

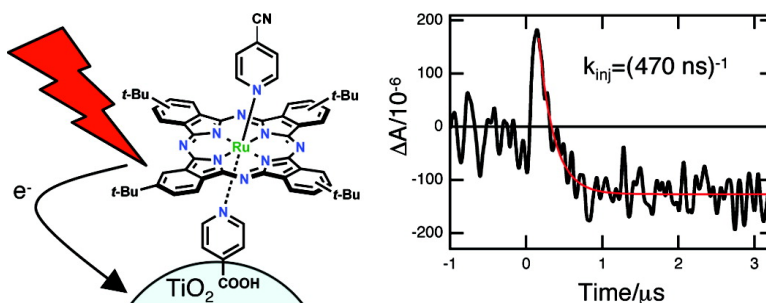
Communication

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Slow Electron Injection on Ru–Phthalocyanine Sensitized TiO₂

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The function of dye sensitized solar cells is based upon photoinduced electron injection from a molecular excited-state into the conduction band of a nanocrystalline metal oxide film. Over the last 10 years, extensive studies of model systems based on dye sensitized metal oxide films have demonstrated that such interfacial electron transfer can occur on remarkably fast time scales.^{1–3} Nevertheless it remains an open question as to whether such ultrafast injection dynamics are necessary for efficient device function. We have recently reported charge injection dynamics on the 100 ps–1 ns time scale for a range of ruthenium bipyridyl dyes adsorbed to TiO₂ in the presence of redox electrolytes.^{4,5} We have suggested that such relatively slow injection dynamics are still fast enough to compete effectively with excited-state decay-to-ground, and therefore are consistent with efficient device function.

In this paper, we extend our studies of the time scale of electron injection necessary to achieve efficient DSSC function to phthalocyanine (Pc) sensitizer dyes and specifically to axially coordinated ruthenium phthalocyanines such as RuPc **1** (Figure 1). Pc's are attractive sensitizers for DSSCs because of their intense red absorbance and excellent photochemical and electrochemical stability.⁶ Moreover, when bearing axial ligands, their aggregation tendency on the surface of the nanocrystalline semiconductor is remarkably reduced.^{7,8} In DSSC with suitable electrolytes, RuPc **1** dye is capable of efficient photocurrent generation, with absorbed photon to current efficiencies (APCE) of up to 45%, consistent with previous studies of analogous⁹ and related¹⁰ dyes. In terms of electron injection, it is interesting to note that the LUMO orbital for RuPc **1** is expected to be delocalized over the conjugated macrocycle of the phthalocyanine ring and therefore spatially well separated from the TiO₂ surface. This contrasts with more widely studied ruthenium bipyridyl dyes, where the LUMO orbital is localized on bipyridine groups in close proximity to the TiO₂. This raises an interesting issue over the time scale and mechanism of charge injection for this class of RuPc dyes. We show herein that electron injection for this efficient sensitizer dye is indeed remarkably slow, with a rate constant of ca. 10⁷ s⁻¹, and discuss the implications of this observation in terms of the requirements on electron injection for efficient DSSC device function.

The new RuPc **1** was synthesized from the corresponding bis-(benzonitrile)tetra-*tert*-butyl RuPc complex,¹¹ which was refluxed in THF in the presence of one equivalent of the 4-cyanopyridine ligand and three of the isonicotinic acid one. The desired compound RuPc **1** with two different axial ligands was isolated in ca. 30% yield.¹²

Steady-state absorption and emission measurements were carried out on RuPc **1** sensitized nanocrystalline TiO₂ films covered with

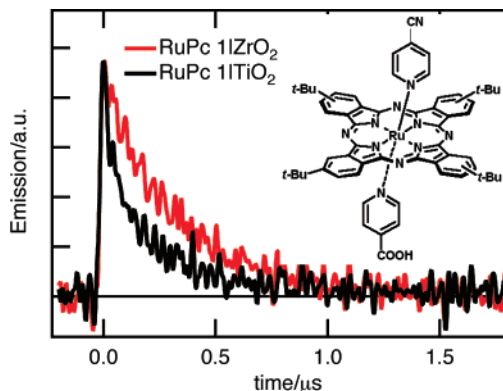


Figure 1. Phosphorescence emission decays of RuPc **1**/ZrO₂ (red) and RuPc **1**/TiO₂ (black) films ($\lambda_{\text{exc}} = 630$ nm, $\lambda_{\text{det}} = 880$ nm). The traces have been normalized for ease of comparison.

a redox inactive electrolyte, 0.6 M LiN(SO₂CF₃)₂ in propylene carbonate and compared against control data employing non-injecting RuPc **1** sensitized ZrO₂ films. Both films exhibited an absorbance maximum at 633 nm, indistinguishable from solution spectra for this dye. For both films, a very weak fluorescence band at ca. 690 nm was observed, in agreement with previous observations that RuPc dyes are only weakly fluorescent.¹³ This weak fluorescence has been assigned to rapid (<100 ps) and efficient singlet-to-triplet intersystem crossing induced by the presence of the heavy Ru atom.^{13,14}

Time-resolved emission measurements (Figure 1) of RuPc **1** sensitized ZrO₂ resolved a phosphorescence emission maximum at 880 nm (see Supporting Information). This emission, assigned to the RuPc triplet state, exhibited a monoexponential decay with a lifetime of 320 ns (Figure 1), consistent with previous reports of RuPc triplet-state lifetimes.^{7,9,14,15} In contrast, for the RuPc **1**/TiO₂ films, this phosphorescence decay is significantly accelerated, with an average emission time constant of 190 ns¹⁶ (Figure 1), consistent with electron injection from RuPc **1** triplet state into the TiO₂ conduction band. We further note that the initial amplitude of the phosphorescence decays for both films were similar, indicating similar triplet yields for both films, and suggesting that singlet electron injection was not efficient.

Transient absorption measurements were undertaken to investigate further these injection dynamics. Figure 2A shows a comparison between the transient absorption spectra observed for RuPc **1**/ZrO₂ at 1 μ s after excitation, assigned to the dye triplet-state absorption and that of RuPc **1**/TiO₂ at 10 μ s, assigned to the charge separated state RuPc **1** cation/TiO₂(e⁻). Both spectra show very good agreement with reported triplet¹⁵ and radical cation spectra⁹ for other RuPc's. Decay kinetics of both spectra (Figure 2, inset)

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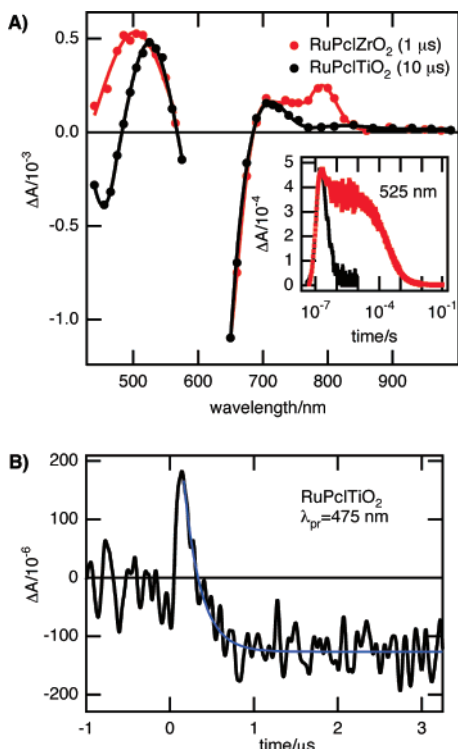


Figure 2. (A) Transient absorbance spectra of (i) RuPc **1**/ZrO₂ (red) at 1 μs after excitation, assigned to RuPc **1** triplet state and (ii) RuPc **1**/TiO₂ (black) at 10 μs, attributed to RuPc **1** cation/TiO₂(e⁻) states. For the sake of comparison, the spectra were normalized at 650 nm. The inset is a comparison of the absorption kinetics for these samples probed at 525 nm. (B) Absorption kinetics of RuPc **1**/TiO₂ film probed at 475 nm. The transient can be fitted by a monoexponential function with a time constant of 200 ns (blue solid line), assigned to electron injection. The excitation wavelength was 630 nm.

confirm these assignments. These spectra can be most unambiguously distinguished at ca. 475 nm, where they exhibit oppositely signed signals. Monitoring the kinetics of RuPc **1**/TiO₂ at this wavelength (Figure 2B), we observe the initial appearance of the positive absorption of the dye triplet state and the subsequent decay of this signal with a 200 ns time constant to give negative signal indicative of formation of the dye cation. These data clearly confirm that charge separation in RuPc **1**/TiO₂ films proceeds from the RuPc **1** triplet state with a lifetime of ca. 200 ns.

The energy levels and dynamics of RuPc **1**/TiO₂ are summarized in Figure 3. Optical excitation of RuPc **1** is followed by intersystem crossing from S₁ to T₁, $k_{ISC} > (100 \text{ ps})^{-1}$. Electron injection from T₁ state into the TiO₂ conduction band proceeds with a rate constant $k_{inj}(T_1) \approx (470 \text{ ns})^{-1}$. Electron injection from the S₁ appears to be relatively inefficient. An estimate of $k_{inj}(S_1)$ can be obtained, knowing $k_{inj}(T_1)$, $E(S_1)$, and $E(T_1)$, and assuming that the density of electron acceptor states in nanocrystalline TiO₂ has an exponential dependence on the energy of the states (see Supporting Information). This estimation gives a value for $k_{inj}(S_1)$ ranging from 600 ps^{-1} to 30 ns^{-1} , too slow to compete with the relaxation of S₁ to T₁ by intersystem crossing, consistent with our experimental observations.

We conclude that for axially substituted RuPc's, the most efficient pathway for electron injection into TiO₂ is from the RuPc triplet state. The long lifetime of this T₁ state enables electron injection to occur on the 100's of nanoseconds time scale, leading

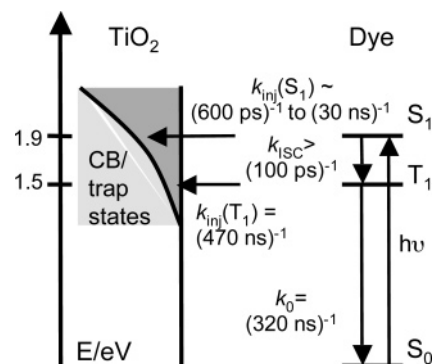


Figure 3. Schematic representation of the energy levels of RuPc **1**/TiO₂.

to APCE values of >45%. It is thus clearly apparent that ultrafast electron injection is not a prerequisite for efficient PV device function. This triplet electron injection is in kinetic competition with T₁ decay-to-ground, and optimization of this kinetic competition is therefore likely to be a key factor in achieving further improvements in the efficiency of RuPc sensitized solar cells.

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Supporting Information Available: Synthetic details, spectroscopic data, and estimate of $k_{inj}(S_1)$ for RuPc **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- In the reaction, the three possible RuPc (**1–3**) bearing different axial pyridine ligands are formed: RuPc **1** is functionalized with two different pyridine ligands (namely, 4-carboxypyridine and 4-cyanopyridine), whereas RuPc's **2** and **3** carry two 4-cyanopyridine and 4-carboxypyridine ligands, respectively. The three compounds can be easily separated by column chromatography (see Supporting Information for more details).
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- In this case, the emission decay presents non-exponential dynamics and an average emission time constant is calculated (see Supporting Information).

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