

Supporting information for:

Surface energy relay between cosensitizer molecules in solid-state dye-sensitised solar cells: co-operative optical and electronic enhancements

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SI Contents:

- S1. Solar Cell Fabrication and Characterisation
- S2. Time-correlated single-photon counting (TCSPC) measurements
- S3. Chemical structure of dye molecules
- S4. TiO₂ PL decays
- S5. Förster Resonant Energy Transfer Calculations

S1. Solar Cell Fabrication and Characterisation

A fluorine-doped tin oxide (FTO) coated glass substrate was partially etched by oxidation of zinc powder in the presence of hydrochloric acid, extant debris was cleaned with soap, acetone and ethanol and finally cleared by oxygen plasma etching for ten minutes. A compact layer of TiO₂ was created by spray pyrolysis deposition at 450 degrees. The mesoporous layers TiO₂ were deposited by doctor blade coating using Dysol 18NRT paste diluted to 1/3 concentration with ethanol. These films were subsequently sintered to 500 degrees for 30 minutes in air to burn out the organic components and form mesoporous structure of ~1.4µm thickness. The cells were then re-sintered to 500 degrees for 45 minutes after being treated with titanium tetrachloride solution (20mM) at 70°C for 60 minutes. Once cooled to 70 degrees the cells were immersed in D102¹ (1mM in a 1:1 mix of tert-butanol and acetonitrile) and/or TT1² (50µM TT1, 0.5 mM Chenodeoxycholic acid in ethanol) for varying periods of time and rinsed in ACN before the application of 2,2', 7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-OMeTAD) in chlorobenzene solution containing Li-TFSI and TBP additives by spin coating³. 150 nm thick silver electrodes were then thermally evaporated onto the active surface of the SDSCs. The active area of the solar cells was ~ 0.12 cm² defined by the overlap of the FTO and Ag electrodes. The cells were illuminated by a 150W ABET Technologies Sun 2000 Class AAB Solar Simulator and measured using a Keithley 2400 Sourcemeter run by a National Instruments LabView program. The solar simulator was calibrated against monocrystalline silicon S1133B KG5 filtered, calibrated reference cell. IPCE measurements were taken illuminated by a Newport 66902 Xenon Lamp linked to an Princeton Instruments ACTON SP2150 monochromator and Keithley 2636 controlled by a National Instruments LabView program. The current density results were calibrated against a reference Si diode with a known spectral response which allowed the calculation of the incident photon-to-electron conversion efficiency for the tested cells. The absorption of the devices was measured using a UV-Visible Spectrophotometer with an integrating sphere accessory (Varian, Cary 300 spectrophotometer).

S2. Time-correlated single-photon counting (TCSPC) measurements

Time-correlated single photon counting was used to measure the photoluminescence from the samples as a function of time after excitation. An excitation pulse with a centre wavelength of 400nm (100fs duration), a fluence of 1.25pJ/pulse and a spot diameter of approximately 50µm was used; the excitation and detection polarisation were parallel throughout. The photoluminescence lifetime was measured using a monochromator attached to a photomultiplier tube, and the instrument response time is approximately 120ps at visible wavelengths. The measured lifetimes were deconvoluted using an instrument response function derived from the scattered excitation pulse.⁴

S3. Chemical structure of dye molecules

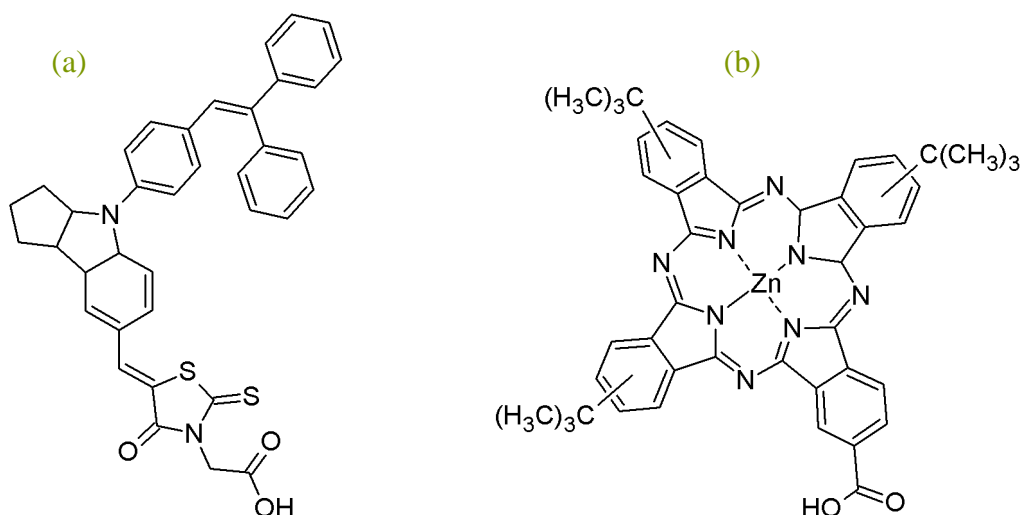


Figure S1 shows the chemical structure of (a) D102¹ and (b) TT1⁵.

S4. TiO₂ PL decays

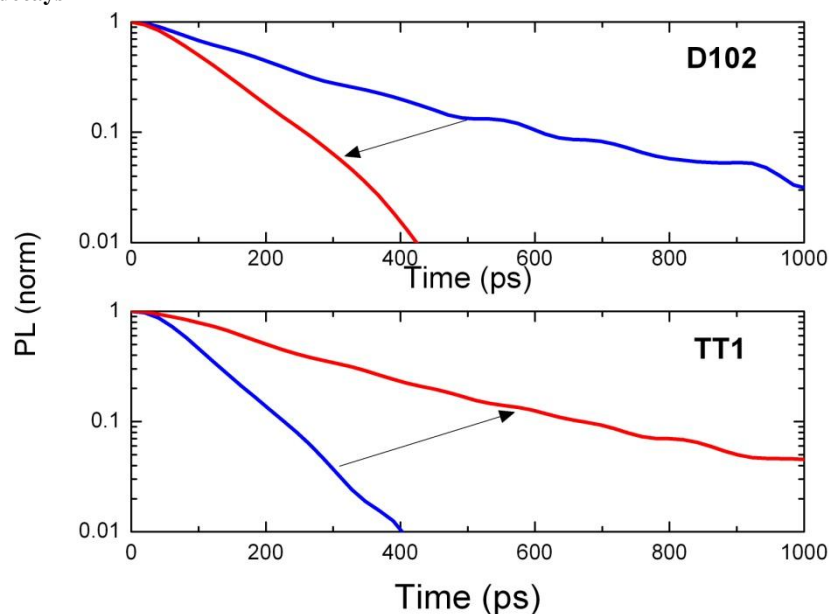


Figure S2. Time-resolved photoluminescence from D102 at 650nm (top) and TT1 at 705nm (bottom) is shown for the case of monosensitized (blue line) and cosensitized (red line) mesoporous TiO₂ films. The arrows show the trend upon cosensitization.

S5. Förster Resonant Energy Transfer Calculations

The FRET radius equation, defining the distance at which the probability of FRET occurring is precisely 50%:⁶

$$R_0^6 = \frac{9000 (\ln 10) \kappa^2 \phi_d}{128\pi^5 N_A n^4} \int_0^\infty F_d(\lambda) \epsilon_a(\lambda) \lambda^4 d\lambda$$

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 normalised fluorescence profile of the donor and ϵ_a is the molar extinction profile of the acceptor molecule.

From the FRET radius, the measured natural fluorescence decay of the donor (k_{fluor}) and an estimation of the inter-dye separation, the rate of energy transfer, and subsequently energy transfer efficiency, can be found:

$$k_{ET} = k_{fluor} \frac{R_0}{r}^6$$

$$\eta_{fret} = \frac{k_{ET}}{k_{ET} + k_{inj}}$$

From the TCSPC study the energy transfer rate and efficiency could also be derived empirically. The TCSPC analysis indicates a k_{ET} of $4.8 \times 10^{10} \text{ s}^{-1}$ and a k_{inj} of $4.5 \times 10^{10} \text{ s}^{-1}$. This suggests a FRET efficiency of ~43%. Using the measured k_{inj} and a k_{ET} of $7 \times 10^{10} \text{ s}^{-1}$ (estimated from the previous equations), the η_{fret} is found theoretically to be ~52%.

A degree of error in the FRET radius calculation derives from the estimated quantum yield of D102 and it must also be noted that the spatial extent of the dye molecules themselves will also contribute to some inaccuracy of this simple model from a real system. As such, it should be stressed that this is a fairly rough estimate and should not be taken verbatim, but as a guideline in lieu of more comprehensive modelling and calculation.

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² Cid, J.-J.; Garcia-Inglesias, M.; Yum, J.-H.; Forneli, A.; Albero, J.; Martinez-Ferrero, E.; Vazquez, P.; Grätzel, M.; Nazeeruddin, M. K.; Palomares, E.; Torres, T. *Chem. Eur. J.* **2009**, *15*, 5130-5137

³ Snaith, H. J.; Humphry-Baker, R.; Chen, P.; Cesar, I.; Zakeeruddin, S. M.; Grätzel, M. *Nanotechnology* **2008**, *19*, 424003

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⁶ Förster, T., *Ann. Phys.* **1948**, *437* (1-2), 55-75.