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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Intramolecular Hole Transfer at Sensitized TiO_2 Interfaces

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Ⓢ *Supporting Information*

ABSTRACT: Three ruthenium compounds with triphenyl amine donors were anchored to nanocrystalline TiO_2 thin films for interfacial electron-transfer studies. Molecular tuning of reduction potentials enabled the extent of hole transfer from the photo-oxidized ruthenium center to the triphenyl amine to be tuned from zero to unity. Kinetic data revealed two new insights into the unwanted interfacial recombination reaction of the injected electrons with the oxidized compounds. First, recombination was highly sensitive to the concentration of oxidized compounds present at the interface. Second, a significant enhancement of the open circuit photovoltage was realized without a change in the recombination kinetics, behavior attributed to translation of the hole away from the interface thereby generating a larger surface dipole.

Light-to-electrical energy conversion in dye-sensitized solar cells is initiated by excited-state electron transfer from a dye molecule to a semiconductor material.[1,2] The oxidized dye that is formed is usually regenerated by outer-sphere intermolecular hole transfer to a donor in solution.[1] A growing class of dye molecules utilizes an intramolecular hole transfer to a covalently linked donor group.[3−8] Studies of such 'dyad'[9] molecules have provided valuable insights into the factors that control the open circuit photovoltage, V_{oc}, the maximum Gibbs free energy that a regenerative solar cell can produce. With some dyads, enhanced V_{oc}s have been directly correlated with decreased rate constants for interfacial charge recombination,[3,10] while in others no correlations were observed.[4] An explanation for such dissimilar behavior is lacking due, at least in part, to the absence of dyads that maintain a common structural motif with redox potentials that can be systematically tuned. Recently such molecules have been synthesized.[11] Herein we report that intramolecular hole transfer yields can be tuned from zero to near unity through molecular level modifications and have quantified how this influences interfacial electron transfer and the stored free energy. The data revealed for the first time that V_{oc} is not always linked to charge recombination as is commonly assumed and that charge recombination kinetics are remarkably sensitive to the concentration of oxidized dyes present at the interface.

The molecules of interest are shown in Figure 1. These ruthenium polypyridyl compounds contain a common terpyridyl ligand with three carboxylic acid/carboxylate groups for surface binding, and a tridentate cyclometalated ligand with a conjugated triaryl amine donor group. The synthesis of the methyl ester derivatives of these compounds was recently reported[11] and converted to the carboxylate forms by saponification reactions in DMF. The dyads were then anchored to mesoporous nanocrystalline TiO_2 or ZrO_2 thin films by reactions in MeOH or EtOH solutions as was previously described and is abbreviated **1−3**/MO_2.[12] The visible absorption spectra of the sensitized films were in good agreement with that measured for the carboxylate form of the compounds in fluid solution. The surface coverages were typically 1×10^{-8} mol/cm^2. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) measurements revealed an antisymmetric CO_2^- stretch at 1600 cm^{-1}, consistent with carboxylate binding to the TiO_2 surface.[13]

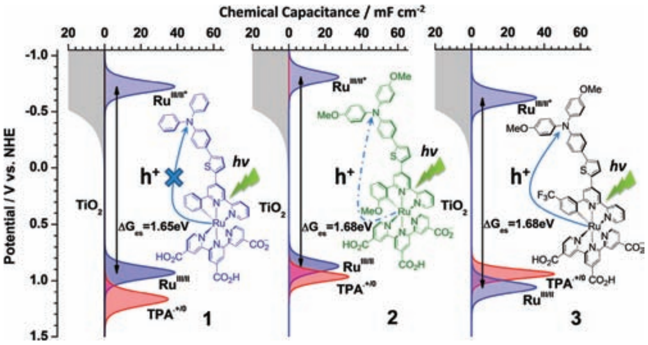

Figure 1. The interfacial density of states for **1**/TiO_2, **2**/TiO_2, and **3**/TiO_2 measured by spectroelectrochemistry in 0.5 M $LiClO_4/CH_3CN$ electrolyte.

Spectroelectrochemistry was used to quantify the interfacial energetics of **1−3**/TiO_2 in 0.5 M $LiClO_4/CH_3CN$ electrolyte. Forward bias resulted in reduction of the TiO_2 thin films and the characteristic absorption spectrum of trapped electrons, herein abbreviated as $TiO_2(e^-)$, as well as small shifts in the absorption spectrum of the molecules due to the surface electric field.[14] Reverse bias resulted in absorption changes consistent with oxidation of the Ru metal center and the triphenylamine group, TPA. In all cases, the redox chemistry was accompanied by reversible absorption changes with the maintenance of isosbestic points that enabled determination of absorption spectra of the one- and two-electron oxidized forms of the compounds. The integrated concentration change associated

Received: February 23, 2012
Published: May 1, 2012

dx.doi.org/10.1021/ja3018175 | *J. Am. Chem. Soc.* 2012, 134, 8352−8355

with sensitizer oxidation measured spectroscopically after a potential step of 15−25 mV was plotted as a chemical capacitance, Figure 1. For **3**/TiO$_2$, TPA was oxidized prior to the ruthenium metal center, while for **1**/TiO$_2$ the Ru metal center was oxidized prior to the TPA group. Compound **2**/TiO$_2$ showed intermediate behavior where oxidation of TPA and Ru occurred concomitantly. The potential at which equal concentrations of the two redox states were present was taken as the formal reduction potential, Table 1. The excited-state reduction potential, Ru$^{III/II*}$, was estimated from thermochemical cycles with the free energy stored in the excited state, ΔG_{es}, abstracted from the corrected photoluminescence spectrum measured for **1−3**/ZrO$_2$. Oxidation of the TPA donor by the metal-to-ligand charge transfer (MLCT) excited state was thermodynamically unfavored.

Table 1. Reduction Potentials and Ideality Factors (a) for 1−3/TiO$_2$

compound	$E_{1/2}$ (Ru$^{III/II}$) (a)^a	$E_{1/2}$ (TPA$^{\cdot+/0}$) (a)^a
1/TiO$_2$	930(1.36 ± 0.06)	1165(1.50 ± 0.06)
2/TiO$_2$	870(1.33 ± 0.03)	960(1.11 ± 0.03)
3/TiO$_2$	1060(1.33 ± 0.04)	940(1.04 ± 0.03)

^{a}Ideality factors were obtained by fitting data to the equation: $x = 1/(1 + 10^{(E_{app} - E^0)/(a \times 59\text{mV})})$, where x is the fraction of molecules in a specified oxidation form and a is the ideality factor. Potentials are in mV versus NHE.

With two notable exceptions, the redox behavior of the sensitized TiO$_2$ thin films was unchanged from that expected in fluid solution. First, the metal-based Ru$^{III/II}$ potentials measured by cyclic voltammetry were 70−90 mV more positive than that measured for the surface anchored compounds. This observation can be rationalized by the conversion of the electron-withdrawing carboxylic acid groups to carboxylates upon surface binding. Second, the interfacial redox chemistry did not follow the Nernst equation. For example, an 80 mV potential step was required to induce an order of magnitude change in the Ru^{III} concentration, which corresponds to an ideality factor a = 1.3, Table 1.

Figure 2A displays transient absorption difference spectra measured 45 ns after pulsed laser excitation of the sensitized thin films. The normalized spectra were time independent, consistent with the formation and loss of one state. Overlaid on the spectra are simulations based on the spectroelectrochemical data that indicated quantitative hole transfer to yield TPA$^{\cdot+}$-Ru^{II}/TiO$_2$(e$^-$) for **3**/TiO$_2$, no hole transfer to yield TPA-Ru^{III}/TiO$_2$(e$^-$) for **1**/TiO$_2$, and partial hole transfer for **2**/TiO$_2$. The absorption band at 740 nm[4,15] was found to be characteristic of TPA$^{\cdot+}$, and the prompt appearance after laser excitation of **2**/TiO$_2$ and **3**/TiO$_2$ indicated that both excited-state electron injection and hole transfer occurred within 10 ns. The relative amplitudes of this absorption indicate that quantum yield for hole transfer in **2**/TiO$_2$ was about 0.2. The extent of hole transfer after excitation of **1−3**/TiO$_2$ is precisely what one would expect based on the interfacial energetics data shown in Figure 1. Note that a reductive quenching mechanism for generation of TPA$^{\cdot+}$-Ru^{II}/TiO$_2$(e$^-$), i.e., where the TPA reduced the MLCT excited state, was not expected or observed in fluid solution or when the compounds were anchored to ZrO$_2$. Therefore, unlike previous dyad studies, hole transfer occurs only after excited-state injection for **2−3**/TiO$_2$.[3−8]

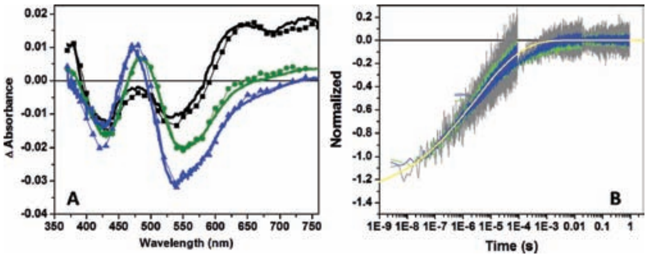

Figure 2. (A) Absorption difference spectra measured 45 ns after pulsed 532 nm excitation (0.2 mJ/cm^2) of **1**/TiO$_2$ (blue), **2**/TiO$_2$ (green), and **3**/TiO$_2$ (black) immersed in 0.5 M LiClO$_4$ CH$_3$CN solution. (B) The absorption change monitored at 550 nm after pulsed laser excitation of **1**/TiO$_2$ (blue), **2**/TiO$_2$ (green), and **3**/TiO$_2$ (gray) normalized at 45 ns; overlaid is a fit to the KWW model (yellow).

The kinetics for interfacial charge recombination to yield ground-state products were nonexponential but were satisfactorily fit to the Kohlrausch−Williams−Watts (KWW) model, $A(t) = A_0 \exp(-(kt)^\beta)$, Figure 2B.[16,17] Comparative studies showed that the rate constant k and the distribution parameter β = 0.26 were independent of the dyad present on the TiO$_2$ surface. Error analysis of the normalized data revealed that the k and β terms were not highly correlated, Figure S1, SI. An average rate constant k_{cr} = 1.9 (±0.3) × 10^4 s^{-1} of the underlying Lévy distribution of rate constants was calculated as the first moment.[17] In fact the time-dependent absorption changes were superimposable after normalization at their initial amplitudes, indicating that charge recombination was within experimental error the same for all three dyads regardless of the kinetic model used to analyze the data. Therefore, translation of the hole from the ruthenium center to TPA did not inhibit charge recombination, presumably because of a trade-off in the free energy change, $\Delta G°$ = −120 mV, with the increased distance to the more remote amine group.[10,18]

The presence of two reversible redox processes in **3**/TiO$_2$ enabled the concentration of oxidized amines to be systematically controlled, Figure 3A. In one extreme, TPA in **3**/TiO$_2$ was almost completely oxidized with an applied bias of +1.02 V. Pulsed MLCT excitation resulted in excited-state electron injection, $k_{inj} > 10^8$ s^{-1}, but hole transfer was now prevented as the amines were already oxidized. The resultant TPA$^{\cdot+}$-Ru^{III}/TiO$_2$(e$^-$) was found to be much shorter lived than the state formed at open circuit, i.e., TPA$^{\cdot+}$-Ru^{II}/TiO$_2$(e$^-$), and was highly dependent on the TPA$^{\cdot+}$ concentration.

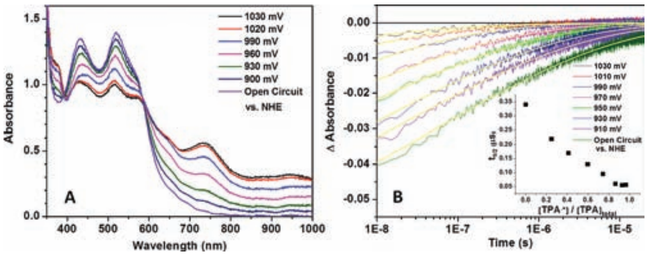

Figure 3. (A) Visible absorption spectra of **3**/TiO$_2$ at the indicated applied potentials. (B) Absorption change monitored at 442 nm after pulsed 532 nm light excitation of **3**/TiO$_2$ at the indicated applied potentials. Overlaid in yellow are the fits to the KWW model. Inset: a $t_{1/2}$ analysis of this data plotted against the fraction of oxidized amines.

A series of experiments were performed where the concentration of the oxidized amines was controlled with an external bias, and photoinduced back electron transfer was quantified spectroscopically, Figure 3B. In all cases, a TPA^{+}-$Ru^{III}/TiO_2(e^-)$ charge separated state was formed within 10 ns of laser excitation. The loss of this state was well described by the KWW model. Significantly, abstracted rate constants increased by around 2 orders of magnitude as the concentration of oxidized amines increased from zero to near unity. Likewise the time required for one-half of the injected electrons to recombine, $t_{1/2}$, also decreased markedly when more oxidized sensitizers were present, Figure 3B inset. This observation is relevant to ongoing studies of $Co^{III/II}$ or other redox mediators with near zero or endergonic free energy changes for sensitizer regeneration.[19,20] Such conditions are optimal for V_{oc}, and hence power conversion efficiencies, but result in equilibrium concentrations of oxidized sensitizers that these data now show can enhance unwanted recombination reactions. Interestingly, the back electron-transfer kinetics shown in Figure 3B did not directly yield ground-state products but rather reduced and doubly oxidized dyads with equal concentrations, i.e., TPA-Ru^{II}/TiO_2 and TPA^{+}-Ru^{III}/TiO_2, that returned to ground-state products on a millisecond time scale with $\Delta G° = -120$ mV by lateral self-exchange across the TiO_2 surface.

Durrant and co-workers[21,22] had previously shown that $t_{1/2}$ decreased markedly when the $TiO_2(e^-)$ concentration was increased with a forward bias. A corresponding rate enhancement with oxidized sensitizer concentration has not been previously reported, presumably because most sensitizers are unstable when oxidized. Collectively these data show that charge recombination kinetic data not only report on transport of the injected electrons but also reflect the concentration of $TiO_2(e^-)$ and oxidized sensitizers.

As the recombination rate constants for **1**−**3**/TiO_2 were within the experimental error, the same when measured at open circuit, one would anticipate that the V_{oc} values would also be the same. This expectation comes from the widely utilized diode equation that requires an order of magnitude decrease in charge recombination rate constant for a 59 mV increase in V_{oc} at constant irradiance and room temperature.[23] Nevertheless, the V_{oc} for **3**/TiO_2 was measured to be 120 ± 20 mV larger than **2**/TiO_2 over 3 decades of irradiance. For example, with 1 sun illumination of 514.5 nm light (100 mW/cm^2), V_{oc} for **3**/TiO_2 was 650 mV, while that for **2**/TiO_2 was 530 mV when measured relative to a Pt pseudoreference electrode. The enhanced V_{oc} did not result from a change in the TiO_2 conduction band edge position that might have accompanied sensitizer binding; spectroelectrochemical data showed that the TiO_2 DOS were sensitizer independent, as would be expected given the homology present in **1**−**3**. The comparative data were obtained under conditions where the ground-state absorption and laser irradiance were closely matched. Therefore, the data show for the first time that even for a series of homologous sensitizers, V_{oc} is not always linked to charge recombination kinetics as is often assumed.

To explain this behavior, one must account for a higher quasi-Fermi level (i.e., closer to the vacuum level) when **3**/TiO_2 was illuminated, even though the steady-state $TiO_2(e^-)$ concentration was the same for **1**−**3**/TiO_2. It is known that the semiconductor band edge positions are not fixed parameters and shift upon illumination, behavior termed band edge unpinning or Fermi-level pinning.[24] This phenomenon occurs when semiconductor materials behave nonideally and the electric field extends over the molecular−semiconductor interface. Recent electroabsorption measurements have shown that fields as large as 270 MV/m are present at related sensitizer−TiO_2 interfaces.[14] The adsorption of cations on the anatase TiO_2 surface, like H^+ or Li^+, are known to screen this field, lower the TiO_2 quasi-Fermi level, and decrease V_{oc}.[2] After excited-state injection, the charge on the sensitizer increases by one unit, and translation of this charge away from the surface would circumvent this unwanted shift. Therefore, intramolecular hole transfer could in itself explain the higher V_{oc} relative to a sensitizer, where the oxidized equivalent remains proximate to the surface.[25] However, the magnitude was remarkably high especially when one considers that over an 100-fold increase in adsorbed cation concentration would be required to observe the same behavior.[26]

Cahen, Zaban, and co-workers have previously shown that the coadsorption of molecules with net dipole moments influence V_{oc} through the electrostatic field that they generate.[27] Dipoles oriented toward the surface increase V_{oc}, while those directed away decrease the value. For benzoic acid monolayers, a 200 mV shift per Debye was most consistent with their data at saturation surface coverage.[27] Theoretical analysis also indicates that oriented dipoles significantly influence V_{oc}.[28] In the dark, the dipole moments for **1**−**3**/TiO_2 are expected to be very similar and oriented toward the surface. After excited-state injection, the dipole moment will increase due to the generation of the oxidized ruthenium center. Molecular models indicate that relative to the carboxyl carbon of the central terpyridyl ring, hole transfer from Ru^{III} to TPA results in translation from 7 to 23 Å. As the dipole moment is linearly proportional to the distance, hole transfer approximately triples the magnitude. Therefore, an enhanced V_{oc} is qualitatively expected based on the large dipole moment generated after excited-state injection and hole transfer to the TPA group.

In conclusion, a comparative study of three dyads attached to TiO_2 surfaces has shown that after excited-state injection, the yield of intramolecular hole transfer to a remote amine group can be controlled through synthetic design and predicted at the molecular level based on measured reduction potentials. The data reveal for the first time that the charge recombination kinetics were sensitive to the concentration of oxidized sensitizers present at the illuminated interface. For this class of dyads, intramolecular hole transfer in itself had no measurable influence on the charge recombination kinetics as might have been expected based on previous studies.[3−6] Nevertheless, quantitative hole transfer did generate a significantly enhanced open circuit photovoltage, i.e., a larger Gibbs free energy was stored in the interfacial charge-separated state. Hence, these comparative studies have shown that an increased V_{oc} can be realized without a change in the recombination kinetics. Hole transfer decreases the net positive charge at the interface and increases the dipole moment resulting in a negative shift in the TiO_2 quasi-Fermi level. Therefore, an increased V_{oc} observed for a molecular sensitizer does not necessarily imply inhibited charge recombination as is commonly assumed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

An error analysis for the charge recombination kinetics of Figure 2B is shown. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The U.S. authors acknowledge support by a grant from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (DE-FG02-96ER14662). C.P.B. and K.C.D.R. are grateful to Canadian Natural Science and Engineering Research Council, Canadian Foundation for Innovation, Alberta Ingenuity and the Canada School of Energy and Environment (CSEE) for support.

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