the rods bound to TiO$_2$ displayed a broad carboxylate band at $\sim$1600 cm$^{-1}$, which is most consistent with bidentate coordination modes. In our previous work with tripodal linkers, the OPE bridge did not directly connect the complexes to the surface, because of either the adamantyl or sp$^3$ carbon unit in the tripodal footprint. With this work, we investigate the effect of an OPE bridge on the electron injection properties of rigid-rod Ru complexes 1–3, which we have studied in solution and bound to nanoparticles. The electron injection behavior of 1–3 is of interest, because OPEs are considered good prototypes of “molecular wires” that may function as exciton and/or charge carriers for device applications. Due to their electronic properties, rigidity, linear geometry, and synthetic accessibility through Pd-catalyzed cross-coupling reactions, OPEs have been frequently used as spacers in numerous energy and electron-transfer studies. The excited-state behavior of OPE oligomers has been recently characterized by Kamat et al. Based on this background, we considered that the bridge in rods 1–3 may act as a mediator of electron transfer through delocalization of the excited state. Furthermore, to our knowledge, no injection

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studies of donor–OPE–semiconductor systems have been reported. The interaction between the Ru complex and the acceptor (in this case the semiconductor), is likely to be mediated by the LUMO of the π-conjugated OPE bridge, and our previous work has indicated that the electronic coupling between the Ru complex and the OPE bridges is strong.

The dyes 1–3 were bound to ∼12 µm thick TiO$_2$ (anatase) nanoparticles films cast on glass slides. The experimental details for the films preparations, binding procedures, and pump–probe measurements are provided in the Supporting Information.

Figure 2 shows the absorption spectra of 1–3 in solution and the overlaid spectra of one of the dyes before and after binding to a TiO$_2$ film. The absorption of the OPE units overlaps with the intense absorption of the TiO$_2$ substrate transparent above ∼370 nm, Figure 2b. The sensitized films were excited at 530 nm, in the MLCT region, and the injection dynamics was probed in the 600–1000 nm range. The 530 nm excitation wavelength was selected in order to deposit a minimum amount of excess energy. The MLCT “state” of Ru(bpy)$_3$ consists of several distinct states. Therefore, exciting close to the red edge of the band should reduce and simplify electronic relaxation between the individual states. The dominant absorbing species at 900 nm is the MLCT triplet state. The similarity of injection rates retrieved from the 670 and 900 nm traces (see the Supporting Information) strongly suggests that we see only injection from the 3$^1$MLCT state. This is consistent with the rates retrieved from the double exponential fitting as even the fast component is considerably slower than the 50–100 fs inter-system crossing rate reported in the literature for the Ru$^{II}$ type sensitizers. The excited-state lifetime for 1–3 in acetonitrile solution was about 2 µs, and binding to TiO$_2$ films resulted in effective quenching of the excited state. It is important to note that none of the traces recorded in solution (Supporting Information) exhibit the decay that is found for the same molecules bound to TiO$_2$. All of this confirms that the observed decays are due to interfacial electron injection. Figure 3 shows the kinetic traces of electron injection into the semiconductor conduction band for 1/TiO$_2$, 2/TiO$_2$, and 3/TiO$_2$ probed at 670 nm. The injection time constants, amplitudes, and $\lambda_{abs}$ of the MLCT band for each rod are reported in Table 1. All injection traces could be fitted with biexponential decays on a measured time scale of 130 ps. Multieponential electron injection and recombination kinetics are characteristic of Ru complexes bound
to TiO₂. This behavior is attributed to a combination of rapid intersystem crossing (ISC) and different injection rates from the 1MLCT and 2MLCT states, and, possibly, from nonthermalized excited states. Multiexponential injection behavior may also derive, at least in part, from the heterogeneity and disorder of the porous nanoparticle films.

Plots of the fast or slow component of 1−3 vs the spacer length yielded a very low value for the attenuation factor (β ~ 0.04 Å−1). Although the dependence is weak, a trend is clearly observable: an increase of the length of the linker results in slower injection rates. Interestingly, both the slow and fast injection components exhibit a remarkably similar distance dependence with β values of 0.044 ± 0.011 and 0.043 ± 0.0008 Å−1, respectively. The relative amplitudes of the components, however, do not exhibit a discernible trend. The fast component can be somewhat speculatively attributed to electron injection from vibrationally hot and incompletely solvated MLCT* states. It is also possible that the distribution of the PF6− counterions within the voids of the film shifts the effective oxidation potential of the Ru center and therefore alters the injection rate. Both the r₁ and r₂ components are sufficiently slow (~7 to 100 ps) to arise from electron injection from the triplet MLCT state, as the intersystem crossing from the initial singlet state occurs as the intersystem crossing from the initial singlet state occurs (~100 fs time scale). The similarity of the slopes of the fast and slow components strongly suggests that they both result from the same, or very similar, electron-transfer pathways. Therefore, the difference is likely to originate from thermodynamic factors (i.e., either incomplete relaxation of the MLCT* state as described above or direct injection into low-lying traps).

The observed β ~ 0.04 Å−1 indicates a much weaker attenuation with distance than predicted. High-level MO calculations place β values for OPE oligomers between 0.39 and 0.96 Å−1, depending whether the phenylene rings are all in plane or perpendicular, respectively. Albinsön and co-workers have experimentally obtained β = 0.20 Å−1 and close to exponential behavior for triplet energy transfer in porphyrin-based donor–OPE–acceptor systems in solutions. It should be remembered that there are examples of donor-OPE-acceptor systems in which the distance dependence is absent or much weaker than that expected on computational grounds. For example, Smalley et al. have observed nonmonotonic distance dependence of electron transfer of ferrocene-OPE systems attached to gold surfaces, and Hammarström et al. reported distance independent energy transfer in Ru-complex-OPE– fullerene models in solution.

It is possible that, in the present case, electron injection from the Ru-bpy complex proceeds through multiple pathways. In the sponge-like environment of the mesoporous film, direct contacts between the conjugated rod and the TiO₂ particles other than that to which the rod is attached are likely. Such contacts can act as short-circuits competing with electron transfer along the full length of the rod, thus leveling the slope of the distance dependence. Unlike Willig and co-workers, we did not observe an ultrafast subpicosecond component of injection that could be convincingly attributed to direct contacts between the redox active chromophore and TiO₂ particles. This, together with other evidence, suggests that the thermalized MLCT state is preferentially localized on the ligand attached to the conjugated rod. Indeed, delocalization of the MLCT state onto the OPE rod may also potentially account for some of the weakness of the electron injection distance dependence.

In conclusion, a weak and monotonic linker length dependence was observed in a series of three Ru-bpy complexes bound to TiO₂ films through linkers made of OPE bridges ending with an isothiophenic acid anchoring unit. This trend had not been observed with other rigid-rod models, demonstrating the importance of anchoring groups in the design of model compounds for electron-transfer studies at the semiconductor interfaces.

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Supporting Information Available: Description of films preparation and properties, the ultrafast laser system, electron injection data at 900 nm, and solution data for all the rods at 670 and 900 nm. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes
(13) The surface coverage was lowest for compound 3. This is reflected in the lower amplitudes at τ = 0 for 3 (Figure 3). We have often observed that structural differences result in difference in binding properties, and that the largest or more lipophilic compounds are most difficult to bind.
(14) The attenuation factor (β) was calculated using the formula β = kᵣ₀ exp(−r²) where r is the C distance.
(15) For the role of the PF₆⁻ counterion on the calculated optoelectronic properties of 1 and 2, see ref 8.
(16) Willig and Gundlach, private communication.