

# Förster Resonance Energy Transfer in Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) offer the potential to make affordable solar power a reality. The limited quantity and harmful nature of our current energy sources are well-known,<sup>1,2</sup> and there is urgent need for a technology that can replace our current energy production infrastructure cheaply, cleanly, and on a global scale. Solar power is the clear favorite, as the “fuel” is delivered free to our doorsteps in gross excess of our needs; every hour the Earth receives enough solar energy to power humanity for an entire year.<sup>2</sup> Of course, the challenge lies in the cheap and efficient conversion of sunlight to chemical fuels<sup>3</sup> or to electric power. DSSCs possess efficiencies comparable to other thin-film technologies but with greatly reduced costs for raw materials and processing methods. Their low toxicity and potential for high-volume production using currently available technology make DSSCs excellent candidates to supply significant fractions of our future power needs, if only moderate increases in efficiency can be achieved. Record-holding liquid-junction cells have demonstrated efficiencies of 11.5%<sup>4</sup> despite the fact that many high-efficiency dyes do not absorb strongly past 700 nm. This problem is exacerbated in solid-state dye-sensitized solar cells (SS-DSSCs), which have an extremely thin absorbing layer. In these cells, light absorption is not nearly as complete. Generally, it is true that one must choose between either a dye with a broad but relatively weak absorbance or one that absorbs strongly in only a small spectral window. In either case, much of the sunlight passes through the cell.

One of the major challenges of DSSCs is to design a cell that can absorb all of the light from 350–1000 nm using a very thin absorbing layer. Unfortunately, there are no dyes available that can achieve both of these goals alone. Efforts have been made

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to extend spectral response by cosensitization with complementary dyes<sup>5,6</sup> but fail to beat the efficiency record set by a single dye. Tandem cells have also been proposed, but the need for current matching makes their realization difficult. While excellent efficiencies have been attained with tandem cells,<sup>7</sup> they are on par with single dye cells because efficient infrared (IR) dyes capable of current matching do not exist. Therefore, they have similar limitations as single-junction cells in terms of spectral response. Moreover, since tandem cells are made by stacking two separate cells in series, the outcome is roughly double the production cost without any increase in efficiency, which is not in line with the goal of developing affordable solar power. It is hoped that high-extinction-coefficient dyes will one day enable thin SS-DSSCs to have efficiencies comparable to much thicker liquid-junction DSSCs; however, a high extinction coefficient often comes at the cost of absorbance in a very limited window of the solar spectrum. Despite much work in the field in the last 19 years, high-efficiency DSSCs<sup>4</sup>

**ABSTRACT** It appears that the efficiency of dye-sensitized solar cells (DSSCs) has reached a ceiling due to the limited absorption spectrum of currently available dyes. To achieve new record efficiencies, light absorption must be extended into the near-infrared region of the spectrum without sacrificing performance in the visible region. No single dye has this ability, but there is greater strength in numbers. Förster resonance energy transfer (FRET) may be used to link two or more materials to provide strong absorption across a broad portion of the solar spectrum. This process has been shown to be effective and efficient, and a recent breakthrough in FRET-enhanced DSSCs is presented in this issue. This Perspective explores the background of this topic and considers directions for future development.

See the accompanying Article by Buhbut *et al.* on p 1293.

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are not fundamentally different from their original incarnation.<sup>8</sup> The next generation of DSSCs must be marked by complete absorption in thin layers ( $\sim 2 \mu\text{m}$ ) over a range comparable to competing semiconductors such as crystalline silicon (wavelengths up to  $1.1 \mu\text{m}$ ). This is a difficult task, but one that is required to attain efficiencies that merit commercial adoption of the technology. One way to achieve this could be by harnessing Förster resonance energy transfer (FRET).

FRET is a mechanism by which one molecule may transfer its excitation energy nonradiatively to another molecule separated by a short distance.<sup>9</sup> The two molecules are coupled through the electric field by a dipole–dipole interaction. Light is first absorbed by a donor molecule, which becomes excited. Before the donor can fluoresce and return to the ground state, its excitation is transferred to a nearby acceptor molecule having a slightly lower excitation energy *via* the exchange of a virtual photon. The donor returns to the ground state as the acceptor gains its excitation. The end result is that the acceptor has become excited due to the indirect absorption of a photon to which it would otherwise be insensitive. FRET is an interesting phenomenon because it requires neither physical contact nor charge exchange. This opens up a great number of possibilities for possible donor/acceptor pairings, as it avoids many of the problems that may result from direct contact of the two and allows for somewhat relaxed rules for compatibility. Nature has already come close to perfecting light harvesting by FRET; it is the means by which chlorophyll transfers excitation to cell reaction centers and has been observed to be 95% efficient in purple bacteria.<sup>10</sup>

The main concepts of FRET are embodied in a few key equations. Most importantly is the description of the Förster radius,<sup>9</sup>  $R_0$ , defined as the separation distance at which the transfer efficiency is 50%

$$R_0^6 = \frac{9000 \ln(10) k^2 \Phi_D}{128 \pi^2 N_A n^4} \left[ \int_0^\infty F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \right]$$

where  $k$  is the orientation factor between donor and acceptor dipoles ( $k^2$  is equal to  $2/3$  for random orientation),  $\Phi_D$  is the donor fluorescence quantum yield in the absence of the acceptor,  $N_A$  is the Avogadro constant ( $6.022 \times 10^{23}$ ), and  $n$  is the index of refraction for the medium surrounding the donor and acceptor. The value for  $\Phi_D$  must be high to achieve useful values of  $R_0$  for DSSC applications. The overlap integral is the most important term because it represents the resonance term. It is the overlap between the fluorescence of the donor, normalized to unity area,  $F_D(\lambda)$ , and the molar absorption spectrum of the acceptor,  $\epsilon_A(\lambda)$ , scaled by wavelength to the fourth power. The stronger this resonance term the more efficient energy transfer will be. The maximization of this term through selection of materials is what will drive research in FRET-enhanced DSSCs.

Once the Förster radius has been calculated, it can be used to estimate other quantities of interest, such as the rate of energy transfer from a single donor to a single acceptor given by

$$k_{\text{ET}} = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6$$

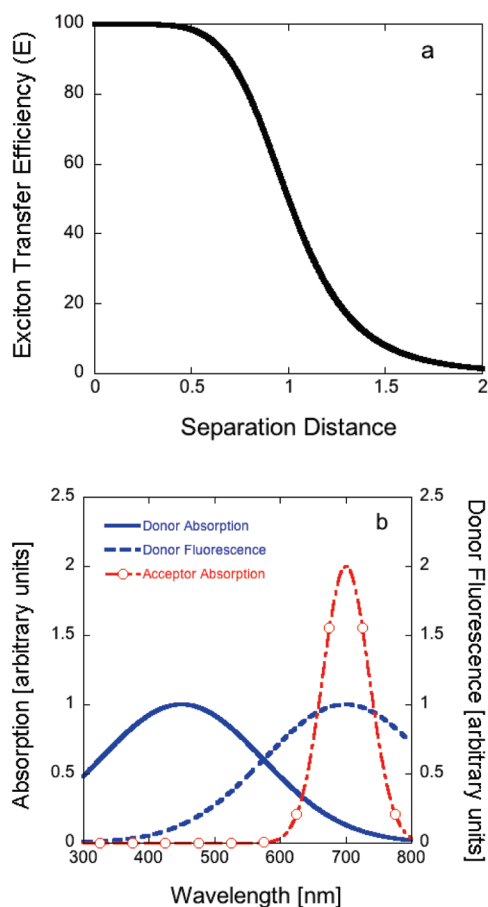
where  $\tau_D$  is the lifetime of the donor excited state in the absence of the acceptor, and  $r$  is the distance between donor and acceptor chromophores. One can also find the energy transfer efficiency  $E$ :

$$E = \frac{R_0^6}{R_0^6 + r^6}$$

which is similarly valid for point-to-point transfer between single donor and acceptor molecules. Because of the strong distance dependence in these formulas, it is clear that the separation distance  $r$  must be as small as possible for efficient trans-

fer to occur. The bulk heterojunction of a DSSC affords a unique structure capable of bringing large amounts of donor and acceptor molecules together while assuring that almost all donors are within a Förster radius of an acceptor. In other words, the nanoscale architecture is the key feature enabling straightforward incorporation of FRET in DSSCs. It is also encouraging to note that the above equations for energy transfer efficiency consider point-to-point transfer, while in most DSSCs, a more accurate description is transfer from a point donor to a sheet of acceptor dye molecules. Energy transfer efficiency from a point donor dipole to an infinite sheet of acceptors decays as  $r^{-4}$  instead of  $r^{-6}$  for dipole to dipole transfer, meaning that a sheet of acceptors can harvest energy over a larger distance.<sup>11</sup>

**The Requirements of FRET.** Many reviews<sup>9,12–14</sup> and books<sup>15–17</sup> giving a deeper and more complete theory of FRET are available. The purpose of this paper is to explore the possibilities for the use of FRET in DSSCs. How can this tool be used to achieve our goal of strong, broad absorption without sacrificing key parameters, such as  $V_{\text{oc}}$  or fill factor? The answer lies in materials selection. In our case, the acceptor material will be a dye anchored to the surface of titania, the same materials that are typically the only sensitizer in DSSCs. We know that excited dye molecules have fast and efficient electron transfer to titania and are therefore a logical place for our donor material to send its excitation. The acceptor material must have a lower excitation energy than the donor, meaning the acceptor will absorb in the red/near-infrared (NIR) while the donor will absorb in the blue/green part of the spectrum. The donor material must fulfill some basic requirements to be successfully incorporated into the cell. The main three requirements are that (1) the donor must be strongly fluorescent, (2) there must



**Figure 1.** (a) Excitation transfer efficiency is high inside a Förster radius and quickly falls off at larger distances. (b) Idealized donor and acceptors showing complementary absorption spectra and strong resonance between donor fluorescence and acceptor absorbance. In this case, donor absorbance is broad, and acceptor absorbance is strong but narrow, characteristic of many organic dyes.

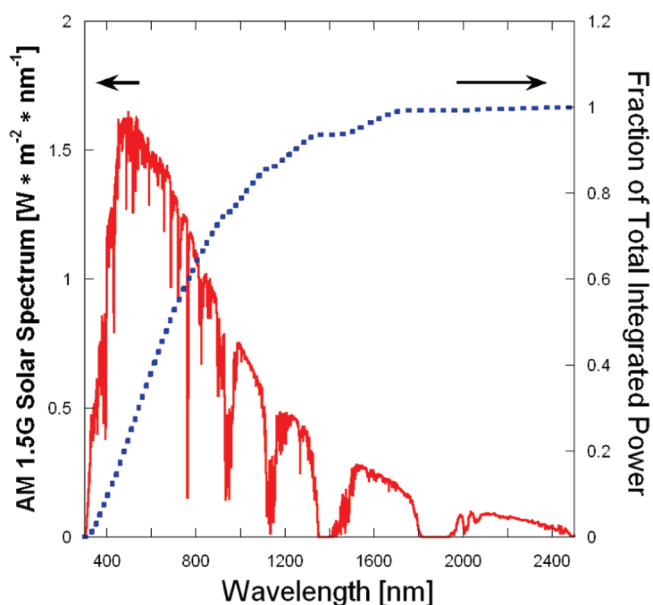
be a large overlap between the donor fluorescence spectrum and the acceptor absorbance spectrum, and (3) the two materials must be within one Förster radius (*i.e.*, several nanometers) of each other. We consider these points below.

The first requirement is that the donor fluorescence should be quenched by energy transfer to the acceptor and not by other materials in the cell. One can verify this experimentally by measuring donor fluorescence with the addition of increasing concentrations of acceptor. Common additives such as triiodide have been shown to be efficient quenchers of donor fluorescence,<sup>4</sup> hence care must be taken that this quenching mechanism does not dominate. The donor must also be highly soluble in the electrolyte to enable high concentrations without aggregation. Gains

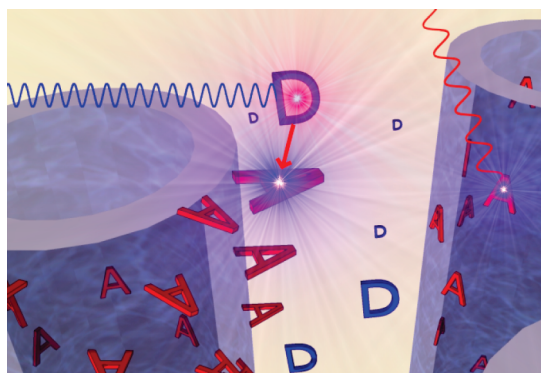
may be seen as more donor is added, until concentration self-

quenching outpaces energy transfer. Donor concentration is a parameter to be optimized for maximum light harvesting before the onset of self-quenching.

The second requirement, that the donor fluorescence spectrum overlap strongly with the acceptor absorbance spectrum, is a measure of the strength of the resonance between the donor and acceptor. This overlap integral scales as  $\lambda^4$ . All things being equal, one can expect a larger Förster radius as the overlap in the spectra is shifted to longer wavelengths. Using high absorption coefficient dyes also enables the use of thin active layers in the device and increases the value of the overlap integral. This requirement can be confusing as it is also a requirement for the more trivial process of photon emission by the donor and subsequent absorption by the acceptor. That is a long-range process following a  $r^{-2}$  dependence and is not directed, as FRET is, and is therefore not useful. Exciton transfer efficiency and an example of ideal donor and acceptor absorption and fluorescence spectra are depicted in Figure 1. The ideal pairing combines two dyes with complementary absorption cover-



**Figure 2.** AM 1.5G solar power spectrum and its integrated power as a function of wavelength. From American Society for Testing and Materials (ASTM) Standard G137.



**Figure 3.** Schematic depicting the absorption of blue light by a donor molecule (D) suspended in the electrolyte, with subsequent excitation transfer to an acceptor molecule (A) anchored to the surface of a TiO<sub>2</sub> nanotube.

ing most of the solar spectrum, along with strong overlap of donor fluorescence and acceptor absorbance.

The final requirement is that the donor and acceptor be in close proximity, within a Förster radius. Because transfer efficiency falls off abruptly, most donors within a Förster radius will transfer their excitation with near unity efficiency. Donors that are too far away will either be quenched by the electrolyte or radiatively decay, emitting a photon that may or may not find its way to an acceptor. This requirement can easily be met in a bulk heterojunction where separation distances of several nanometers are common.

**Using FRET in the Design of DSSCs.** The task ahead for the development of FRET-enhanced DSSCs is to identify or to design new donor/acceptor materials. One of the main goals should be to extend overall absorption to longer wavelengths. The currently used window (350–650 nm)

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accounts for roughly 42% of the total solar energy available (Figure 2). Another 33% of the solar spectrum energy lies in the 650–1000 nm range. In order to utilize this portion of the solar spectrum, new dyes must be developed that can efficiently absorb this portion of the spectrum, and donors must be developed that can efficiently absorb over a complementary spectrum and transfer the energy to the red/NIR absorbing dye. This means one material can only be developed while keeping the other in mind. Interest should be limited to materials with very high absorption coefficients that would enable SS-DSSCs to attain a high absorptance with a thin active layer. FRET may be an enabling technology to allow high efficiencies in SS-DSSCs by combining many high-extinction materials together to cover the whole solar spectrum.

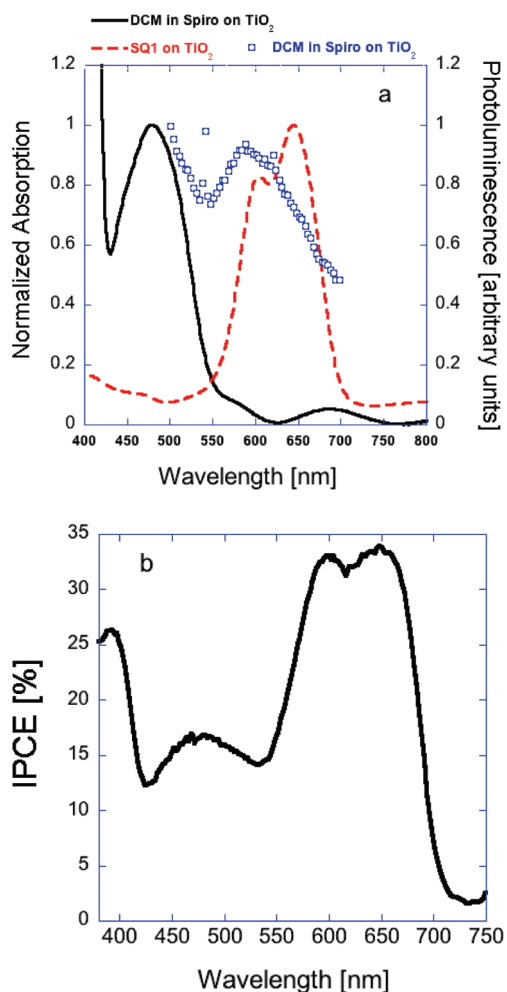
The use of FRET in DSSCs is a relatively new idea,<sup>18–20</sup> but a few interesting examples have been presented. Proof-of-concept was demonstrated by Shankar and coworkers<sup>21</sup> by dissolving a zinc phthalocyanine based dye in the electrolyte of a liquid-junction DSSC sensitized by “Black Dye” (N-749). This work established the presence of FRET from a donor dye molecule suspended in the electrolyte to an acceptor dye anchored to the surface of TiO<sub>2</sub> nanotubes. This design, generalized in Figure 3, is interesting because cell characteristics are dominated as usual by the dye,

electrolyte, and TiO<sub>2</sub> substrate and not by addition of the donor. Overall current enhancement is however limited by the narrow, though strong, absorption of zinc phthalocyanine.

Grätzel, McGehee, and collaborators developed a tailor-made donor material that can be employed in the same fashion in liquid-junction DSSCs<sup>22</sup> and SS-DSSCs.<sup>23</sup> The perylene derivative perylene tetracarboxylic diimide (PTCDI) significantly improves absorption from 400 to 600 nm by employing FRET from PTCDI to the zinc phthalocyanine acceptor dye, which is otherwise weakly absorbing in the blue/green part of the spectrum. Roads to improvement include the reduction of donor quenching and design of an improved acceptor dye.

Recent work in our lab has shown that 4-dicyanomethylene-2-methyl-6-*p*-dimethylamino-styryl-4*H*-pyran (DCM), a common laser dye, can be used as a donor in SS-DSSCs in tandem with a squaraine acceptor dye (SQ1) using Spiro-OMeTAD as the hole conductor. Excitation transfer efficiencies in optimized devices of an astonishing 80% are observed, as well as an 89% increase in photocurrent due to addition of DCM. Donor quenching is observed to be comparatively low in this system, enabling efficient harvesting of donor excitation. Fill factor and  $V_{oc}$  remain high (61% and 675 mV, respectively), almost unaffected by the addition of DCM. Efficiencies of 1.6% are seen in nanotube films only 500–600 nm thick; much higher efficiencies are expected once the process is optimized for thicker cells (roughly  $\geq 2$   $\mu\text{m}$ ). Incident photoconversion efficiency (IPCE) gains due to DCM, shown in Figure 4, can increase with cell thickness as the absorption of blue photons is not complete with the 500–600 nm thick cells. In fact, DCM is only one of a great many off-the-shelf fluorescent compounds available that could be used in this way. We believe considerable time could be saved by employing other





**Figure 4.** (a) Absorbance spectra of dye molecule DCM dissolved in pure Spiro-OMeTAD spin-coated onto TiO<sub>2</sub> nanotubes, squaraine acceptor dye (SQ1) absorbed to TiO<sub>2</sub> nanotubes, and the fluorescence spectrum of DCM dissolved in pure Spiro-OMeTAD. There is an excellent overlap of DCM fluorescence and SQ1 absorbance. (b) Incident photoconversion efficiency (IPCE) of a cell employing DCM as donor, SQ1 as acceptor, and Spiro-OMeTAD as hole conductor on a 500–600 nm thick transparent TiO<sub>2</sub> nanotube array.

well-studied commercial products including organic light-emitting diodes (OLEDs) and polymer laser dyes.

In this issue, Zaban and co-workers demonstrate a new architecture in which quantum dots are incorporated inside the TiO<sub>2</sub> anode to act as donors, while an asymmetrical squaraine dye (SQ2) is anchored to the TiO<sub>2</sub> surface to act as an acceptor. In this device, FRET truly is the enabling mechanism. The quantum dots, having a low band gap core and high band gap shell, form quantum wells that are unable to donate an electron to TiO<sub>2</sub> and therefore fluoresce with high efficiency. Size tuning of the core enables the appropriate fluo-

rescence spectrum to be achieved, allowing a maximization of the overlap integral of donor fluorescence and acceptor absorbance. Being isolated from the electrolyte, the quantum dots do not suffer from excessive quenching, yet they are still close enough to the dye layer for energy transfer. Harnessing FRET is a solution to many of the problems that have previously hindered the use of quantum dots in DSSCs, including charge injection to TiO<sub>2</sub> and stability in the electrolyte. It is in fact a general technique that could be applied to quantum dots of many different materials coupled to any acceptor dye. In particular, the ease with which the fluorescence spectrum can be tuned

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makes it especially useful for providing a good match to an arbitrary acceptor dye. Additionally, the strong and broad absorption of quantum dots gives them the potential to cover the whole visible spectrum, making up for the shortcomings of IR dyes that may absorb weakly in the visible region.

#### FUTURE OF FRET FOR DSSCS

Future research in this area will focus on the development of donor–acceptor pairs. Of primary concern are maximization of spectral coverage, the maximization of energy transfer efficiency and minimization of quenching, and the development of new dyes that can push absorbance further into the IR region. Broader absorption may be realized by simply finding a donor with broad yet strong absorption, as is the case for the semiconductor nanoparticles mentioned above. In the case of molecular dyes, it may be necessary to employ three (or more) materials, such that the sum of the absorption of all three may provide complete coverage of the solar spectrum. Energy transfer would follow a cascade from the bluest absorber to the reddest. Of course, in this case, transfer efficiencies must be very high for benefits to be seen because of the multiplicative nature of transfer losses.

The problem of quenching could be solved by physical isolation, as in the case of capped quantum dots. A similar strategy might also apply to donor micelles in a liquid electrolyte that do not allow for contact between excited donor and electrolyte. A more fundamental approach may also be taken by adjusting HOMO/LUMO levels of the donor so that it cannot be quenched as easily by the electrolyte. The development of new dyes may be the most difficult piece of the puzzle, as there are few dyes currently available that offer strong IR absorption and efficient electron injection into TiO<sub>2</sub>. Pushing absorption out to 1000 nm will be difficult, but the gains to be made are obvious. Whatever the challenges, FRET offers an exciting opportunity to overcome many obstacles to efficiency improvements and may likely be a key process in future DSSCs.

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