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Interfacial Charge-Transfer Switch: Ruthenium–dppz Compounds Anchored to Nanocrystalline TiO_2

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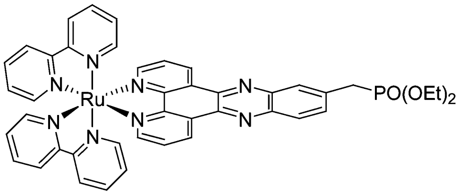
The compound $Ru(bpy)_2(dppz\text{-}R)(PF_6)_2$, where bpy is 2,2′-bipyridine and dppz-R is 11-(diethoxyphosphorylmethyl)dipyrido[3,2-*a*:2′,3′-*c*]phenazine, was prepared and anchored to mesoporous nanocrystalline (anatase) TiO_2 thin films as a probe of the effects of interfacial water on excited-state charge transfer processes at semiconductor interfaces. In nitrogen-saturated fluid acetonitrile, the $Ru(bpy)_2(dppz\text{-}R)(PF_6)_2$ compound was found to be highly photoluminescent. Water was found to quench the excited state by a mechanism adequately described by the Perrin model, from which the radius of quenching was abstracted, 75 ± 2 Å. The $Ru(bpy)_2(dppz\text{-}R)(PF_6)_2$ compounds were found to bind to the TiO_2 thin films in high surface coverages, 5×10^{-8} mol cm^{-2}. When these films were immersed in acetonitrile, long-lived excited states ($\tau = 825$ ns) that were quenched by the addition of water were observed. About 30% of the excited states could not be quenched by water. Efficient electron injection, $\phi_{inj} = 0.8$, was observed after light excitation of $Ru(bpy)_2(dppz\text{-}R)/TiO_2$ in a 0.1 M $LiClO_4$/acetonitrile solution. The addition of large concentrations of water, >0.5 M, was found to decrease the injection yield to $\phi_{inj} = 0.3$.

Ruthenium diimine compounds based on the dppz ligand, dipyrido[3,2-*a*:2′,3′-*c*]phenazine, have been widely used as luminescent probes since Sauvage and co-workers first reported their novel photophysical properties.[1] Compounds such as $Ru(bpy)_2(dppz)^{2+}$ are nonemissive in aqueous solution but have long-lived photoluminescent excited states in nonprotic environments. When the phenazine nitrogens of the dppz ligands are shielded from water, the compounds become highly emissive, and this enhancement gives rise to the celebrated "light-switch" effect.[2] Here we communicate a related effect wherein excited-state charge transfer at a semiconductor surface can be reversibly tuned with the interfacial water concentration. The studies provide direct information on the molecular environment and provide new insights into excited-state charge transfer processes at semiconductor interfaces.

Chart 1



The compound of interest is $Ru(bpy)_2(dppz\text{-}R)(PF_6)_2$, where bpy is 2,2′-bipyridine and dppz-R is 11-(diethoxyphosphorylmethyl)dipyrido[3,2-*a*:2′,3′-*c*]phenazine (Chart 1). The dppz-R ligand was prepared as previously described.[3] The compound was synthesized by methods analogous to that used for the unsubstituted dppz compounds[1] and was characterized by ^{1}H NMR, IR, UV−vis, and elemental analysis. In cyclic voltammetry experiments, the compound displayed a quasi-reversible[4] $E°(Ru^{III/II})$ wave at 1.37 V vs Ag/AgCl and a ligand-based reduction $E°(Ru^{2+/+})$ at −0.92 V vs Ag/AgCl in a 0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile electrolyte. The ligand reduction was assigned to the dppz ligand and occurred at ~300 mV more positive than the first ligand reduction on $Ru(bpy)_3^{2+}$ or $Ru(phen)_3^{2+}$.[5] Mesoporous nanocrystalline TiO_2 thin films were prepared by a previously described method.[6] Unless otherwise stated, measurements were performed at saturation surface coverages of 5×10^{-8} mol cm^{-2}.

The compound shows broad and intense metal-to-ligand charge-transfer absorption bands in acetonitrile: $\lambda_{max} = 447$ nm and $\epsilon = 20,100$ M^{-1} cm^{-1}. Light excitation into these bands gives rise to intense room-temperature photoluminescence (PL) in nitrogen-saturated acetonitrile: $\phi_{PL} = 0.067$,

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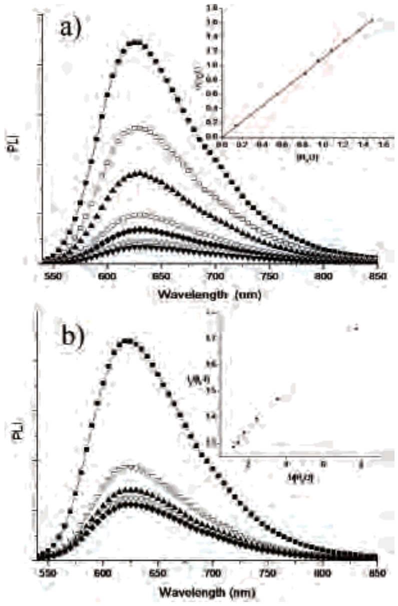

Figure 1. (a) SSPL spectra of complex $Ru(bpy)_2(dppz\text{-}R)(PF_6)_2$ (■) in neat acetonitrile and with (□) 0.3 M, (▲) 0.5 M, (○) 0.8 M, (◆) 1.1 M, and (△) 1.3 M water. The inset shows a Perrin model plot. (b) SSPL spectra of $Ru(bpy)_2(dppz\text{-}R)/TiO_2$ (■) in neat acetonitrile and with (▽) 0.13 M, (▲) 0.3 M, (○) 0.4 M, and (◆) 0.5 M water. The inset shows a modified Stern−Volmer plot.

$\tau = 750$ ns, $k_r = 8.9 \times 10^4$ s^{-1}, and $k_{nr} = 1.3 \times 10^6$ s^{-1}. The quantum yields were determined by the optically dilute technique.[7] Shown in Figure 1 are photoluminescence spectra in acetonitrile as a function of the water concentration. Stern−Volmer plots for the quenching process were found to be nonlinear and upward-curving.

The Perrin model gave an excellent fit to the experimental data, as was previously reported for $Ru(phen)_2(dppz)^{2+}$, where phen is 1,10-phenanthroline[8] (eq 1). Here [Q] is the

$$I_0/I = \exp([Q]VN) \qquad (1)$$

molar water concentration, V is the volume of the quenching sphere, and N is the number of molecules per millimole, 6.02×10^{20}.[9] In this model, excited states within a sphere of radius r of a water molecule are completely nonemissive, while those further away do not interact with the excited state.[9]

The compounds were also photoluminescent when anchored to nanocrystalline titanium dioxide thin films immersed in a neat acetonitrile solution. Here the quenching data could not be fit to the Perrin model but were adequately described by a modified Stern−Volmer model that takes into account two populations of excited states, with only one of them accessible to the water quenchers[9] (eq 2). Here f_a is

$$\frac{I_0}{I_0 - I} = \frac{1}{f_a} + \frac{1}{f_a K_a [Q]} \qquad (2)$$

the fraction of the initially formed excited states that were accessible to water, and K_a is the Stern−Volmer quenching constant of the accessible fraction. The results of the steady-state data are summarized in Table 1.

Table 1. Water Quenching of $Ru(bpy)_2(dppz\text{-}R)^{2+}$*

	acetonitrile solution[a]		TiO$_2$/acetonitrile[b]	
	slope (M^{-1})	r (Å)	K (M^{-1})	f_a[c]
SSPL	1.1 ± 0.02	75 ± 2	7 ± 1	0.7 ± 0.1
TRPL	0.97 ± 0.01	73 ± 1	7 ± 1	0.7 ± 0.1

[a] The Perrin model was used (eq 1). [b] A modified Stern−Volmer function that takes into account a population of excited states inaccessible to the quencher (eq 2). [c] The fraction of excited states accessible to the quencher.

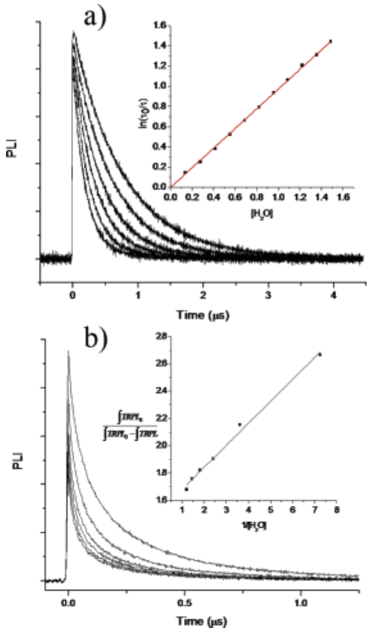

Figure 2. (a) TRPL spectra of $Ru(bpy)_2(dppz\text{-}R)(PF_6)_2$ in neat acetonitrile and with 0.3, 0.5, 0.8, 1.1, and 1.3 M water. The inset shows a Perrin plot. (b) TRPL spectra of $Ru(bpy)_2(dppz\text{-}R)/TiO_2$ in neat acetonitrile and with 0.14, 0.3, 0.5, 0.8, and 1.1 M water. The inset shows a modified Stern−Volmer plot.

Pulsed-laser excitation of $Ru(bpy)_2(dppz\text{-}R)(PF_6)_2$ in acetonitrile reveals long-lived excited states (Figure 2a). Excited-state relaxation was first-order with a notably long lifetime of 750 ns. Assuming an intersystem crossing yield of unity,[5,10] radiative and nonradiative rate constants $k_r = 1.1 \times 10^5$ s^{-1} and $k_{nr} = 1.2 \times 10^6$ s^{-1} were calculated. The addition of water led to a decrease in the lifetime and a small decrease in the amplitude. Perrin analysis of the lifetime change revealed a radius of quenching very similar to that extracted from steady-state photoluminescence (SSPL) data.

Excited-state decay for $Ru(bpy)_2(dppz\text{-}R)(PF_6)_2$ anchored to TiO_2 nanoparticles was nonexponential but was adequately described by a parallel first- and second-order kinetic model.[11] The first-order component arises from radiative and nonradiative decay $\tau = 825$ ns, and the second-order component is a result of triplet−triplet annhilation reactions that are facilitated by rapid intermolecular energy transfer between the surface-bound compounds.[12] The addition of

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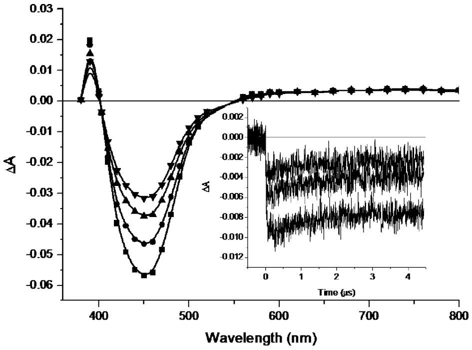

Figure 3. Time-resolved absorption difference spectra of Ru(bpy)$_2$(dppz-R)/TiO$_2$ in a 100 mM LiClO$_4$/acetonitrile solution after pulsed-laser 532.5-nm light excitation. The spectra are shown at delay times of 10 ns (■), 100 ns (◆), 500 ns (▲), and 2 μs (▼). The inset shows absorption transients monitored at 405 nm with water concentrations of 0, 0.3, and 0.5 M. The amplitudes of the signal directly report on the excited-state injection yield.

water resulted in both static and dynamic quenching of the excited state as evidenced by the decreased amplitude and shorter "lifetime" (Figure 2b). The integrated area under the time-resolved photoluminescence (TRPL) decays were also fit to the Stern−Volmer model.[9] The fraction of excited states accessible to quenchers was found to be approximately the same as that extracted from steady-state data, $f_a = 0.7 \pm 0.1$.

The addition of 0.1 M LiClO$_4$ to the external acetonitrile solution lead to efficient excited-state conduction band quenching.[13] Lithium cations are known to be potential determining ions that shift the energetic position of the conduction band edge, making excited-state quenching more favorable.[13] Figure 3 shows transient absorption spectra that were assigned to the charge-separation state Ru(bpy)$_2$(dppz)$^{3+}$|TiO$_2$(e$^-$). Comparative actinometry measurements revealed a high injection quantum yield, $\phi_{inj} = 0.8$.[14] The addition of water to the 0.1 M LiClO$_4$/acetonitrile bath resulted in a decrease in the electron injection quantum yield. For example, when the water concentration was 0.5 M in acetonitrile, the injection quantum yield was ~0.3. Higher water concentrations of up to 1.3 M did not lower the injection yield further. This was consistent with the photoluminescence quenching data, where about 30% of the excited states could not be quenched by water.

Taken together, the excited-state quenching of Ru(bpy)$_2$(dppz-R)(PF$_6$)$_2$ by water was very similar to that reported for the Ru(phen)$_2$(dppz)(PF$_6$)$_2$ compound. Our results agree well with those of Murphy and co-workers,[8] who also utilized the Perrin model to quantify the concentration dependence. The inclusion of a methylene spacer between the dppz ligand and the phosphonate binding group did not decrease the excited-state lifetimes and allowed for high surface stability in acetonitrile/water mixtures.

A surprising result was the finding that about 30% of the Ru(bpy)$_2$(dppz-R)/TiO$_2$ excited states remained unquenched by the addition of a large excess of water, >0.5 M. Because all measurements were made at saturation surface coverage, this 30% could correspond to specific environments wherein the phenazine nitrogens were protected from the aqueous water.[2] However, we have previously shown that rapid intermolecular energy transfer occurs and Monte Carlo simulations indicate an energy-transfer hopping rate of (30 ns)$^{-1}$.[11] The second-order component observed in the excited-state decay of Ru(bpy)$_2$(dppz-R)/TiO$_2$ is evidence that energy migration does indeed occur. Therefore, with long-lived (825-ns) excited states, the putative population inaccessible to water should have been capable of energy transfer to regions of the film that were accessible. While additional studies are needed to fully understand this behavior, we speculate that energy transfer to this population is inhibited perhaps because the emissive sensitizers are present in necking regions between the anatase nanoparticles.

The addition of potential determining ions such as lithium to acetonitrile is known to shift the conduction band edge of TiO$_2$ positively[13] (on an electrochemical scale), thereby favoring excited-state injection. A commonly accepted value of the TiO$_2$ conduction band edge in 100 mM LiClO$_4$/acetonitrile is −1.0 V vs SCE.[15] This is about 100 mV above our estimated reduction potential of the photoluminescent excited state $E°(\mathrm{Ru}^{III/II*}) = -0.9$ V vs SCE. The measured injection yield of 0.8 is therefore surprisingly high and may indicate involvement of vibrationally hot excited states.[16,17] The addition of water was found to decrease the injection yield to about 30% at 0.5 M. Future studies will be directed toward determining whether the decreased injection stems from water quenching the excited state or shifting the semiconductor conduction band by partioning lithium cations off the TiO$_2$ surface. These findings also indicate that sensitizers with dppz ligands may be utilized for efficient energy conversion in dye-sensitized solar cells.[18]

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