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Decreased Interfacial Charge Recombination Rate Constants with N3-Type Sensitizers

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ABSTRACT Interfacial charge separation and recombination were quantified at sensitized mesoporous nanocrystalline TiO_2 interfaces immersed in acetonitrile electrolyte. Two sensitizers contained a phenylenethynylene spacer between a cis-$Ru(NCS)_2$ core and TiO_2 anchoring groups, and a third sensitizer did not contain the spacer, cis-$Ru(dcb)(bpy)(NCS)_2$, where bpy is 2,2′-bipyridine and dcb is 4,4′-$(CO_2H)_2$-bpy. Excited-state injection occurred with approximately the same yield for all these sensitizers and was rapid with $k_{inj} > 10^8$ s^{-1}. Representative charge recombination rate constants from nanosecond transient absorption data were quantified by a distribution analysis, based on the Kohlrausch–Williams–Watts model, and were found to be 3 times slower for the sensitizers with the phenylenethynylene spacer. Slow recombination kinetics manifested itself as an increased open circuit photovoltage, V_{oc}. The V_{oc} values measured experimentally were contrasted with calculated values abstracted from the diode equation with ideality factors around 3 and the rate constants for charge recombination measured spectroscopically.

SECTION Energy Conversion and Storage
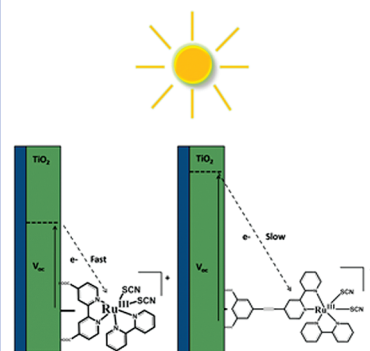
Photocurrent generation in dye-sensitized solar cells (DSSCs) is well understood on the molecular level. Structural optimizations of dyes have been carried through, so that nearly every absorbed solar photon is converted into current with sensitizers such as N3, cis-$Ru(dcb)_2$-$(NCS)_2$ where dcb is 4,4′-$(CO_2H)_2$-2,2′-bipyridine.[1−3] However, the open circuit voltage, V_{oc}, which represents the maximum Gibbs free energy that can be achieved under steady state irradiation, remains low, and the molecular events that control it are poorly understood. In 11+% confirmed efficiency cells, V_{oc} represents less than half of the free energy stored in the sensitizer excited state.[4] Light excitation of sensitizers that undergo intramolecular hole transfer reactions to covalently linked electron donor groups are known to inhibit interfacial charge recombination and increase V_{oc}.[5,6] However, a considerable loss in free energy accompanies hole transfer from the sensitizer to the donor, and the V_{oc} enhancement is thus far from optimal. Here we report for the first time that long-lived charge separation *and* enhanced V_{oc} can be realized without energy losses associated with hole transfer to an electron donor. Charge recombination rate constants and V_{oc} data were quantified with sensitizers that contained a phenylenethynylene spacer between a cis-$Ru(NCS)_2$ core and the surface anchoring groups (Chart 1).

All the sensitizers displayed an intense absorption band between 500 and 700 nm attributed to metal-to-ligand charge-transfer (MLCT) transitions and the expected π−π* transitions in the UV region.[7] Compounds **2** and **3** also displayed

Chart 1. The Sensitizers Used in This Study
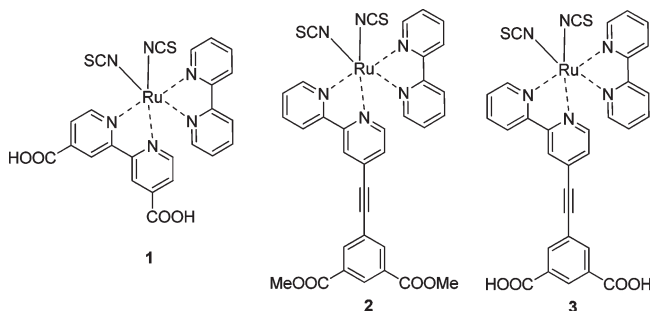
an intense 350 nm absorption band that has been previously observed for compounds with oligo-phenylenethynylene motifs.[8] The extinction coefficients at the MLCT maxima were ~10 000 M^{-1} cm^{-1} when measured in dimethyl sulfoxide (DMSO) (Figure 1). Visible light excitation into the MLCT absorption leads to a very weak photoluminescence with corrected maxima of 760 ± 5 nm for **2** and **3** and 770 ± 5 nm for **1**. The photodecomposition quantum yields were estimated to be 2 × 10^{-6}. Nanosecond transient absorption

measurements at $-30\ °C$ in CH_3CN were consistent with an MLCT excited state, with maintenance of isosbestic points and first-order relaxation with $\tau = 40\ ns$ (**1**) and $\tau = 55\ ns$ (**2**). The poor solubility of **3** precluded transient absorption studies in solution. The sensitizers were anchored to mesoporous nanocrystalline TiO_2 thin films by overnight reactions in methanol or DMSO to yield $\sim 10^{-9}\ mol/cm^2$ surface coverages.

Pulsed 532 nm light excitation of the sensitized films immersed in a 0.1 M $LiClO_4$ acetonitrile electrolyte at the open circuit condition resulted in the prompt appearance of an absorption transient that was reasonably assigned to a charge-separated state comprised of an electron in TiO_2 and the oxidized sensitizer. An instrument response limited absorption change indicated that excited state injection occurred with $k_{inj} > 10^8\ s^{-1}$. Assuming 10 000 $M^{-1}\ cm^{-1}$ extinction coefficients for the TiO_2 anchored sensitizers, comparative actinometry measurements 10 ns after pulsed laser excitation (< 1 mJ/pulse) indicated that the excited state injection yield of **1** and **2** were the same, while that for **3** was about 30 % lower. Steady-state absorption measurements before and after laser excitation revealed no evidence for photodecomposition when the sensitizers were anchored to TiO_2.

Charge recombination to yield ground state products was nonexponential and required milliseconds for completion (Figure 2). The transient data were well described by the Kohlrausch–Williams–Watts (KWW) kinetic model, where β takes values between zero and unity and is inversely related to the width of a stretched Levy distribution of rate constants, and I_0 and I_f are the initial and final amplitudes, respectively (eq 1).[9]

The first moment of the KWW function is given by eq 2, where Γ is the gamma function.[10]

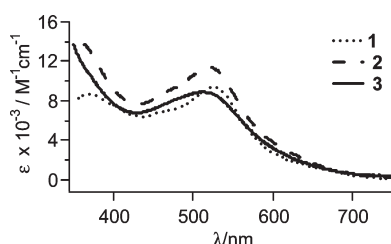$$I = (I_0 - I_f) \times \exp[-(k_{obs} \times t)^\beta] + I_f \qquad (1)$$

A representative charge recombination rate constant, k_{cr}, was taken as the reciprocal of $\langle \tau_{ww} \rangle$.

$$\langle \tau_{ww} \rangle = \frac{1}{k_{obs}\beta}\Gamma\left(\frac{1}{\beta}\right) \qquad (2)$$

Measurements from multiple sensitized films with this distribution analysis revealed that the charge-separated states of **2** and **3** were significantly longer-lived than the corresponding state of **1** (Table 1). The increased lifetimes were apparent in the observed experimental data and were not an artifact of the kinetic modeling. Furthermore, the kinetic modeling was consistent over a range of incident irradiations. We note also that recent simulations require nonlinear recombination kinetics, presumably through a distribution of trapping states, to accurately model observed photoelectrochemical behavior.[11,12] Thus the presence of the phenylenethynylene spacer, and presumably a longer average sensitizer–semiconductor distance, induced slower recombination.

An advantage of the KWW function is that the inverse Laplace transform is analytically known for discrete values of β and has been approximated for others. This enables one to directly examine the distribution of rate constants that underlie the experimental data. The distributions in Figure 3 were generated from the best-fits to eq 1 with a series approximation.[10] On the basis of these distributions, it is clear that the average rate constant has increased for compound **1**, which does not contain a phenylenethynylene spacer. We also note that because β is nearly the same ($\beta = 0.4 \pm 0.04$ for all three sensitizers), this simplifies the distribution analysis considerably. Meaningful comparisons and discussion of "average rate constants" would have been much more difficult had the shapes of the distributions changed significantly (i.e., different β values) for each sensitizer.

Figure 1. Electronic absorption spectra for **1**, **2**, and **3** in DMSO.

Table 1. Open Circuit Photovoltage (Measured at 1 mW/cm^2), Ideality Factor i, Representative Charge Recombination Rate Constants k_{cr}, and β Parameters Abstracted from a Distribution Analysis of Transient Absorption Data[a]

sensitizer	V_{oc} (mV)	i	β	k_{cr} (s^{-1})
1	100	2.0	0.36 ± 0.03	$7.1 \pm 3.6 \times 10^5$
2	300	3.3	0.44 ± 0.04	$2.8 \pm 1.4 \times 10^5$
3	280	3.0	0.43 ± 0.06	$2.6 \pm 1.3 \times 10^5$

[a] All measurements were performed at room temperature in 0.1 M $LiClO_4$ acetonitrile solution. The indicated uncertainties in kcr represent the maximum and minimum values obtained from individual fits of time-resolved data from multiple samples.

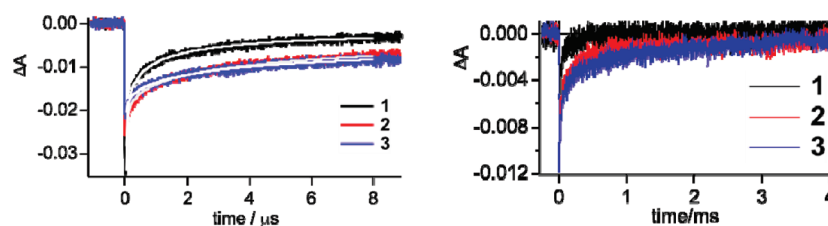**Figure 2.** Absorption changes recorded at 460 nm after pulsed 532 nm laser excitation (~ 2 mJ/pulse, 5 ns full width at half-maximum (fwhm)) of the indicated sensitizer anchored to nanocrystalline TiO_2 thin films immersed in 0.1 M $LiClO_4$ acetonitrile electrolyte on microsecond (left) and millisecond (right) time scales. Overlaid fits to the KWW function are shown in white in the left panel.
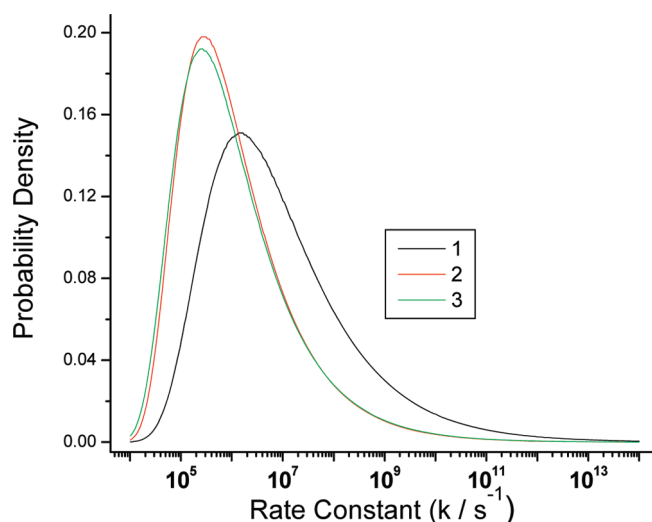
Figure 3. The distribution of charge recombination rate constants abstracted from KWW fits of the data shown in Figure 2.
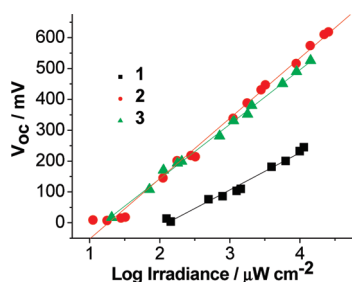

Figure 4. Open circuit voltage, V_{oc}, measured as a function of 514.5 nm light irradiance for **1** (squares), **2** (circles), and **3** (triangles), obtained in 0.1 M LiClO$_4$ acetonitrile electrolyte. Straight lines are overlaid best fits to eq 3.

The smaller charge recombination rate constants measured for **2** and **3** suggested that they would yield higher V_{oc} values than **1**. Figure 4 shows typical V_{oc} data for all three sensitizers measured over three decades of 514.5 nm irradiance versus a Pt pseudoreference electrode in 0.1 M LiClO$_4$ acetonitrile. The ester and carboxylic acid-terminated rigid rods exhibited very similar V_{oc} values, which were indeed consistently larger than **1** (Table 1).

Irradiance dependent V_{oc} data has previously been modeled by the so-called "diode equation" (eq 3), which relates V_{oc} to the natural logarithm of the flux of electrons into the semiconductor, I_{inj}, divided by the summation of recombination rate constants of electrons, n, to acceptors, A_j, at any temperature T.[13-17] When the ideality factor i equals 1, this equation predicts a 59 mV increase in V_{oc} for an order of magnitude decrease in charge recombination at room temperature.[1,2]

$$V_{oc} = i \times \left(\frac{kT}{e}\right) \times \ln\left[\frac{I_{inj}}{n \sum_j k_{cr}[A]_j}\right] \quad (3)$$

In the absence of redox mediators, the predominant electron acceptor is the oxidized sensitizer present in equal numbers to the injected electrons. Ideality factors greater than unity were required to fit the data in Figure 4 to eq 3. The value of $i = 2$ measured for **1** is typical of those reported in the DSSC literature.[14,15] However, the value of $i = 3.0-3.3$ measured for **2** and **3** is, to our knowledge, the highest value reported. The factors that control ideality factors are unknown, and the observation here indicates that they can be controlled and understood on a molecular level. The average recombination rate constants measured spectroscopically were almost an order of magnitude slower for the rigid-rod sensitizers than for **1**. With an ideality factor difference of $\Delta i = 1$, a 59 mV larger V_{oc} is predicted per decade of irradiance for **2** and **3** relative to **1**.

In conclusion, we have shown that incorporation of a spacer (in this case a phenylenethynylene unit) between a bipyridine ligand and the surface anchoring groups significantly decreased charge recombination rate constants with the already highly optimized cis-Ru(NCS)$_2$-type sensitizers.[3] The enhanced lifetime of the interfacial charge-separated state directly resulted in improved open circuit photovoltages as predicted by the diode equation with notably large ideality factors. These enhancements come *without* the need for surface blocking layers[17,18] or the significant energy loss associated with hole transfer to a covalently bound donor[5,6] or to iodide.[16] The use of rigid spacers thus appears to be a viable strategy for optimization of the free energy stored in charge-separated states at sensitized nanocrystalline interfaces.

EXPERIMENTAL SECTION

Mesoporous nanocrystalline TiO$_2$ thin films were prepared as previously described.[19] The sensitizers were anchored to base-treated TiO$_2$ from concentrated methanol or DMSO solutions. All transient spectroscopic measurements and photovoltage determinations were performed in 0.1 M LiClO$_4$ acetonitrile solutions at room temperature. The solutions were purged with argon gas prior to data collection. Time-resolved spectroscopic measurements were performed with a nanosecond flash photolysis system described in detail elsewhere,[20] with 532 nm laser excitation at a frequency of 1 Hz. Open circuit photovoltages were measured in nonregenerative solar cells containing 0.1 M LiClO$_4$ acetonitrile electrolyte. The photovoltages were recorded using a BASi Epsilon-EC. Incident light was achieved with a 514.5 nm line of an Innova Ar$^+$ laser with a Thorlabs BE 10X beam expander, and the incident irradiance was altered using Newport neutral density filters. The area exposed to illumination in photoelectrochemical measurements was typically 3 cm^2.

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