

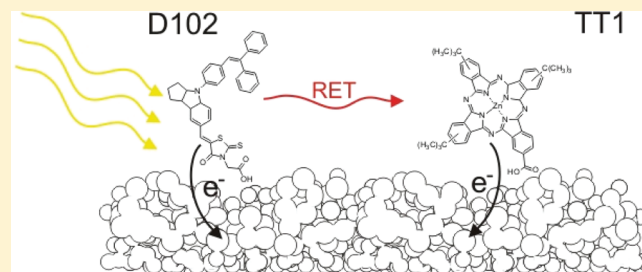
Surface Energy Relay Between Cosensitized Molecules in Solid-State Dye-Sensitized Solar Cells

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Supporting Information

ABSTRACT: We employ cosensitization of a visible absorbing organic sensitizer and a near IR absorbing Zn-phthalocyanine complex to significantly enhance the optical bandwidth in spiro-OMeTAD based solid-state DSCs. The cosensitized cells exhibit greatly enhanced performance, with full sun AM1.5 power conversion efficiencies of 4.7%, as compared to 3.9% for the best monosensitized device. Unexpectedly, further to broadening the spectral response, the addition of the near IR sensitizer greatly enhances the spectral response in the visible region. Through both electronic and spectroscopic investigations, we demonstrate that resonant energy transfer occurs from the visible to the near IR sensitizer. This unforeseen charge generation route works in conjunction with direct electron transfer from the visible sensitizer, improving the overall charge generation efficiency and explaining the panchromatic enhancements with the cosensitized system. This previously unobserved mechanism for charge generation relaxes the design criteria for visible absorbing sensitizers, providing a second, and possibly primary, channel for efficient charge generation.



Rising global energy demands are inspiring a mounting interest in renewable energy research. Among the new technologies, dye-sensitized solar cells (DSCs) are a promising concept, having good photovoltaic conversion while remaining cost-effective.¹ Solid-state DSCs (SDSCs) using molecular hole-transporters are an attractive alternative to liquid electrolyte based cells, but efficiency is limited to a large extent by poor light harvesting, both in extinction strength and bandwidth.² Optimizing absorption is critical in SDSCs, since the thickness of the device appears limited by inefficient pore filling of structures over 2–4 μm thick.^{3,4} Panchromatic sensitizers tend to have low absorption strengths⁵ making them nonideal in thin dye-sensitized films, while organic dyes tend to have narrower yet stronger absorption bands. The coadsorption of complementary dyes has been shown to be promising for extending the photovoltaic response in electrolyte based cells,⁶ but should be most advantageous for these SDSCs where limited optical extinction is critical. Here, we extend the absorption spectrum of solid-state dye sensitized solar cells sensitized with a visible absorbing indoline based dye^{7,8} by further sensitizing with a near-IR absorbing Zn-phthalocyanine dye, termed TT1.^{9,10} SDSCs incorporating the indoline sensitizer exhibit a full sun conversion efficiency of 3.9%, incorporating the Zn-phthalocyanine sensitizer they exhibit 1.1%, and remarkably this is enhanced to 4.7% with an optimized cosensitized system. This by itself is noteworthy, but more intriguingly, we observe that the improvements with cosensitization amount to more than that expected from the superior light harvesting. Förster resonant energy transfer (FRET) is an energy transfer process that can occur between photoactive molecules

over a distance regime of many nanometers.¹¹ Through photoluminescence investigations, we demonstrate that FRET occurs from the visible absorbing dye to the Near IR sensitizer. For dye-sensitized metal oxides there is usually a heterogeneous, or multiphase electron transfer process. The “ultrafast component” is very efficient, however electron injection in the slower phases, competes with nonradiative, noninjecting decay channels. This results in the species undergoing slow electron transfer, not transfer charges with unity efficiency. The surface energy relay observed here enables the slower injecting photoexcited states to transfer to the near IR dye prior to decaying, which opens a second channel for charge generation from the visible absorbing dye improving overall efficiency.

SDSCs using 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) as the hole-transporter were fabricated and characterized as previously described.³ Mesoporous TiO₂ was sensitized with a visible absorbing indoline based dye, termed D102, for 1 h in a 0.2 mM ACN:*tert*-Butanol 1:1 solution, and with a Zinc Phthalocyanine based sensitizer, termed TT1, for 1 h in a 50 μM in EtOH + 10 mM chenodeoxycholic acid (CDCA) solution. For cosensitization the films were first sensitized with D102 for 48 min followed by TT1 for 12 min. Chemical structures and UV–vis absorption spectra are shown in Figure 1 (further experimental details are presented in the Supporting Information, SI).

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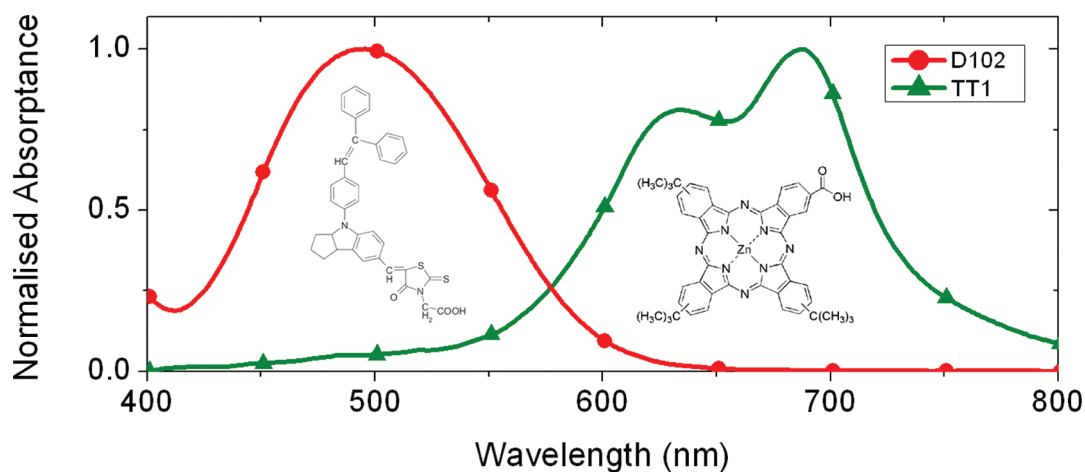


Figure 1. Normalized absorbance spectra of D102 (circles) and TT1 (triangles) adsorbed on mesoporous TiO₂ films. The molecular structure of the dyes employed are inset under the respective absorption curves.

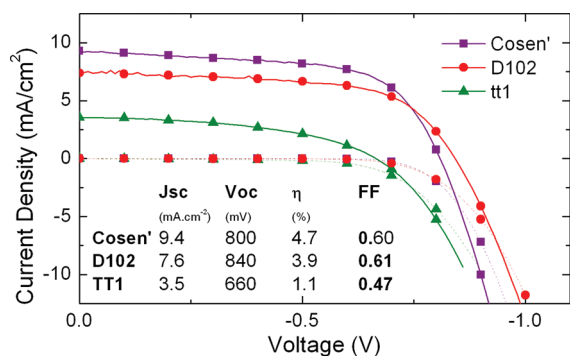


Figure 2. Current density–voltage (*J*–*V*) characteristics of SDSCs sensitized with D102 (circles), TT1 (triangles), and cosensitized with both D102 and TT1 (squares) measured under simulated AM1.5 sunlight of 100 mW cm⁻² and in the dark (same symbols with dotted lines).

In Figure 2, we present the current–voltage curves for SDSCs measured under simulated AM1.5 sun light of 100 mW cm⁻². Devices incorporating TT1 are observed to have a short-circuit current density of 3.5 mAcm⁻² and an efficiency of just over 1%, comparable with that previously reported for SDSCs incorporating Zn-phthalocyanines.¹² Devices incorporating D102 deliver a short-circuit current density of 7.6 mAcm⁻² and convert 3.9% of the solar energy to electrical power, again, consistent with previous reports.⁷ Cosensitization improves the current density further still to 9.4 mAcm⁻², with the overall power conversion efficiency increased to 4.7%. It is noted that when D102 devices were made incorporating equivalent proportions of CDCA, the spacer molecule present in the TT1 solution, no significant increase in performance was observed as compared to the standard D102 SDSC.

In order to verify that the increased photocurrent in the cosensitized devices is due to increase light harvesting in the Zn-PC dye, we have performed spectral response measurements. The photovoltaic action, presented in Figure 2, does display an extension into the near IR for the cosensitized cell, as compared to “mono-sensitization” with D102, but the actual photoresponse in this extra IR region from 650 to 750 nm is relatively low. However, there is also an unexpected increase in the photo conversion efficiency in the visible region, where D102 already absorbs strongly.

In order to disentangle the influence of enhanced light absorption, from improved operational processes, we have quantified the absorbed photon-to-electron conversion efficiency (APCE): We have estimated the light absorption in the device by measuring the reflectance spectra from silver backed devices in an integrating sphere¹³(see SI), and subsequently divided the IPCE by the fraction of light absorbed to determine the APCE. Indeed, the conversion efficiency from the visible absorbing dye is panchromatically enhanced by the presence of the TT1 dye. We note here a few peculiarities of the absorption spectra: For the TT1 only devices we would expect negligible absorption in the 450 to 550 nm region, however, from the reflectance measurements there is around 30% of the light absorbed in two passes of light through the film (reflectance). Furthermore, for the D102 only devices, we would expect negligible absorption in the region >650 nm, where we actually measure around 20% absorption in reflectance. This is likely to be due to partially oxidized spiro-OMeTAD, which absorbs in this region.³ This implies that the APCE values derived are a lower estimation of the conversion efficiency from light absorbed in the dye, especially in the near IR region where the absorption from the sensitizer does not compete as strongly with the absorption in the “doped” spiro-OMeTAD than in the visible region of the spectrum.

The reason for the enhanced efficiency from D102, with the addition of the near IR absorbing Zn-PC sensitizer is not clear. However, the indoline-based dyes (such as D102) are prone to aggregation and or formation of multi layers on the TiO₂ surface, and this may render electron-transfer from photoexcited dye less than ideal.^{14,15} A possibility is that the cosensitization process is breaking apart aggregates or desorbing nonbound dye. The TT1 dye solution contains approximately 2 mM of chenodeoxycholic acid, specifically introduced to reduce aggregation of the TT1 molecules. To probe if this is also improving the D102, we soaked the D102 sensitized films in a 2 mM chenodeoxycholic acid solution for 12 min to mimic the effect under the cosensitization process. In this instance, however, we observed no significant increase in photocurrent of the constructed solar cells, indicating that the presence of the TT1 is directly influencing the photo-induced charge generation from light absorbed in the D102.

We postulate that energy transfer from D102 to TT1 could be responsible for enhancing the charge generation efficiency: If electron transfer from the photoexcited D102 is heterogeneous,¹⁵

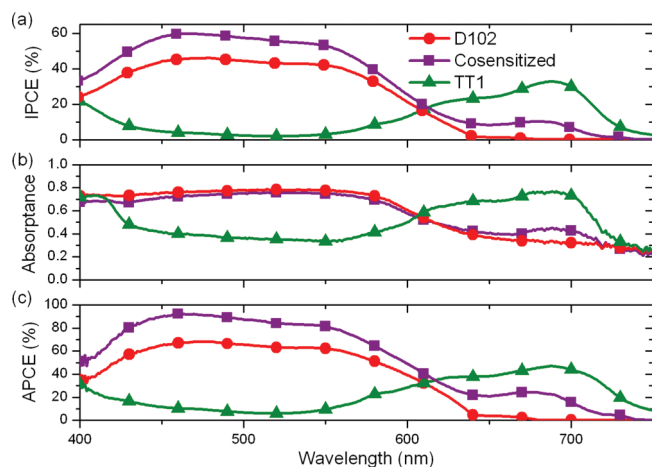


Figure 3. (a) Photovoltaic action spectra for the same cells as presented in Figure 1 showing incident photon-to-electron conversion efficiency (IPCE). (b) Fractional light absorbed in the complete devices, measured in reflectance in an integrating sphere with first order correction for absorption in the FTO glass. (c) Absorbed photon-to-electron conversion efficiency (APCE) calculated by dividing the IPCE by the absorbance.

then a certain fraction of the excited states will undergo fast and very efficient charge generation, and the remaining slower injecting species may not compete effectively with the natural decay of the excited state. In the literature the fraction of the fast (efficient) component versus the slow (inefficient) component can vary from 30 to 100% depending on the sensitizer and oxide. If this slow-injecting inefficient phase can transfer its energy to the near IR dyes prior to exciton decay, then this would, in essence, “recycle” the exciton and enable a second chance for electron transfer to the TiO₂ through the TT1 sensitizer, even if the TT1 sensitizer is less efficient in the first place. To probe whether surface energy transfer occurs in this system we performed time-resolved photoluminescence (PL) measurements on sensitized mesoporous TiO₂ and Al₂O₃ substrates (the Al₂O₃ substrates are acting as noninjecting references). The films were excited at 400 nm under vacuum (further details are given in the SI).

The photoluminescence spectra for D102, TT1 and cosensitized films are shown in Figure 4a. D102 has a broad visible to near IR emission. On both TiO₂ and Al₂O₃ (Comparable measurements on Al₂O₃ are shown in the SI), the visible emission from D102 is significantly quenched by cosensitization with TT1. The emission onset for the cosensitized film is almost identical to pure TT1, consistent with highly efficient energy transfer occurring from the emissive species in D102 to TT1. We also measured the PL spectra for D102 after soaking in an equivalent solution of CDCA; which in contrast shows a marginal increase in PL intensity and no change to the spectral shape. This confirms that CDCA does not play a significant role in quenching of the luminescence, although it may further aid energy transfer to the TT1 by increasing the PL intensity from the D102. We note that the light absorption in TT1 at 400 nm is very weak and the absolute emission at 700 nm has increased ~10-fold in the cosensitized films as compared to pure TT1 sensitization. The PL tail observed in pure TT1 films is due to the reduced sensitivity combined with very low emission signals. The results on TiO₂ and Al₂O₃ follow the same trend though the overall PL intensity is higher on Al₂O₃ due to elimination of the electron transfer channel.

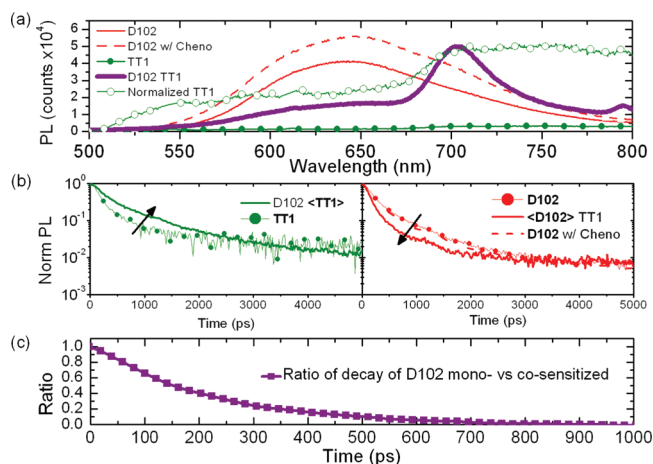


Figure 4. (a) The time integrated photoluminescence spectrum of sensitized mesoporous TiO₂. All PL spectra are shown without normalization—a normalized version of the TT1 PL spectra is also shown for ease of interpretation. Note that the PL response of molecular TT1 singly sensitized was observed to be significantly lower than for the organic D102. Dye adsorption was performed as for the SDSCs. (b) Time-resolved photoluminescence from TT1 at 705 nm (left) and D102 at 650 nm (right) is shown for the case of monosensitized (line and symbol) and cosensitized (solid line). All measurements were performed with Al₂O₃ as a substrate to avoid ambiguity due to electron injection. The arrows show the trend upon cosensitization. The D102 panel also shows the time-resolved PL for D102 containing chenodeoxycholic acid (CDA) in equivalent concentration to a cosensitized film (dashed line). (c) The ratio of emission from D102 in the cosensitized to monosensitized films; the decay is indicative of energy transfer, with an exponential lifetime of 210 ps (line).

The transient PL decay curves for sensitized Al₂O₃ are shown in Figure 4b. The D102 emission (at 650 nm) decays significantly faster in the cosensitized film than in the monosensitized film. The TT1 PL (at 705 nm) decays faster in the monosensitized film than when cosensitized with D102. This is consistent with excitation energy transferring from D102 to TT1 which “replenishes” the TT1 excitons as they undergo their natural decay, slowing down the overall observed decay. The PL decays are faster on TiO₂ than on Al₂O₃ consistent with electron transfer to the TiO₂. However, we observe identical trends, which are shown in the SI. Importantly here, the D102 emission decays significantly faster in the cosensitized films on TiO₂, indicating that long-lived D102 excited states contributing to the emission are more effectively quenched via energy transfer to TT1 than via electron transfer to TiO₂ for times longer than 10 ps. Figure 4c also shows the ratio of the D102 PL on the Al₂O₃ in the cosensitized to monosensitized films. If this quenching of the D102 emission is due to resonant energy transfer to the TT1, then the exponential decay in Figure 4c fits with an energy transfer lifetime of 210 ps.

The Förster radius (R_0) is the distance between a donor and acceptor at which there is a 50% probability of FRET occurring and is defined by the following:¹¹

$$R_0^6 = \frac{9000(\ln 10)\kappa^2\phi_d}{128\pi^4N_A n^4} \int_0^\infty F_d(\lambda)\epsilon_a(\lambda)\lambda^4 d\lambda$$

where κ^2 is the orientation parameter, typically taken to be 2/3 for random orientation; N_A is Avogadro’s number; ϕ_d is the quantum yield of the donor; F_d is the normalized fluorescence

profile of the donor, and ϵ_a is the molar extinction profile of the acceptor molecule. From the time-integrated photoluminescence spectra, the steady state absorption spectra, an estimated fluorescence quantum yield of 2%.¹⁴ and using the refractive index for the host material (spiro infiltrated titania) as reported in reference¹⁶ (see SI for further details) we estimate R_0 to be 3.5 nm \pm 0.4 nm. Using this Förster radius, our estimated dye loading values, and the measured natural fluorescence rate (k_{fluor}) the FRET rate (K_{ET}) can be modeled,¹⁷ in addition to the value previously estimated from the TCSPC data by the following:

$$k_{\text{ET}} = k_{\text{fluor}} \left(\frac{R_0}{r} \right)^6$$

Where r is the average dye separation, estimated from dye loading values derived from the measured absorption spectra. A FRET rate of $\sim 7 \times 10^{10} \text{ s}^{-1}$ is calculated, which, taken as a rough estimate, is consistent with the measured value of $\sim 5 \times 10^{10} \text{ s}^{-1}$. Both the modeled and measured FRET rate estimates suggest a FRET efficiency of around 50%.

These results indicate that an inferior performing sensitizer molecule can provide greater than expected performance improvements when used in conjunction with a previously well-established dye sensitizer. We also note that TT1 has recently been shown to act as an effective “energy sink” when combined with an energy relay dye suspended within the electrolyte of a DSC and also in combination with a small molecular donor in the solid-state DSC.^{17,18} Furthermore, energy transfer has been shown between dye molecules adsorbed to the same titania surface.^{4,19,20} In the work of Hardin et al. in electrolyte cells and Yum’s route in the solid-state DSCs, the “energy relay dye” is suspended in the hole-transport medium and channels all its useful excitation energy through the low band gap sensitizer. In contrast, here we report that visible absorbing dyes can function as both sensitizers and energy relay dyes simultaneously, enabling dual channels for charge generation. We also note that an argument in favor of using an energy relay dye suspended within the hole-transport/electrolyte phase, is that it does not take up space on the oxide surface which can therefore be used for increased sensitization. However, since most of the current generation of nearIR dyes suffer from aggregation issues, in their optimized configuration they are spaced apart with more than 100 fold the molarity of chenodeoxycholic acid. This implies that the energy relay dye on the surface can replace the cheno deoxycholic acid, or indeed act as a spacer itself for the nearIR dye and not reduce the sensitization density. We note, that although our experimental results are consistent with resonant energy transfer from photoexcited D102 to TT1, there may still be a fraction of direct electron, hole or exciton transfer between adjacent molecules which will also contribute to the energy and charge transfer in this system.

In summary, we have utilized cosensitization as a tool to significantly enhance the optical bandwidth and efficiency in solid-state DSCs with respect to the lone visible absorbing system employed here. A combination of electron transfer into the TiO_2 , and efficient energy transfer from the visible absorbing dye to the near IR sensitizer is observed to occur, with subsequent conventional charge generation from the near IR sensitizer. This novel charge generation route proves to be remarkably useful, since it gives a second chance for charge generation to species which would have otherwise decayed prior to electron transfer. This broadens possibilities to enhance the

performance of existing visible sensitizers, potentially relaxes issues with aggregation of visible sensitizers, but more excitingly opens the design criteria for a new family of highly emissive, strongly absorbing visible sensitizers: With this energy relay mechanism, it should be possible to create surface-tethered dyes optimized for light absorption strength and bandwidth, neglecting the previous requirement to maximize their electron transfer efficiency by inducing electron push–pull characteristics.

■ ASSOCIATED CONTENT

S Supporting Information. Additional material as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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