Supplementary Information for 'Highly Soluble Energy Relay Dyes for Dye-Sensitized

Solar Cells'

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Dye Synthesis and Characterization



Synthesis of 1: A mixture of 2-tert-butyl-6-methyl-4H-pyran-4-one (1.16 g, 7.00 mmol) and malononitrile (0.56g, 8.5 mmol) in 5 mL of acetic anhydride was stirred and heated to 120 °C for 12 h under nitrogen atmosphere. The reaction mixture was then quenched by deionized water and the solution was extracted with chloroform. The organic layer was washed with brine solution followed by drying over anhydrous MgSO₄. Recrystallization from ethanol gave the product as peachy fibrous solid. Yield: 97% (1.45 g). ¹H NMR (CDCl₃, 400 MHz, [ppm]): δ 6.56 (s, 1H), 6.55 (s, 1H), 2.34 (s, 3H), 1.30 (s, 9H); GC-MS: m/z 214, calcd 214.11.

Synthesis of **BL302**:¹ A mixture of **1** (0.3 g, 1.40 mmol), diethylaminobenzaldehyde (0.248 g, 1.40 mmol), and piperidine (0.20 mL, 2.00 mmol) was placed in a flask containing dry acetonitrile (10 mL) under nitrogen atmosphere. The mixture was heated to reflux for 24 hours. After cooling, the reaction was quenched by water and was extracted with dichloromethane. The combined organic layer was dried over anhydrous MgSO₄ and evaporated under vacuum. The mixture was purified by silica gel column chromatograph with dichloromethane as eluent. 0.335 g of the neon red solid of product was collected (64% yield). ¹H NMR (CDCl₃, 400 MHz, [ppm]): δ 7.42 (d, 2H, *J* = 8.99 Hz), 7.35 (d, 1H, *J* = 15.83 Hz), 6.67 (d, 2H, *J* = 8.99 Hz), 6.58 (d, 1H, *J* = 2.08 Hz), 6.51 (d, 1H, *J* = 2.08 Hz), 6.48 (d, 2H, *J* = 15.83 Hz), 3.45 (m, 4H), 1.37 (s, 9H), 1.23 (m, 6H); LC-MS: m/z 374.2250,

calcd 373.22. Anal. Calcd for C₂₄H₂₇N₃O: C, 77.18; H, 7.29; N, 11.25. Found: C, 77.6; H, 7.49; N, 11.24.



Synthesis of **2**:² A mixture of 4-bromoaniline (5.15 g, 30 mmol), 2-bromoethyl ethyl ether (7.67 g, 68 mmol), K₂CO₃ (9.4 g, 68 mmol) and KI (0.63 g, 3.8 mmol) was placed in a flask containing butanol (20 mL) under nitrogen atmosphere, and the mixture was stirred under nitrogen at 120 °C for 6 d. The reaction was cooled to room temperature and filtered through Celite® and the residue was washed with IPA. The filtrate was concentrated under reduced pressure and the remaining oil was heated with acetic anhydride (1.5 mL) in butanol (15 mL) at 120 °C for 15 min (the mono alkylated by-product reacted to give the acetylated product.) The reaction was cooled to room temperature and filtered through Celite® and the residue was concentrated under reduced pressure and the residue to room temperature and filtered through Celite® and the residue washed with IPA. The filtrate was concentrated under reduced product.) The reaction was cooled to room temperature and filtered through Celite® and the residue washed with IPA. The filtrate was concentrated under reduced pressure and crude oil was purified by silica gel column chromatograph with hexane:ethyl acetate (4:1) as the eluent. The desired product was obtained as a slightly yellow viscous oil (8.145 g, 85%). ¹H NMR (CDCl₃, 400 MHz, [ppm]): δ 7.26 (d, 2H, *J* = 9.12 Hz), 6.60 (d, 2H, *J* = 9.12 Hz), 3.57 (m, 8H), 3.49 (m, 4H), 1.19 (t, 6H, *J* = 14.02 Hz); GC-MS: m/z 315, calcd 315.08.

Synthesis of **3**: A 25 ml flask was charged with **2** (2.05 g, 6.5 mmol), 2-thiophene boronic acid (0.90 g, 7 mmol), Pd(PPh₃)₄ (0.15 g, 0.13 mmol) and toluene (10 mL), and degassed with nitrogen for 15 min. 3.3 mL of 3M K₂CO₃ was added, and reaction mixture was heated at 90 °C for 24 h and then cooled down at room temperature and quenched with 2M HCl. The

product was extracted with dichloromethane and the combined organic layers were washed with plenty of water. The organic extracts were then dried over anhydrous MgSO₄, evaporated and purified with column chromatography on silica gel with hexane:ethyl acetate (95:5) as the eluant to give yellow viscous oil. Yield: 88% (1.82 g). ¹H NMR (CDCl₃, 400 MHz, [ppm]): δ 7.47 (d, 2H, *J* = 8.99 Hz), 7.13 (t, 2H, *J* = 10.70 Hz), 7.03 (dd, 1H, *J* = 8.89 Hz), 6.72 (d, 2H, *J* = 8.99 Hz), 3.60 (s, 8H), 3.53 (dd, 4H), 1.20 (t, 6H, *J* = 14.03 Hz); GC-MS: m/z 319.2, calcd 319.16.

Synthesis of **4**: 0.17 mL (1.85 mmol) of phosphorus oxychloride (POCl₃) was added to N,N-dimethylformamide at 0 °C, and the solution was stirred for 30 min. **3** (0.50 g, 1.57 mmol) in 10 mL of dichloroethane was added to the above solution and stirred at 80 °C for 3 h. After cooling to room temperature, 1 M sodium hydroxide was added and the mixture was stirred vigorously for 1 h for neutralization. The solution was extracted with dichloromethane, and the combined organic extracts were washed with brine and dried over MgSO₄. After removal of the solvents under reduced pressure, the residue was purified by flash column chromatography with dichloromethane to give yellow viscous oil. Yield: 74% (0.405 g). ¹H NMR (CDCl₃, 400 MHz, [ppm]): δ 9.81 (s, 1H), 7.68 (d, 1H, *J* = 3.93 Hz), 7.54 (d, 2H, *J* = 8.82 Hz), 7.23 (d, 1H, *J* = 3.93 Hz), 6.74 (d, 2H, *J* = 8.82 Hz), 3.61 (s, 8H), 3.53 (dd, 4H, *J* = 20.93 Hz), 1.20 (t, 6H, *J* = 14.04 Hz); GC-MS: m/z 347, calcd 347.16.

Synthesis of **BL315**: A mixture of **1** (0.25 g, 1.17 mmol), **4** (0.40 g, 1.16 mmol), and piperidine (0.17 mL, 1.70 mmol) was placed in a flask containing dry acetonitrile (10 mL) under nitrogen atmosphere. The mixture was heated to reflux for 24 hours. After cooling, the reaction was quenched by pouring water and it was extracted with dichloromethane. The combined organic layer was dried over anhydrous MgSO₄ and evaporated under vacuum. The mixture was purified by silica gel column chromatograph with dichloromethane as eluent. The clay red solid of product was then collected (0.469 g, 74% yield). ¹H NMR (CDCl₃, 400 MHz, [ppm]): δ 7.49 (m, 3H), 7.19 (d, 1H, *J* = 3.89 Hz), 7.13 (d, 1H, *J* = 3.89 Hz), 6.75 (d, 2H, *J* = 8.92 Hz), 6.61 (d, 1H, *J* = 1.99 Hz), 6.52 (d, 1H, *J* = 1.99 Hz), 6.43 (d, 1H *J* = 15.38 Hz), 3.61 (s, 8H), 3.53 (dd, 4H, *J* = 20.78 Hz), 1.37 (s, 9H), 1.22 (t, 6H, *J* = 14.15 Hz); LC-MS: m/z 544.2383, calcd 543.26. Anal. Calcd for C₃₂H₃₇N₃O₃S: C, 70.69; H, 6.86; N, 7.73; S, 5.90. Found: C, 70.43; H, 7.01; N, 7.67; S, 6.06.



Fig. S1. ¹HNMR spectrum of **BL302**.



Fig. S2. ¹HNMR spectrum of **BL315**.



Fig. S3. Absorption and emission spectra of DCM (black), BL302 (red), and BL315 (blue) dyes in CH_2Cl_2 (c = 10^{-5} M).



Fig. S4. Cyclic Voltammogram of BL302 (red), and BL315 (blue) dyes. From the curves, it was found that $HOMO_{BL302}=5.12$ eV, $LUMO_{BL302}=3.07$ eV, $HOMO_{BL315}=5.05$ eV, $LUMO_{BL302}=3.23$ eV.

Calculation of FRET Radius

The FRET Radius, R₀, between two chromophores is given by

$$R_o^6 = \frac{9000 \cdot \ln(10) \kappa^2 Q_{\rm D}}{128 \cdot \pi^5 n^4 N_{\rm A}} \int F_{\rm D}(\lambda) \varepsilon_{\rm A}(\lambda) \lambda^4 \,\mathrm{d}\lambda$$

Where κ^2 is a geometrical factor (taken to be 2/3 for random orientations), Q_D is the PL quantum efficiency, n is the refractive index of the medium (~1.5 for benzonitrile), N_A is Avogadro's number, $F_D(\lambda)$ is the normalized emission profile of the donor and $\varepsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor. It is known from literature that Q_D for DCM is 0.43 in methanol,³ and due to the difficulty of accurately measuring photoluminescence quantum yield is assumed to be the same in acetonitrile. From our steady state PL measurements, the emission of BL302 in benzonitrile is actually slightly higher than DCM in acetonitrile (Fig. S5). Thus it is suspected that the emission quantum yield of BL302 in benzonitrile may be actually higher than 0.43 – if the ratio of the peak heights is indicative of the quantum yield, Q_D for BL302 in benzonitrile is approximately 0.49.



Fig. S5. Relative PL emission of 1 mM DCM in acetonitrile and benzonitrile and 1 mM BL302 in benzonitrile excited at 514 nm by an argon ion laser.

Fig. S6 shows the relative emission spectra of BL302 and BL315. From the areas under the curves, the PL efficiency for BL315 can be estimated. If BL302 is assumed to have a PL efficiency of approximately 0.49, this method results in a PL efficiency of approximately 0.28 for BL315 in benzonitrile.



Fig. S6. a) Relative PL emission of 1 mM BL315 and 1 mM BL302 in benzonitrile excited at 514 nm by an Ar laser. b) Normalized absorption of TT1. Molar extinction coefficient of TT1 at peak is 191500 M⁻¹cm⁻¹.

Using the estimated PL efficiencies and spectra in conjunction with the absorption spectrum of TT1 in solution, the FRET radius can be calculated for BL302 and BL315 to TT1, resulting in values of 5.84 nm and 4.92 nm, respectively. Once again, these values are only

estimates, as the true PL efficiency is difficult to measure, but an error of even 100% in some of the factors (such as PL efficiency) doesn't greatly alter the FRET radius, which goes as $Q_d^{1/6}$. Hence we only cite FRET radii to one significant digit.

Measurement of Dye Absorptance

To calculate the amount transmitted through the FTO during device operation, the absorptance of the FTO was measured using an integrating sphere to account for reflections and scattering. This allowed for measurement of the absorptance (ABS) of the FTO at 520 nm (~5%). The total transmission through the FTO is given by 1-ABS-R, where R is the reflection off the glass front contact (~4%). This gives our measurement of transmission through the FTO electrode as 91%. Directly measuring transmission through the FTO electrode is also possible, but it should be considered that transmission through the electrode creates 2 reflections (front and back) at air-glass and FTO-air interfaces, while during device operation, the refractive index of the electrolyte matches the index of the FTO relatively well – leading to little reflection at this surface.



Fig. S7. Absorptance of FTO as measured with an integrating sphere to account for scattering and reflection.

Measurement of IQE_{SD}

By measuring the transmission through a FTO substrate and subtracting the transmission through a TT1-sensitized film, the dye absorptance, or ABS_{SD} can be calculated (Fig. S8). The TT1 sensitized film was obtained by breaking open the DSSC device and measuring the actual used substrate, to ensure any device fabrication variation did not cause any errors. The peak absorptance is slightly blue-shifted from the EQE peak, presumably due to solvation effects of the electrolyte. In order to measure the IQE of the sensitizing dye, given by,

$$IQE_{SD} = \frac{EQE_{SD}}{ABS_{SD}},$$

the peak EQE is divided by the peak absorptance, ignoring any spectral shifts caused by the electrolyte. This resulted in IQEs for the TT1 dye in the range of 0.82-0.85.



Fig. S8. EQE of TT1 Device with 180 mM BL302 and difference between transmission of TT1 sensitized substrate and FTO substrate (which is the sensitizing dye absorptance).

Dynamic Quenching Rates and Theoretical ETE

A theoretical investigation of the energy transfer efficiency of ERDs has been previously published.⁴ The ETE depends on the ratio of so-called critical radius R_C and the pore radius, with the numerically calculated dependence given in Ref. 4. The critical radius is given by

$$R_c = \left(\frac{R_0^6 C_A}{Q}\right)^{1/4}$$

where R_0 is the FRET radius, C_A is the sensitizing dye surface coverage (in units of length⁻²), and Q is the dynamic quenching factor (ie. if the PL is quenched by a factor of 2, then Q=2). R_0 was previously determined previously to be approximately 6 nm for BL302, and C_A can be estimated to be approximately 1 nm⁻². The dynamic quenching factor, Q, comes from two sources: dynamic concentration quenching and dynamic electrolyte quenching (Fig. S9). Multiplying the quenching rate from having 180 mM concentration of BL302 and the effects of 100% electrolyte concentration gets a final Q value of 6.9 for BL302. This gives a critical radius, R_C , of 9.1 nm.



Fig. S9. a) Dynamic quenching of BL302 dye in 85:15 benzonitrile:valeronitrile mixture as measured by time-resolved photoluminescence. τ is the Fluorescence lifetime and τ_0 is the fluorescence lifetime at 0 electrolyte concentration. b) Dynamic quenching of BL302 due to high concentrations of dye in benzonitrile solvent. Here, τ is the fluorescence lifetime and τ_0 is the fluorescence lifetime at 1 mM dye concentration.

ETE Loss by desorbed dyes

If a sensitizing dye desorbs from the TiO_2 , energy relay dyes can FRET to the desorbed dye, resulting in lost photocurrent. To model the energy loss, a desorbed dye was placed a distance x from the center of a 17nm pore (Fig S10). The ERD's can be considered to be homogenously distributed in order to calculate the average energy transfer efficiency to the desorbed dye.



Fig. S10. Schematic diagram of desorbed dye a distance x from the center of a spherical sensitizing-dye-lined pore.

Consider a volume element, dV, of ERD at position (x_1,y_1,z_1) , the rate of energy transfer from that dye element to the desorbed dye is given by

$$k_{FRET,dd}(\mathbf{x}_1, \mathbf{y}_1, \mathbf{z}_1) = \frac{1}{\tau_{PL}} \frac{R_{FRET}^6}{((x_1 - x)^2 + y_1^2 + z_1^2)^3}$$

where R_{FRET} is the calculated FRET radius, and τ_{PL} is the photoluminescence lifetime. The FRET rate of the same ERD volume element to the SD's on the surface is given by

$$k_{FRET,sd}(\mathbf{x}_1, \mathbf{y}_1, \mathbf{z}_1) = \iint \frac{1}{\tau_{PL}} \frac{R_{FRET}^6 C_{SD} dS}{((x-d)^2 + y^2 + z^2)^3}$$

Where C_{SD} is the surface coverage of sensitizing dye, dS is the surface area element of the pore, S is the pore surface and $d = \sqrt{x_1^2 + y_1^2 + z_1^2}$ is the distance of the ERD volume element from the center of the pore. In spherical coordinates, $x = rsin(\theta)cos(\varphi)$, $y = rsin(\theta)sin(\varphi)$ and $z = rcos(\theta)$, and the surface area element is given by $dS = r^2sin(\theta)d\theta d\varphi$ (where r is simply the pore radius). Substituting and integrating θ from 0 to π and φ from 0 to 2π gives the relative FRET rate of the ERD volume element to the surface. From here, we can integrate the relative energy transfer rates over the volume of the pore to find what percentage of the ERDs in the pore energy transfer to the desorbed dye, ERD_{Loss},

$$ERD_{Loss}(x) = \frac{1}{V} \int \frac{k_{FRET,dd}(\mathbf{r},\varphi,\theta)}{k_{FRET,sd}(\mathbf{r},\varphi,\theta) + k_{FRET,dd}(\mathbf{r},\varphi,\theta)} dV$$

It should be noted that exact knowledge of R_{FRET} and τ_{PL} is not necessary to calculate to losses due to desorbed dyes, as these cancel in the calculation of ERD_{Loss} above. The percentage of ERD excitation lost, as a function of the distance of the desorbed dye from the pore center, x, is shown in Fig. S11.



Fig. S11. Fraction of ERD excitation lost as a function of the distance of the desorbed dye from the center of the pore for a 17nm diameter pore with 1 sensitizing dye per nm^2 surface coverage. When the dye is near the center, the r^6 nature of the FRET interaction causes a large amount of ERDs in its vicinity to preferentially FRET to the desorbed sensitizer.

As can be seen in Fig. S11, the percent of excited ERD energy that is transferred to the desorbed dye varies from 3.4% in the center of the pore down to approximately 0.1% for a dye near the surface. Under the assumptions that desorbed dyes will be homogenously distributed other than the outside 2nm of the pore (since dyes on the surface take up physical volume) the ETE loss can be averaged over the volume to get an average ETE loss of approximately 1.75%. If two dyes are desorbed, then the total ETE loss would be slightly less than twice 1.75%, and would require calculation of the FRET rates for both dyes and the surface. With many dyes, this calculation because relatively intractable fairly quickly, and a monte carlo simulation would be the easiest approach to estimating the ETE loss. However, for only a few dyes, a reasonable estimate of the ETE loss is simply the number of dyes times the average loss for one dye, as the dyes are unlikely to be in the same neighborhood of eachother. Thus for 2.03 desorbed dyes per pore, a reasonable estimate of the ETE loss is 2.03*1.75%=3.6%.

Comparison of Dynamic and Static Quenching

As discussed in the main text, time-resolved and steady-state PL quenching measurements can be used to differentiate between static and dynamic quenching. While the electrolyte causes both dynamic collisional quenching and static quenching in the case of BL302, there is no such static quenching in the case of DCM in either acetonitrile or benzonitrile electrolytes, as shown in Fig. S12. Since the steady-state and time-resolved quenching measurements show that the PL lifetime is decreased by the same amount as the overall steady-state PL signal, the only quenching that occurs in the DCM-electrolyte system is dynamic quenching.



Fig. S12. a) Comparison of time-resolved and steady-state quenching of 5 mM DCM in acetonitrile electrolyte. b) Comparison of time-resolved and steady-state quenching of 8.5 mM DCM in benzonitrile electrolyte.

BL302 Dynamic and Static Concentration Quenching

High concentrations of ERD can also cause both static and dynamic photoluminescence quenching. Just as previously, the time-resolved and steady-state quenching can be compared to deconvolute the amount of static and dynamic quenching, as shown in Fig. S13. The decrease in steadystate PL quenching is the same as the decrease in the PL lifetime until 60 mM. However, at 180 mM, the steady-state PL is quenched by a factor of 5.6, while the time-resolved PL goes down by only a factor of 3.3. This means that significant number (approximately 41%) of dyes are statically quenched. It is possible that this also contributes to the 30% ETE loss seen with using 180 mM BL302 in the electrolyte. However, it is also possible that high concentrations of ERD cause some ERD to crash out of solution and form unsoluble aggregates. These aggregates would cause static quenching, but might not be able to go inside the small pores of the DSSC. Thus it cannot be said for certain how much of a loss this static concentration actually causes.



Fig S13. Comparison of time-resolved and steady-state quenching of BL302 in benzonitrile with varying concentration.

The ETE was measured for devices with 20 mM and 60 mM BL302, in exactly the same way as previously: the absorptance of the ERD (ABS_{ERD}) estimated using Beer's law,

and the ETE calculated from the EQE_{ERD}, IQE_{SD} and ABS_{ERD}. Since the absorptance is not near 0.91 (the transmission of the FTO), it can depend relatively strongly on the porosity of the substrates used. The average calculated ETE for 20 mM and 60 mM BL302 devices with 17 nm pores comes out to 76% for both concentrations, when using a porosity of 0.5 to estimate the absorption. Even using a porosity of 0.4 in the calculation of absorptance, a value lower than the porosity of the substrate, the calculated ETE is below 90%. Hence, it stands to reason that the ETE is still well below 100% even without the effects of dye concentration quenching, but still possible that concentration quenching can be a factor in further lowering the ETE slightly.

Impedance Spectroscopy Measurements

Impedance spectroscopy has been widely used to investigate the various charge-transport and charge-transfer processes which take place in DSSCs.^{5–7} In order to clearly see the part of the impedance spectrum that corresponds to mass transport of the redox shuttle within the electrolyte, the DSSC impedance spectrum needs to be taken at far forward bias. Shown below in Fig. S14 are the Nyquist plots of TT1-sensitized DSSCs with and without 180 mM BL302, and their respective impedance fits. The equivalent circuit used for fitting is shown in Fig. S15, and is typically used for fitting impedance spectra of DSSCs in far forward bias.



Fig. S14. Nyquist plots (taken at 0.8 V forward bias) and impedance fits (using the circuit shown in Fig. S15) for TT1 sensitized DSSCs employing a benzonitrile electrolyte without any ERD (a) and with 180 mM BL302 (b).



Fig. S15. Equivalent circuit modeling the operation of a DSSC in far forward bias.

The element in the equivalent circuit (Fig. S15) describing the diffusion of the redox shuttle through the electrolyte is the warburg element, whose impedance is given by

$$Z = R \frac{\tanh(\sqrt{t_{\rm d}}\omega)}{\sqrt{t_{\rm d}}\omega}$$

Where ω is the frequency and R and t_d are fit parameters. The best fit values of (R, t_d) were found to be (12.8 Ohms, 0.21 s) and (15 Ohms, 0.25 s) for the no ERD and 180mM BL302 devices, respectively. As these values are very close, it can be concluded that the addition of large amounts of ERD does not significantly hinder mass transport of the Γ/I_3^- electrolyte. Impedance experiments were also performed on TT1 sensitized cells with a acetonitrile electrolyte and fit to the same model at a bias of 0.9 V (no feature due to diffusion was visible at 0.8 V). This resulted in significantly lower (R, t_d) values of (2.1 Ohms, 0.06 s), showing the effect of changing the electrolyte solvent is much more important than the effects of adding ERD.



Fig. S16. J-V curves of DSSCs with various concentrations of BL302 (left) and BL315 (right).

Aggregates in solution can often cause a change in the absorption/emission spectrum of a chromophore. Since it is hypothesized that the static quenching seen with BL302 is caused by the formation of aggregates, UV-Vis measurements and PL measurements were done to investigate any changes in absorption or emission spectra. For absorption measurements, the strong absorption of the electrolyte does not allow resolution of any spectral changes below 500 nm (Fig. S17). Increasing the dye concentration past 10 mM saturates the UV-Vis measurement even at path lengths as low as tens of µm, making it hard to increase the dye concentration higher to try to see spectral changes. As for the PL spectrum, it remains unchanged (Fig. S18) – most likely because any statically quenched ERDs do no photoluminesce.



Fig. S17. Absorption of 10 mM BL302 with and without electrolyte in an approximately 25 μ m thick 'cuvette' made by sealing 2 pieces of glass with a surlyn spacer (25 μ m) and filling with ERD solution. The absorption was too high to be measured with a standard (0.5 mm or longer) path length cuvette. Any changes to the dye absorption peaks cannot be made out due to the strong absorption of the electrolyte below 450 nm.



Fig. S18. Photoluminecence spectrum of 10 mM BL302 with electrolyte. 25% and 50% corresponds to 25% and 50% of the concentrations of ions that is used in the DSSC electrolyte. As can be seen, there is no significant change in shape of the photoluminescence spectrum – likely because any aggregates do not photoluminesce. There is a slight redshift, but this may be caused by the addition of ions to the solvent.

Experimental Details

Materials were purchased from commercial suppliers (Aldrich, Acros) and used as received unless otherwise noted.

Device Fabrication: Nanoporous titania DSSC substrates were prepared as previously described in detail.⁸ Substrates were fabricated with 6 µm thick active layer made with 20 nm particles and a peak pore diameter of 17 nm. Substrates utilizing 12nm9,10 and 32 nm average pore diameters were also fabricated as previously described in the literature. Devices were fabricated by heating to 500 °C to remove any water/organics, cooling back to room temperature, and then immediately immersing in 0.1 mM TT1 solution in ethanol with 10 mM CDCA (chenodeoxycholic acid). The devices were allowed to sit in solution for 4.5 hours and then were sealed with a platanized FTO back electrode using a 25 nm surlyn spacer by heating and pressing on a 125 °C hotplate. The platanized back electrode was made by drilling a 1 mm hole in FTO, then covering with a solution of chloroplatinic acid hydrate in isopropyl alcohol and heating to 125 °C. The electrolyte was vacuum backfilled and the entire DSSC sealed with surlyn and a glass coverslip. The 'benzonitrile-based' electrolyte was composed of 0.6 M 1-methyl-3-propylimidazolium iodide, 0.04 M I₂, 0.28 M 4-tert-0.025 M LiI and 0.05 M guanidinium thiocyanate in 85:15 butylpyridine, benzontrile:valeronitrile. The 'acetonitrile-based' electrolyte was the same components (0.6 M 1-methyl-3-propylimidazolium iodide, 0.04 M I₂, 0.28 M 4-tert-butylpyridine, 0.025 M LiI and 0.05 M guanidinium thiocyanate) in 85:15 acetontrile:valeronitrile.

*Thickness measurements:*TiO₂ layer thicknesses were measured using a Veeco Dektak³ ST surface profiler profilometer.

IV Measurements: J-V curves were taken with a Keithley 2400 sourcemeter, under simulated AM 1.5G illumination with a Spectraphysics model 91160 solar simulator which has been

callibrated using a hamamatsu Si photodiode with KG5 filter. The DSSC was was masked with a 0.159 cm² area machined mask during J-V measurements.

EQE and absorptance measurements: EQE was measured at a chopping frequency of approximately 2 Hz. For the chopped EQE beam, a Newport Apex monochromator illuminator was focused on a Princeton Instruments monochromator and subsequently put through a filter wheel. The signal from the DSSC was amplified with a home-built transimpedance amplifier and recorded on a Stanford Instruments lock-in amplifier. The EQE was calibrated against a calibrated photodiode of known EQE. Additionally, the EQE beam was split with a 50:50 beam splitter into a 2^{nd} 'reference' photodiode that was used to correct for any fluctuations in the illuminator source intensity.

Experimental set-up for absorptance measurements have also been reported.¹¹ Device absorptance measurements were performed using the same light source/monochromator setup as the EQE and measured using an integrating sphere with an attached silicon photodiode attached to a Kiethley sourcemeter. Care was taken to ensure that the incidence angle of the light should be as close to normal as possible.

Absorption measurements: Absorption measurements were made using a Cary 6000i UV/Vis spectrophotometer.

Photoluminescence measurements: Steady-state photoluminescence measurements were made using an Ar-ion laser for illumination at 488 nm. The resultant photoluminescence was focused onto a monochromator and measured with a CCD, correcting for the CCD response. Time resolved photoluminescence measurements were performed using a Picoharp 300 time-correlated single photon counting system with a picoquant PDL 800-B pulsed laser diode driver with a picoquant model LDH-P-C-485 laser for 485 nm excitation with <1 ns rise time at a frequency of 10 Mhz, detected with an avalance photodiode (PDM 100CT SPAD).

Impedance spectroscopy measurements: Impedance spectroscopy was performed with a Biologic SA model VMP3 potentiostat. Fits were made using EC-Lab software.

References

- 1. R. Andreu, L. Carrasquer, J. Garín, M. J. Modrego, J. Orduna, R. Alicante, B. Villacampa, and M. Allain, *Tetrahedron Lett.*, 2009, **50**, 2920–2924.
- W. D. Oosterbaan, P. C. M. van Gerven, C. A. van Walree, M. Koeberg, J. J. Piet, R. W. A. Havenith, J. W. Zwikker, L. W. Jenneskens, and R. Gleiter, *Eur. J. Org. Chem.*, 2003, 2003, 3117–3130.
- 3. J. M. Drake, M. L. Lesiecki, and D. M. Camaioni, *Chem. Phys. Lett.*, 1985, **113**, 530–534.
- 4. E. T. Hoke, B. E. Hardin, and M. D. McGehee, *Opt. Express*, 2010, 18, 3893–904.
- 5. Q. Wang, J.-E. Moser, and M. Grätzel, J. Phys. Chem. B, 2005, 109, 14945–53.
- 6. F. Fabregat-Santiago, G. Garcia-Belmonte, I. Mora-Seró, and J. Bisquert, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9083–118.
- 7. F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo, and A. Hagfeldt, *Sol. Energy Mater. Sol. Cells*, 2005, **87**, 117–131.
- 8. S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin, and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613–4619.
- 9. J. M. Szeifert, D. Fattakhova-Rohlfing, J. Rathouský, and T. Bein, *Chem. Mater.*, 2012, **24**, 659–663.
- J. M. Szeifert, D. Fattakhova-Rohlfing, D. Georgiadou, V. Kalousek, J. Rathouský, D. Kuang, S. Wenger, S. M. Zakeeruddin, M. Grätzel, and T. Bein, *Chem. Mater.*, 2009, 21, 1260–1265.
- 11. G. F. Burkhard, E. T. Hoke, and M. D. McGehee, Adv. Mater., 2010, 22, 3293-7.