Energy and Hole Transfer between Dyes Attached to Titania in Cosensitized Dye-Sensitized Solar Cells

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Supporting Information

ABSTRACT: Cosensitization of broadly absorbing ruthenium metal complex dyes with highly absorptive near-infrared (NIR) organic dyes is a clear pathway to increase near-infrared light harvesting in liquid-based dye-sensitized solar cells (DSCs). In cosensitized DSCs, dyes are intimately mixed, and intermolecular charge and energy transfer processes play an important role in device performance. Here, we demonstrate that an organic NIR dye incapable of hole regeneration is able to produce photocurrent via intermolecular energy transfer with an average excitation transfer efficiency of over 25% when cosensitized with a metal complex sensitizing dye (SD). We also show that intermolecular hole transfer from the SD to NIR dye is a competitive process with dye regeneration, reducing the internal quantum efficiency and the electron lifetime of the DSC. This work demonstrates the general feasibility of using energy transfer to boost light harvesting from 700 to 800 nm and also highlights a key challenge for developing highly efficient cosensitized dye-sensitized solar cells.

1. INTRODUCTION

Dye-sensitized solar cells comprised mainly of abundant, nontoxic materials offer an inexpensive route to develop highly efficient photovoltaic cells.1–4 Currently, the most efficient sensitizing dyes are ruthenium-based, metal ligand complexes (e.g., C106 and N719),5,6 which absorb light in the visible portion of the solar spectrum, have excellent charge injection properties, and produce a high open-circuit voltage, $V_{oc}$, which is defined as greater than 750 mV. It should be possible to further increase the power conversion efficiency of DSCs by harvesting light in the near-infrared red portion of the spectrum. Cosensitization of titania by dyes with complementary absorption spectra has been demonstrated to broaden the spectral response of organic dye-based DSCs in the visible portion of the spectrum, but not beyond 720 nm.7–10 Designing near-infrared sensitizing dyes with high internal quantum efficiencies is challenging because reducing the band gap requires more precise alignment of the LUMO and HOMO levels and short conjugated ligands to facilitate charge transfer. To date, only two NIR sensitizing dyes (i.e., peak absorption >700 nm) have demonstrated good charge injection efficiencies in DSCs, but neither dye has a $V_{oc}$ greater than 450 mV.11,12 Recombination from the electrons in titania with holes in the dye and triiodide in the electrolyte plays a key role in determining the open-circuit voltage.13 Organic dyes typically experience higher recombination rates resulting in a lower $V_{oc}$.14 The great challenge of designing a cosensitized DSC system using NIR dyes will be maintaining a $V_{oc}$ greater than 700 mV.

Two NIR dye design strategies could result in higher power conversion efficiencies. First, it may be possible to use highly absorptive NIR-sensitizing dyes that directly inject charges even if NIR-SDs have higher recombination rates by using low surface concentrations (<10%) of NIR-SDs to minimize $V_{oc}$ losses. DSC systems where cosensitized dyes do not electronically interact with one another are expected to have an electron recombination rate equivalent to the weighted average of the individual dye DSC systems. However, intermolecular charge transfer from dyes with a low recombination rate to dyes with a higher recombination rate can significantly increase the overall electron recombination rate between oxidized dyes and electrons in the titania, which can disproportionately reduce the open-circuit voltage of the cosensitized DSC system.

A second strategy is to electronically insulate the NIR dye from the TiO$_2$ surface to reduce the recombination rate, which would maintain the $V_{oc}$ but also prevent electron injection. In this case, the NIR dye would act as an energy relay dye (ERD) requiring efficient intermolecular energy transfer to the metal complex SD to generate photocurrent, as shown in Scheme 1.
Scheme 1. NIR Dye Attached to the Titania Surface Absorbs Near-Infrared Photons and Uses Short-Range Energy Transfer To Excite a Neighboring Sensitizing Dye, Which Is Responsible for Electron Transfer into the TiO2 (k\textsubscript{\text{intr}}) and Hole Regeneration with the Electrolyte (k\textsubscript{\text{reg}})

address the feasibility of using NIR-ERDs, we must first determine how effectively NIR-ERDs can transfer energy to SDs in a cosensitized system.

Conventional DSCs are solely dependent on charge transfer mechanisms for current generation, while plants often incorporate a variety of energy transfer processes to increase light harvesting during photosynthesis. Developing systems that incorporate both Förster resonant energy transfer (FRET) and Dexter energy transfer allow greater flexibility in the design of potential light harvesting candidates. Energy relay dyes (ERDs) have been used previously to increase light harvesting in the blue portion of the solar spectrum. Blue ERDs, which absorb high energy photons and undergo FRET to sensitizing dyes, can efficiently transfer energy when placed inside the electrolyte or cosensitized on nanocrystalline TiO2. Grimes et al. recently demonstrated that ERDs unattached to the titania and slightly red-shifted relative to the sensitizing dye peak absorption were able to undergo FRET to the SD. However, the low FRET radii (e.g., 1–4 nm) due to the poor overlap between ERD emission and SD absorption prevents efficient energy transfer from occurring when ERDs are placed inside the electrolyte. For DSC systems where energy transfer is weak (i.e., FRET radii <4 nm), NIR-ERDs should be within the FRET radius of the SD to efficiently transfer energy, which requires tethering between dyes or cosensitization on the TiO2 surface.

2. RESULTS AND DISCUSSION

2.1. Charge Transfer Rates and Energy Transfer Estimates in the Cosensitized C106/AS02 System. To verify that energy transfer occurs from the NIR dye to the SD, we have designed a zinc naphthalocyanine-based dye (AS02) that cannot regenerate with the electrolyte and produce photocurrent independently. The absorption, emission, and the chemical structure of C106 and AS02 in dimethylformamide (DMF) are shown in Figure 1. C106 has a peak molar extinction coefficient of 18 700 M\textsuperscript{-1} cm\textsuperscript{-1} at 550 nm with an absorption tail that extends weakly out to 800 nm. C106 has a broad emission spectrum with a peak at 786 and a natural fluorescence decay lifetime of 85 ns in DMF (see Supporting Information S5). The photoluminescence quantum efficiency of Ru-based metal complexes is between 0.2% and 0.02%. AS02 has a peak molar extinction coefficient of 100 000 M\textsuperscript{-1} cm\textsuperscript{-1} at 773 nm with a narrow emission peak at 782 nm with a fluorescence natural decay lifetime of 2.75 ns in DMF. The photoluminescence quantum efficiency of Zn-based naphthalocyanines is between 10% and 30%. Photoelectron spectroscopy in air (PESA) was used to determine that the HOMO level of AS02 (−4.60 eV) is high relative to the iodide potential (−4.85 eV), which has previously been shown to prevent dye regeneration for a similar Zn-based naphthalocyanine sensitizing dye. AS02 has a HOMO level of −5.27 eV. Intermolecular hole transfer is thermodynamically favorable from the C106 to the AS02; the rate of transfer will be dependent upon the HOMO level offset and the separation distance between molecules. The Förster radius (R\textsubscript{f}) is the distance between the donor and acceptor dye when Förster resonant energy transfer is 50% likely. The FRET R\textsubscript{f} from the donor to the acceptor dye is primarily determined by the donor photoluminescence quantum efficiency, the molar extinction coefficient of the acceptor, and the overlap between the donor emission and acceptor absorption spectra (see the Supporting Information). Traditional energy transfer systems are designed to funnel energy from a donor chromophore whose absorption is blue-shifted relative to the acceptor dye absorption (i.e., C106 to AS02) so that donor emission can overlap with the peak acceptor absorption to provide the largest possible FRET radius. The FRET radius from C106 to AS02 is estimated to be between 1.5 and 2.2 nm, which is fairly short and primarily due to the low photoluminescence quantum efficiency of the C106 dye. Despite the weak emission/absorption overlap of the AS02 emission and C106 absorption, the FRET radius from the NIR dye (AS02) to the SD (C106) is estimated to be between 1.5 and 1.8 nm. The rate of Förster energy transfer (k\textsubscript{\text{FRET}}) between isolated chromophores, known as point-to-point transfer, is given by k\textsubscript{\text{FRET}} = k\textsubscript{0}(R\textsubscript{f})\textsuperscript{6}/r\textsuperscript{6}, where r is the separation distance and k\textsubscript{0} is the natural
fluorescence decay rate, $k_0 = 1/\tau_0$. The separation distance can be approximated on the basis of the sensitizing dye surface concentration, which was measured by desorbing the C106 from titania using 0.15 M tetrabutylammonium hydroxide in DMF and found to be 1 dye/nm$^2$ on the 17 nm diameter TiO$_2$ nanoparticles with an estimated roughness factor of 100/μm (see the Supporting Information). When the NIRDye molecules intimately mix with the C106, the average separation between dyes is estimated to be approximately 1 nm. The FRET rate from the AS02 to C106 is predicted to be between $7.1 \times 10^9$ and $2.3 \times 10^{10}$ s$^{-1}$ ($\tau_{\text{FRET,AS02}} = 44 \pm 130$ ps) based on an average separation distance of 1 nm, while the FRET rate is estimated from C106 to AS02 to be between $1.3 \times 10^8$ and $1.3 \times 10^9$ s$^{-1}$ ($\tau_{\text{FRET,C106}} = 0.75 \pm 7.5$ ns). Interestingly, the FRET rate from the NIR dye (AS02) to the visible sensitizing dye (C106) is an order of magnitude faster than in the opposite direction due to the differences in the fluorescence decay rates between chromophores. The $k_{\text{FRET}}$ rates should be considered rough approximations because the FRET radius calculation is based on a random orientation (i.e., dyes rotating freely in solution), which would not be the case when anchored on the TiO$_2$ surface. Given the short length scale, Dexter energy transfer may also play an important role in intermolecular energy transfer. Meyer et al. have demonstrated near unity lateral Dexter energy transfer from Ru-based metal complex SDs to Os-based metal complex SDs across a semiconductor interface$^{28}$ and have also estimated Dexter energy transfer rates between Ru metal complex SDs to be on the 30 ns time scale.$^{29}$ Calculating the Dexter transfer rate between AS02 to C106 requires calculating the inner and outer sphere reorganization energies and is beyond the scope of this work.$^{29}$

### 2.2. Excitation Transfer Efficiency Calculations.

The excitation transfer efficiency, $\text{ETE}$, is the probability that a dye will undergo energy transfer. ETE is determined by the rate of intermolecular energy transfer ($k_{\text{ETT}}$) relative to the combined rates of all decay pathways, which includes the electron injection rate ($k_{\text{inj}}$) and the nonradiative decay rate ($k_{\text{nr}}$) of the attached dye as shown in eq 1.

$$
\text{ETE} = \frac{k_{\text{ETT}}}{k_{\text{ETT}} + k_{\text{inj}} + k_{\text{nr}}}
$$

The excitation transfer efficiency from NIRDye to the SD is estimated to be between 60% and 80% on the basis of the charge kinetics of the AS02 the FRET radius and an average separation distance of 1 nm. DSCs cosensitized with all organic dyes have previously demonstrated an energy cascade efficiency, where intermolecular energy transfer occurs from the high band gap to the lower band gap SD.$^{31}$ However, energy transfer from the metal complex SD to the NIRDye is not likely because the rate of electron injection of C106 is several orders of magnitude faster than energy transfer processes, efficiently splitting the excitation before energy transfer can occur.

### 2.3. Intermolecular Energy Transfer from AS02 to C106.

To verify that intermolecular energy and hole transfer occurs in this DSC system, we cosensitized transparent 6.5 μm thick TiO$_2$ mesoporous films and measured the optical and electrical properties using methods similar to those in the literature.$^{32}$ Showa Denko 17 nm diameter TiO$_2$ particles were deposited on...
fluorine-doped tin oxide glass (TEC 15 Ω/square, 2.2 mm thick, Pilkington) via screen printing, sintered at 450 °C, and subsequently treated with TiCl4. Figure 2A shows the optical density (OD) versus wavelength during different stages of cosensitization. The titania films were first dipped in a 0.1 mM AS02 solution in acetonitrile for 18 h (red dashed line). TiO2 films dipped in the C106 cation (red dash dot) bleaches at 550 nm and has enhanced absorption at 800 nm, while the AS02 cation (green) bleaches at 780 nm and has an absorption increase at 1000 nm.31,32 Light absorption by C106 at 780 nm was considered negligible. The estimated ETE was determined to be 26%; it should be noted that the measured IQE (72.1%) is an average value of all C106 dyes, but the IQE is most likely lower for C106 dyes that are in close proximity to AS02, which have a higher probability of transferring holes to the AS02 before dye regeneration. Thus, the calculated ETE represents the minimum bound estimate for the C106 + C106 DSC system. AS02 is not an ideal NIR-ERD because the electron injection rate (τinj < 230 ps) is competitive with energy transfer, which reduces the excitation transfer efficiency. For NIR-ERDs with LUMO levels above the conduction band of TiO2, an insulating ligand should be added to retard charge injection. If AS02 electron injection is significantly retarded, then the ETE would increase to over 70%. The measured energy transfer rate (kET) is a combination of both Dexter and FRET energy transfer. On the basis of the kinj and knr of AS02 and the minimum bound ETE of 26%, the measured rate of energy transfer (kET) is >1.76 × 109 s−1 (ET < 568 ps) using eq 1.

\[ EQE_{ERD} = \eta_{ABS, ERD} \cdot IQE \cdot ETE \]  

where EQE_{ERD} is the external quantum efficiency contribution caused by the NIR-ERD at 780 nm (9.4%), \( \eta_{ABS, ERD} \) is the fraction of light absorbed by the NIR-ERD, and IQE is the internal quantum efficiency. The calculated ETE was determined to be 26%; it should be noted that the measured IQE (72.1%) is an average value of all C106 dyes, but the IQE is most likely lower for C106 dyes that are in close proximity to AS02, which have a higher probability of transferring holes to the AS02 before dye regeneration. Thus, the calculated ETE represents the minimum bound estimate for the C106 + C106 DSC system. AS02 is not an ideal NIR-ERD because the electron injection rate (τinj < 230 ps) is competitive with energy transfer, which reduces the excitation transfer efficiency. For NIR-ERDs with LUMO levels above the conduction band of TiO2, an insulating ligand should be added to retard charge injection. If AS02 electron injection is significantly retarded, then the ETE would increase to over 70%. The measured energy transfer rate (kET) is a combination of both Dexter and FRET energy transfer. On the basis of the kinj and knr of AS02 and the minimum bound ETE of 26%, the measured rate of energy transfer (kET) is >1.76 × 109 s−1 (ET < 568 ps) using eq 1.

2.4. Intermolecular Hole Transfer from C106 to AS02.

Photoinduced transient absorption (PIA) spectroscopy, shown in Figure 3, was performed on C106, AS02 + C106, and AS02 sensitized films without the presence of the electrolyte to probe the photogenerated charge species. Steady-state PIA, which measures the change in absorption of the oxidized dye species, was chopped at a frequency of 9 Hz using a 470 nm light bias using methods previously described in the literature. Briefly, the C106 cation (red dash dot) bleaches at 550 nm and has enhanced absorption at 800 nm, while the AS02 cation (green) bleaches at 780 nm and has an absorption increase at 1000 nm. For AS02 + C106 dyed (black) films, the C106 absorbs over 80% of the photons at the illumination wavelength (470 nm), but the PIA signal is dominated by the AS02 cation, indicating intermolecular hole transfer from C106 to AS02.

AS02 is an ideal dye to measure the fraction of holes from C106 dyes that transfer to NIR dyes in the cosensitized DSC system. Charge transfer between SDs in cosensitized systems has
been previously discussed, but could not be verified nor quantified because both dyes are capable of hole regeneration. Because AS02 cannot regenerate with the electrolyte, all holes transferred to AS02 must recombine with the electrons in the TiO₂ and cannot contribute to photocurrent. For this system, the fraction of holes from C106 that transfer to AS02 can be estimated on the basis of the reduction in the internal quantum efficiency of the AS02 + C106 DSC. The internal quantum efficiency is defined by eq 3, which can be defined as the probability of hole transfer to the electrolyte, electron transfer to the titania, and the charge collection efficiency (η_CCE). For C106, the electron injection rate is extremely fast relative to the nonradiative decay rate and is not expected to change with cosensitization. The η_CCE was estimated to be 94% for C106 only but was reduced to 83% for the AS02 (56%) + C106 (44%) DSC system (see the Supporting Information). Further changes in the IQE will be primarily due to competition between hole transfer (k_{HT}) and regeneration (k_{reg}) of the oxidized dye by the electrolyte.

$$\text{IQE} = \frac{k_{reg}}{k_{HT} + k_{reg} + k_{rec} + k_{nr} + k_{cc}} \times \eta_{cc}$$

(3)

An equivalent surface concentration of AS02 reduced the IQE from 88% for the C106 control to 47% for AS02 (56%) + C106 (44%) DSC (see the Supporting Information). On the basis of the IQE and η_CCE reduction and C106 k_{reg} and k_{rec} rates, the effective hole transfer lifetime, τ_{HT}, is 5.4 μs. It should be noted that this is an averaged rate over all C106 dyes cosensitized on the TiO₂ surface; the intermolecular hole transfer rate may significantly vary depending on how C106 and AS02 pack with one another on the surface. While the IQE reduction caused by AS02 is an extreme case, regeneration rates can be slower for organic dyes, and NIR dyes in particular will likely have a lower driving force for hole regeneration. The k_{HT} indicates that >40% holes can be transferred from C106 dyes near AS02. Intermolecular hole migration to NIR dyes has important implications for hole regeneration. The electron lifetime was studied to determine the effects of intermolecular hole migration on the recombination. The electron lifetime was measured using electrochemical impedance spectroscopy for various fractional AS02/C106 surface concentrations to better understand the change in V_{oc}. Impedance measurements were performed with an Autolab PGSTAT30 (EcoChemie B.V., Utrecht, Netherlands) over a frequency range from 1 MHz to 0.1 Hz at bias potentials between −0.2 and −0.8 V (with a 10 mV sinusoidal AC perturbation); all measurements were done at 20 °C and in the dark. The resulting impedance spectra were analyzed with ZView software (Scribner Associate Inc.) on the basis of the two-channel transmission line model. The electron lifetimes of various AS02 + C106 cosensitized DSC systems are plotted against conductivity of the TiO₂ and are shown in Figure 4. C106-only DSCs have an electron lifetime of 500 ms, while AS02-only DSCs have an electron lifetime of 2 ms near open-circuit voltage conditions. If the dyes do not electronically interact in the cosensitized DSC system, then one might expect the electron decay rate to be the weighted average of the individual dye systems. However, in the AS02 (14%) + C106 (86%) cosensitized DSC system, the electron lifetime is 50 ms, which is nearly 3 times lower than the weighted lifetime of 140 ms. The disproportionate change in electron lifetime may be caused by hole transfer from the C106 to AS02. The V_{oc} change is not related to a reduction in the overall dye loading on the TiO₂, which actually increases during cosensitization (see the Supporting Information). It should be noted that recombination between electrons in the titania and the I₃⁻ electrolyte is generally considered to be the V_{oc}-determining recombination mechanism when using Ru-based metal complex dyes, which have relatively fast regeneration rates. However, recombination from electrons in TiO₂ to oxidized dye species may become the critical mechanism for NIR dyes whose ground-state redox potentials are less favorable for regeneration. A complete study of the recombination kinetics of fully functioning NIR-SD is required to determine which recombination mechanism plays a dominant role under V_{oc} conditions for cosensitized DSC systems.

2.5. Negative Effects of Intermolecular Hole Transfer in Cosensitized Dye-Sensitized Solar Cells. A 80 mV drop in V_{oc} was observed for the cosensitized AS02 (14%) + C106 (86%) DSC (V_{oc} = 650 mV) system relative to the C106 control DSC (V_{oc} = 730 mV) (see the Supporting Information). Because the V_{oc} is also affected by the reduction in the photocurrent density, the electron lifetime was studied to determine the effects of intermolecular hole migration on the recombination. The electron lifetime was measured using electrochemical impedance spectroscopy for various fractional AS02/C106 surface concentrations to better understand the change in V_{oc}. Impedance measurements were performed with an Autolab PGSTAT30 (EcoChemie B.V., Utrecht, Netherlands) over a frequency range from 1 MHz to 0.1 Hz at bias potentials between −0.2 and −0.8 V (with a 10 mV sinusoidal AC perturbation); all measurements were done at 20 °C and in the dark. The resulting impedance spectra were analyzed with ZView software (Scribner Associate Inc.) on the basis of the two-channel transmission line model. The electron lifetimes of various AS02 + C106 cosensitized DSC systems are plotted against conductivity of the TiO₂ and are shown in Figure 4. C106-only DSCs have an electron lifetime of 500 ms, while AS02-only DSCs have an electron lifetime of 2 ms near open-circuit voltage conditions. If the dyes do not electronically interact in the cosensitized DSC system, then one might expect the electron decay rate to be the weighted average of the individual dye systems. However, in the AS02 (14%) + C106 (86%) cosensitized DSC system, the electron lifetime is 50 ms, which is nearly 3 times lower than the weighted lifetime of 140 ms. The disproportionate change in electron lifetime may be caused by hole transfer from the C106 to AS02. The V_{oc} change is not related to a reduction in the overall dye loading on the TiO₂, which actually increases during cosensitization (see the Supporting Information). It should be noted that recombination between electrons in the titania and the I₃⁻ electrolyte is generally considered to be the V_{oc}-determining recombination mechanism when using Ru-based metal complex dyes, which have relatively fast regeneration rates. However, recombination from electrons in TiO₂ to oxidized dye species may become the critical mechanism for NIR dyes whose ground-state redox potentials are less favorable for regeneration. A complete study of the recombination kinetics of fully functioning NIR-SD is required to determine which recombination mechanism plays a dominant role under V_{oc} conditions for cosensitized DSC systems.

3. CONCLUSION

This study demonstrates the need to refine design rules for NIR-SDs and NIR-ERDs. NIR-SDs should have sufficient
LUMO and HOMO levels for charge injection and a high molar extinction coefficient (>100 000 M⁻¹ cm⁻¹). Planar NIR-SDs that pack well with metal ligand SDs may lose substantial Voc due to intermolecular hole transfer, negating the potential power conversion efficiency gain with high Voc losses. NIR-SDs should be physically separated from the metal complex SD either via long alkyl side chains or via selective positioning⁹,¹⁰ to prevent intermolecular hole transfer to maintain high open-circuit voltage.

NIR-ERDs do not require precise LUMO level alignment and short conjugated ligands for rapid electron charge injection. However, NIR-ERDs must intimately mix with metal complex SDs. The ability to both sensitize and transfer energy from NIR-ERDs to metal complex sensitizing dyes to electronically transfer energy and must therefore have a HOMO level below the iodide potential to regenerate the electrolyte. Ideally, NIR-ERDs should be designed with an insulating ligand that is long enough to prevent electron backflow for helpful discussions. This work was primarily supported by P.W. thanks the Key Scientific Program (No. 2007CB936700).

ACKNOWLEDGMENT

B.E.H. would like to thank Jun-Ho Yum for preparing the TiO₂ films, Jason Bloking for PESA measurements, and Eric Hoke for helpful discussions. This work was primarily supported by the Office of Naval Research contract no. N00014-08-1-1163. P.W. thanks the Key Scientific Program (No. 2007CB936700).

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