

# Phosphorescent energy relay dye for improved light harvesting response in liquid dye-sensitized solar cells

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**Energy transfer from phosphorescent ruthenium complex N877 dissolved in the liquid electrolyte to the squaraine sensitizer SQ1 anchored on the titanium oxide surface resulted in a four fold increase in external quantum efficiency in the blue part of the visible spectrum despite complete quenching of the luminescence of N877 by the iodine in the electrolyte.**

The need to develop inexpensive renewable energy sources continues to stimulate new approaches for the production of efficient low-cost photovoltaic devices. In this respect, dye-sensitized solar cells (DSSCs) based on nanocrystalline semiconductors have been intensively studied due to their potential low-cost, easy processing and a high performance.<sup>1</sup>

The sensitizer is the key component in the DSSCs, harvesting the solar radiation and converting it to electric current. Over the last 17 years, ruthenium complexes have maintained a clear lead in performance amongst thousands of dyes that have been scrutinized. Their validated efficiency record under standard air mass 1.5 conditions stands presently at 11.1%.<sup>2</sup> Although high efficiency devices have an internal quantum efficiency of  $\sim 100\%$ ,<sup>3</sup> they have short circuit current densities,  $J_{sc}$ , of  $<20 \text{ mA cm}^{-2}$  because they do not absorb all of the photons from the visible and near infrared (NIR) domain. In

order to reach power conversion efficiencies above the state of the art, DSSCs must absorb  $>80\%$  of the light from 400–900 nm.

Therefore, the optimal sensitizer for solar cell applications should be panchromatic and absorb all the light from the visible to the near infrared (NIR) domain. Molecular engineering of ruthenium complexes that absorb from 400 to 900 nm for TiO<sub>2</sub>-based solar cells presents a challenging task as several requirements have to be fulfilled by the dye which are very difficult to meet simultaneously. The LUMO and HOMO have to be maintained at levels where photo-induced electron transfer in the TiO<sub>2</sub> conduction band and regeneration of the dye by iodide can take place at practically 100% yield. This restricts greatly the options available to accomplish the desired red-shift of the metal-to-ligand charge transfer transitions (MLCT) to about 900 nm. To overcome this issue, several strategies have been developed, e.g. co-sensitization,<sup>4</sup> utilizing scattered light,<sup>5</sup> and down and up conversion.<sup>6</sup>

One of these strategies, the use of Förster resonance energy transfer between energy donor molecules covalently attached to the sensitizing dye anchored on the TiO<sub>2</sub>, has been developed.<sup>7</sup> We recently demonstrated a new DSSC architecture where highly luminescent energy relay dyes (ERDs) dissolved inside the electrolyte absorb higher energy photons and transfer their energy to the sensitizing dye via Förster resonance energy transfer (FRET).<sup>8</sup> A highly fluorescent perylene derivative is used as ERD and it is noted that a short lifetime of excited state,  $\tau_0$ , is important for minimizing the luminescence quenching.

We report now the use of the system SQ1 as sensitizer and N877, a phosphorescent ruthenium complex, as the unattached ERD in a device based on liquid electrolyte (see molecular structures of dyes in Fig. 1). This system has been reported recently for its application in solid-state devices.<sup>9</sup> It should be noted that the system based on perylene<sup>8</sup> or another based on quantum dots as the energy relay dye, with a phthalocyanine sensitizing dye, do not work in solid-state

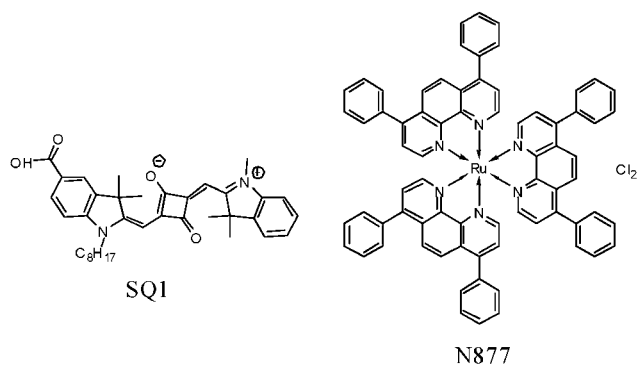
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## Broader context

Molecular engineering of sensitizers that absorb from 400 to 900 nm for TiO<sub>2</sub>-based solar cells presents a challenging task as several requirements have to be fulfilled by the dye which are very difficult to meet. Förster resonant energy transfer between unattached energy relay dye that is excited by higher energy (blue) photons to the sensitizing dye, which absorbs in the near IR region, is an interesting approach for panchromatic response. Here we present a study of energy transfer from a highly phosphorescent ruthenium complex dissolved in the liquid electrolyte to the squaraine sensitizer (SQ1) anchored on the titanium oxide surface resulting in a four fold increase in external quantum efficiency in the blue part of the visible spectrum despite complete quenching of the luminescence of the ruthenium complex by the iodine in the electrolyte. Therefore, the judicious choice of highly phosphorescent energy relay dyes that are not greatly quenched by the electrolyte with complementary absorption spectra to tailor light absorption inside the device in the blue has the potential to improve dye-sensitized solar cell efficiency significantly.

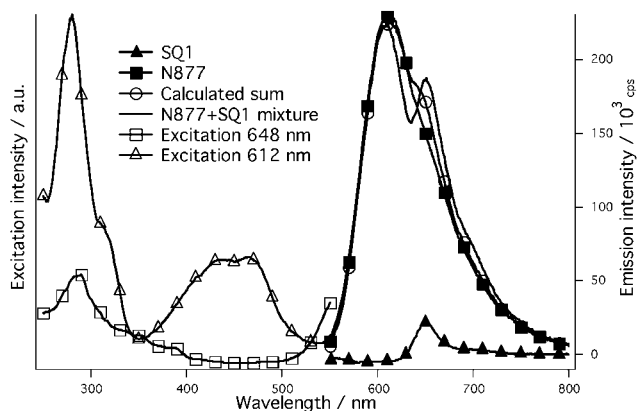


**Fig. 1** Molecular structures of the sensitizer **SQ1** and the energy relay dye **N877**.

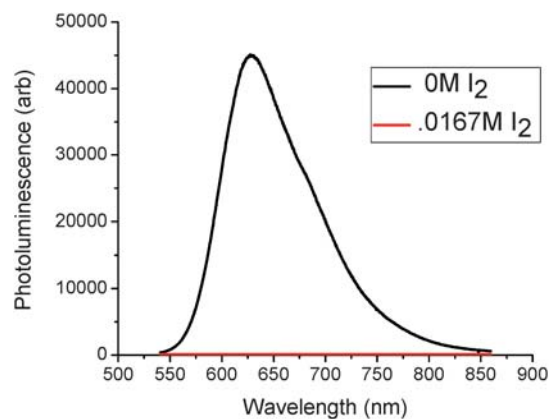
cells.<sup>10</sup> To shed light on the reasons of such a failure, obtaining a successful sensitizer/ERD system both with solid-state and liquid electrolyte is appealing. To our surprise, despite the complete quenching of **N877** emission by iodine and an excited state lifetime three orders of magnitude longer than the perylene ERD, the system **SQ1/N877** leads to improved device efficiency due to increase of blue photon harvesting.

**SQ1** solution in ethanol shows an absorption maximum at 636 nm with a high molar extinction coefficient ( $\epsilon = 158\,500\text{ M}^{-1}\text{ cm}^{-1}$ ).<sup>11</sup> The absorption matches the emission of **N877** (broad emission with a maximum at 612 nm).<sup>12</sup> On the other hand, **N877** shows broad absorption between 400 and 500 nm, with maximum at 460 nm of  $33\,000\text{ M}^{-1}\text{ cm}^{-1}$ , where **SQ1** does not absorb. Fig. 2 shows emission spectra of **SQ1** ( $10^{-6}\text{ M}$  EtOH solution), of **N877** ( $10^{-5}\text{ M}$  EtOH solution), and of a mixture in ethanol containing **SQ1** and **N877** at  $10^{-6}\text{ M}$  and  $10^{-5}\text{ M}$  respectively. The calculated sum of the **SQ1** and of the **N877** emission spectra does not match the emission observed from the mixture of **SQ1** and **N877**, in particular the peak corresponding to the squaraine emission maximum is more intense. In addition when the excitation spectrum is measured while following this emission maximum (648 nm), no signal corresponding to **N877** is observed, pointing to efficient FRET.

In the presence of hole transporting material Spiro-MeOTAD, the luminescence of **N877** is significantly quenched.<sup>9</sup> In the liquid cell, the iodine species play the role of hole transporting material. Iodide and triiodide are highly mobile ions that have a near unity probability of



**Fig. 2** **SQ1** ( $10^{-6}\text{ M}$  in EtOH,  $\lambda_{\text{ex}} = 450\text{ nm}$ ), **N877** ( $10^{-5}\text{ M}$  in EtOH,  $\lambda_{\text{ex}} = 450\text{ nm}$ ), calculated sum, and **SQ1** + **N877** mixture ( $10^{-6}\text{ M}$  and  $10^{-5}\text{ M}$  respectively in EtOH) emission spectra.

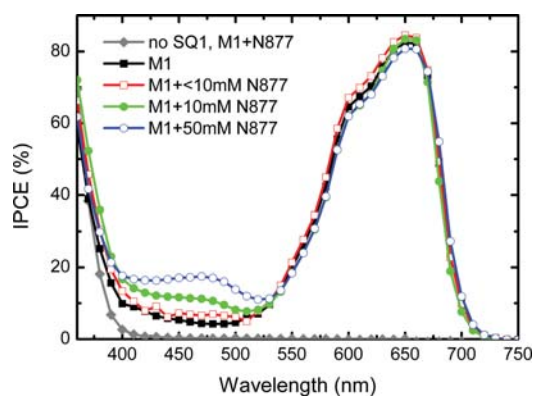


**Fig. 3** **N877** ( $10^{-4}\text{ M}$ ) photoluminescence spectrum without  $\text{I}_2$  and with  $0.0167\text{ M}$   $\text{I}_2$ .

quenching the excited state when they collide with a chromophore. Fig. 3 shows that the phosphorescence of **N877** is almost completely quenched by iodine, already at a concentration much lower than what is present in the electrolyte used for the cell, which is  $0.05\text{ M}$ . A low estimate of the quenching efficiency of the phosphorescence of **N877** by iodine leads to an observed  $>3000$  times reduction of emission intensity.

For the solar cell fabrication, a  $6\text{ }\mu\text{m}$  thick transparent mesoporous  $\text{TiO}_2$  was prepared and treated with a  $40\text{ mM}$  titanium tetrachloride solution using a previously reported procedure.<sup>13</sup> A scattering layer was not incorporated in order to look into the effect of energy transfer from **N877**. The films were heated at  $500\text{ }^\circ\text{C}$  in air and calcined for 30 min before use. **SQ1** solutions were prepared in ethanol at a concentration of  $0.10\text{ mM}$ . The films were immersed into the dye solution for 4 h at room temperature and then they were rinsed with acetonitrile to remove any un-adsorbed dye and used as such for photovoltaic measurements in completely sealed devices. Fig. 4 shows the incident monochromatic photon-to-current conversion efficiency (IPCE) for **SQ1** sensitized solar cells as a function of **N877** concentration in the electrolyte. The IPCE at the maximum absorption wavelength reaches above 83% conversion efficiency in **SQ1** sensitized solar cells. Upon adding **N877**, a new IPCE peak proving new electron injection by photons was generated and reached up to 17% at 470 nm, which is coincident with the absorption peak of **N877**. This photo-generated electron could be caused by direct injection from **N877** to  $\text{TiO}_2$ . However, **N877** doesn't have any anchoring groups by which photo-generated electrons can transfer to  $\text{TiO}_2$ . So, we can speculate that the direct electron injection from **N877** is very unlikely. In addition, if direct electron injection from **N877** was indeed happening, the IPCE of the device without **SQ1** should show the peak between 400 and 550 nm, which corresponds to the absorption spectral region of **N877**. The gray line in Fig. 4 is the IPCE of DSSCs without **SQ1** but incorporating **N877** in the electrolyte, and it shows no photo-generated electrons from visible photons. Therefore, the direct electron injection from **N877** is not possible and the new IPCE from 400 nm to 530 nm is definitely caused by energy transfer which results from **SQ1** absorbing additional photons due to photoluminescence of **N877**. Table 1 shows the photovoltaic performance with various concentrations of **N877**.

The **SQ1** sensitized solar cell shows a good efficiency under solar simulated light irradiation ( $100\text{ mW cm}^{-2}$  1.5 AM Global) of 3.51% with an  $J_{\text{sc}}$  of  $7.48 \pm 0.1\text{ mA cm}^{-2}$ , an open-circuit voltage ( $V_{\text{oc}}$ ) of

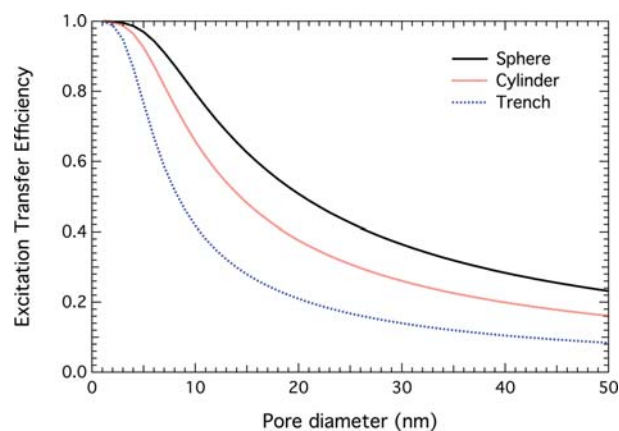


**Fig. 4** IPCE spectrum (top) of **SQ1** sensitized solar cell based on volatile electrolyte (active area of 0.2 cm<sup>2</sup>). The redox electrolyte was **M1** composed of 0.6 M 1-butyl-3-methyl-*N*-butylimidazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.5 M tertiary butylpyridine in a 15/85 (v/v) mixture of valeronitrile and acetonitrile with various concentrations of **N877**.

638.5 ± 10 mV, and a fill factor (FF) of 0.73 ± 0.01. As a result of **N877**,  $J_{sc}$  was enhanced due to additional photon to electron conversion from **N877** to **SQ1**. When 10 mM of **N877** was added in the electrolyte,  $J_{sc}$  increased to 7.98 mA cm<sup>-2</sup>. With a higher concentration, 50 mM of **N877** in the electrolyte,  $J_{sc}$  is almost saturated without any further increase. This is presumably caused by filtering photons of **N877** being transferred to **SQ1** because IPCE at 650 nm decreased to 80% and further decrease was obtained with higher concentrations of **N877**. Indeed at high loading, the low-energy absorption tail of **N877** ultimately decreases the number of red photons available for **SQ1**. The excitation transfer efficiency, (ETE),<sup>8</sup> is the fraction of excited unattached chromophores (*i.e.* **N877** dyes) that transfer their energy to the sensitizing dye (*i.e.* **SQ1**). Fig. 4 shows a peak EQE of 17% with a 50 mM concentration of **N877** and ~8% EQE with just the sensitizing dye, giving a  $\Delta$ EQE = 9%. For a film thickness of 6  $\mu$ m, porosity of 0.60, and a peak molar extinction coefficient of 33 000 M<sup>-1</sup> cm<sup>-1</sup> of **N877**, the light harvesting yield is estimated to be 79% at peak wavelength. Assuming that the internal quantum efficiency (IQE) of **SQ1** is 83% at the maximum absorption wavelength, the ETE is 14%. It should be noted that the internal quantum efficiency (IQE) is estimated to be the same as the EQE. The excitation transfer efficiency is fairly high considering how greatly quenched it is by the electrolyte. However, the ETE is lower than half of 32% based on SpiroMeOTAD,<sup>9</sup> which confirms that one of the most important parameters in this new DSSC architecture is the quenching rate of ERDs by the electrolyte. No matter how strongly the PL of **N877** with liquid electrolyte is quenched, the system **SQ1/N877** was confirmed to work well in both liquid and solid electrolytes. The FRET rate is strongly dependent upon the distance between ERD and sensitizer. Fig. 5 shows a predictable ETE as function of pore size for spherical, cylindrical, and trench geometries. This plot

**Table 1**  $J$   $V^{-1}$  characteristics of **SQ1** sensitized solar cell based on **M1** + **N877** volatile electrolyte

<b>N877</b> concentration	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF (%)	Efficiency (%)
0 mM	7.48	638.54	0.73	3.51
< 10 mM	7.75	638.96	0.73	3.60
10 mM	7.98	638.22	0.72	3.67
50 mM	7.87	635.74	0.74	3.67



**Fig. 5** Modelled average excitation transfer efficiency as a function of pore diameter for spherical, cylindrical, and trench pores.

takes into account 6.0 nm FRET  $R_0$ , a quenching rate of 3000 times, and dye coverage of 0.39 dye nm<sup>-2</sup>. The dye molecules within 15 nm of the wall have a > 60% chance of transferring FRET energy. Given a homogenous distribution of dye molecules in 30 nm pores, there is a > 40% chance for ETE. If the ERD is present in the proximity of the sensitized TiO<sub>2</sub> surface, the FRET will occur at a faster rate than the quenching. This plausibly explains that our system is working in both solid and liquid electrolytes. A more detailed study about the FRET mechanism in DSC is currently under way.

In conclusion, we have demonstrated the use of phosphorescent energy relay dye in DSSC based on liquid electrolytes. **SQ1** sensitized solar cells with **N877** yields 83% of IPCE at 650 nm and 17% of IPCE at 470 nm caused by direct electron injection from **SQ1** by incoming photons and energy transfer from **N877**, respectively. This makes the system **SQ1/N877** the first sensitizer/ERD pair to be successful with both solid and liquid electrolyte. Despite photoluminescence being completely quenched by iodine and excited state lifetime being in the microsecond range, **N877** turns out to be a good ERD. This shows that those photophysical parameters are important for the high impact of the energy transfer approach to the device efficiency, but not fundamental to the occurrence of the process. Careful attention to redox properties of the ERD is believed to be a key issue as photoinduced charge transfer will be detrimental to the energy transfer performances. ERDs are now optimized along these lines of reasoning.

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