Supporting Information for

Measured binding coefficients for iodine and ruthenium dyes; implications for recombination in dye sensitised solar cells

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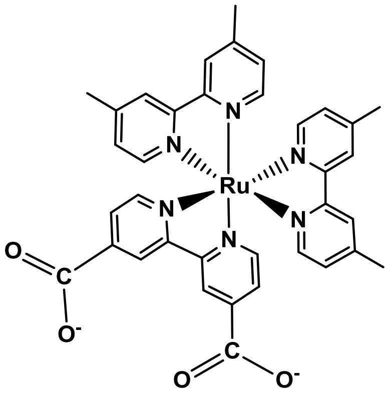
Dye Z995 structure



Scheme S1 Chemical structure of dye Z995.

I_2 titration of N719/TiO_2 films in dichloromethane (DCM)

To determine the dye-iodine binding constant in DCM, a series of I_2 solution (2, 5, 10, 15, 20, 30, 50, 70 and 100 μL) from 0.01 M stock solution was added to 2 mL DCM solution in a 10 mm path length cuvette with a piece of N719/TiO_2 film, and the UV-Vis spectra of film in and out of beam were measured. The absorption spectra of dye-sensitised films were obtained by subtracting the absorption of iodine in solution from the total absorption using equation 1, as shown in Figure S1.

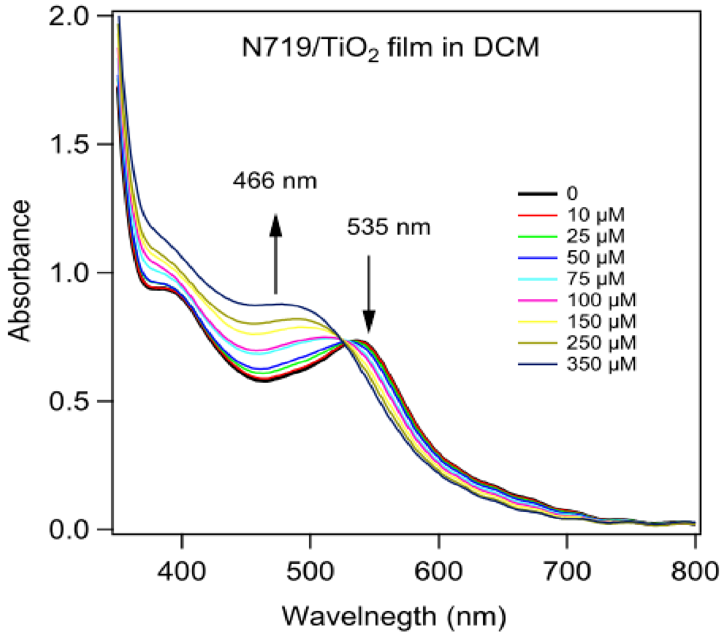
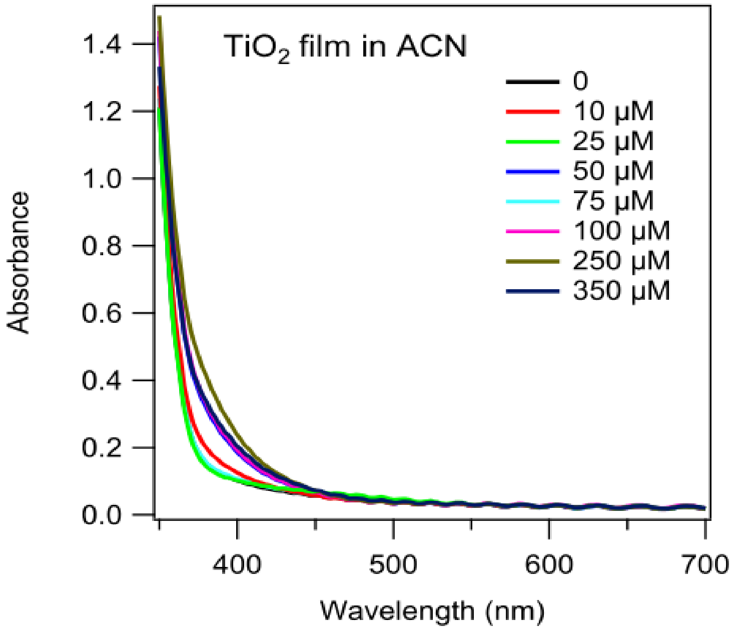


Figure S1 Absorption spectra of the N719/TiO_2 film in DCM upon iodine titration.

I_2 titration of bare TiO_2 and Al_2O_3 films in acetonitrile (ACN) and dichloromethane

In the control experiments with TiO_2 and Al_2O_3 films in ACN and DCM (no dyes), there is no peak/change observed above 450 nm (Figure S2) which means that the TiO_2 and Al_2O_3 films have no effect on dyes to I_2 binding in the range of 450~700 nm.



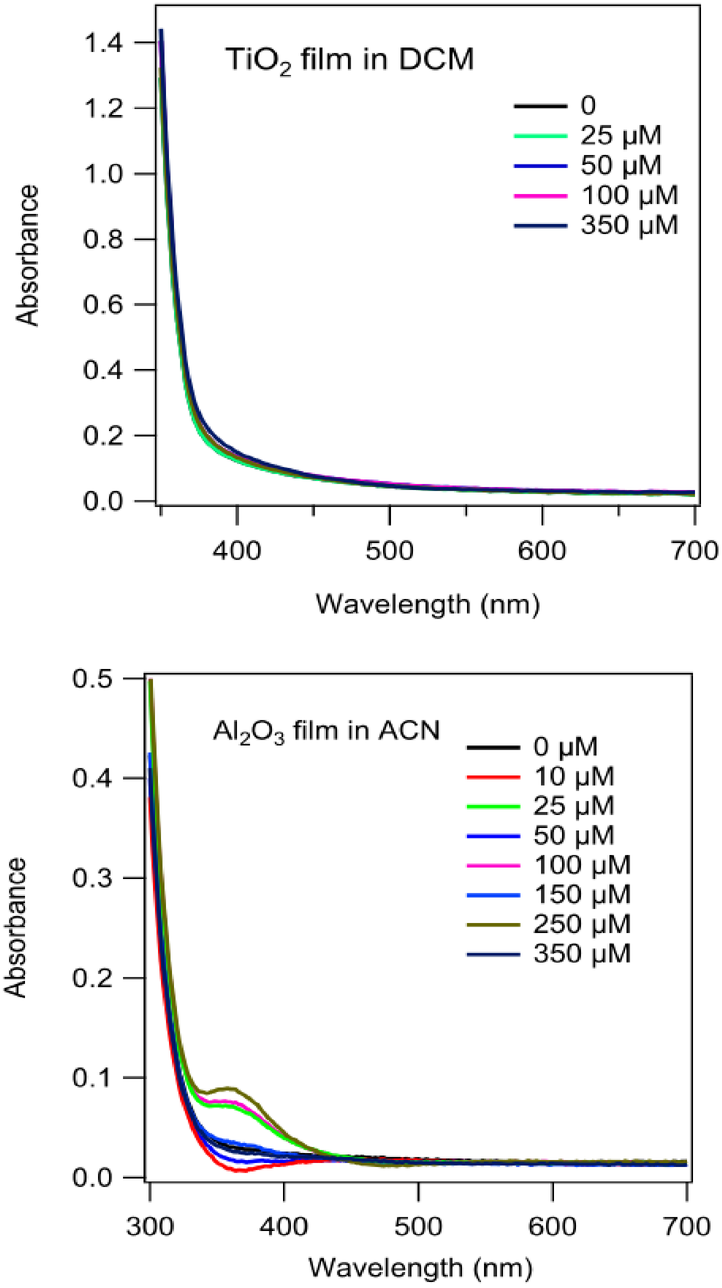


Figure S2 The absorption spectra of the bare TiO_2 film upon the iodine titration in ACN and DCM. Absorption spectra of bare alumina film in ACN with iodine titration.

FTIR of C101/TiO_2 in the presence and absence of iodine

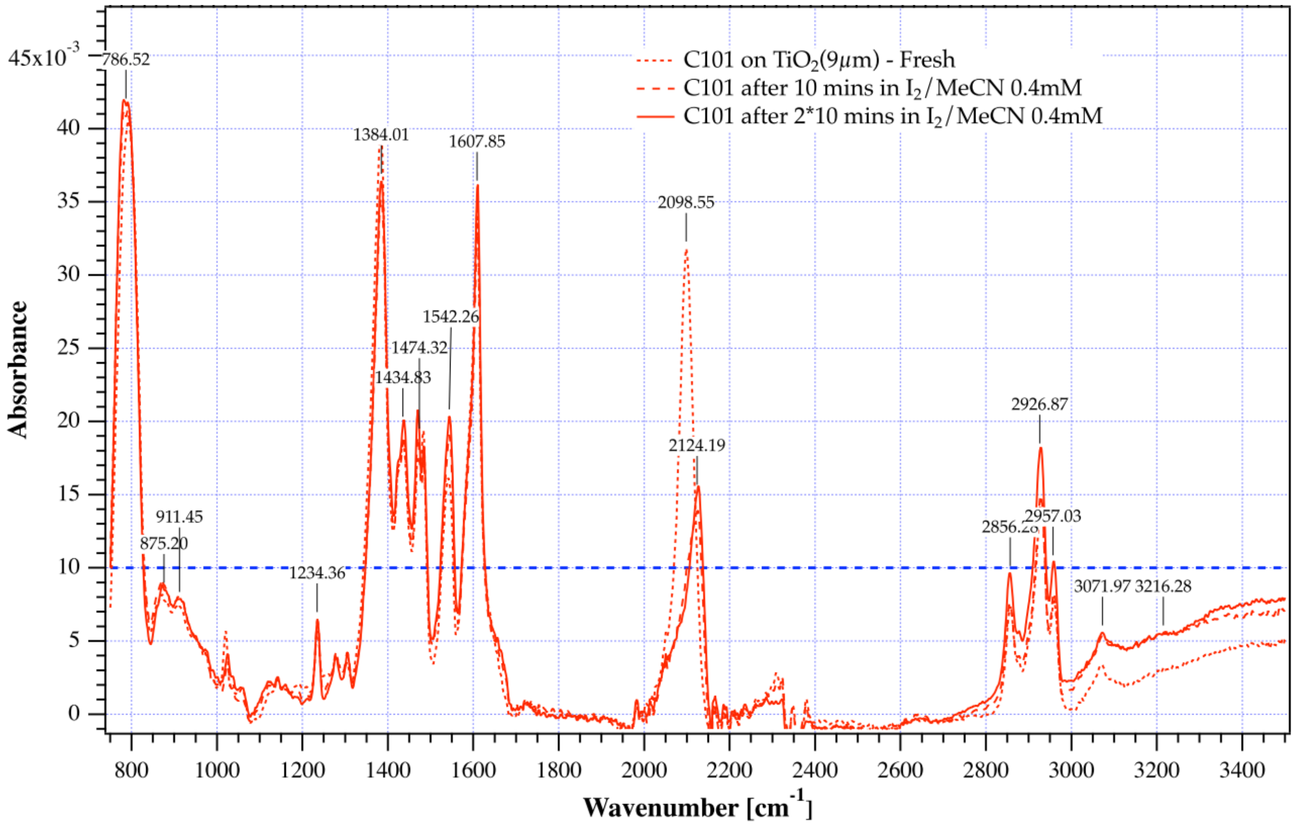


Figure S3 FTIR of C101 on the TiO_2 surface in the presence and absence of iodine.

Similar to N719, the NCS peak appears at 2099 cm^{-1}. In the presence of the iodine the NCS peak is diminished in intensity and a new peak appears at a slightly higher frequency 2124 cm^{-1}.

Dye iodine binding constant

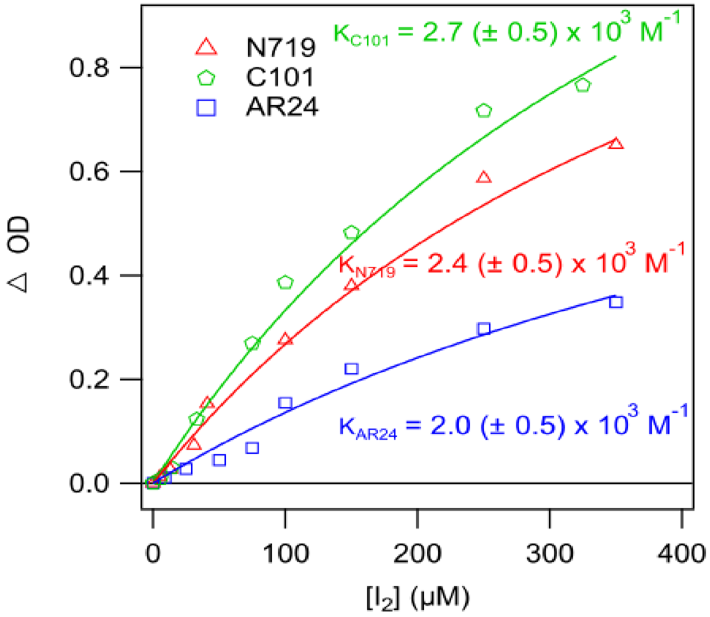


Figure S4 The absorbance changes of the blue shifted MLCT peak ($\Delta OD=A-A_0$) *vs.* the iodine concentration for N719/TiO_2 film, C101/TiO_2 film and AR24/TiO_2 film. Fit are to the Langmuir isotherm equation.

Iodine titration of N719/TiO_2 Film in DCM

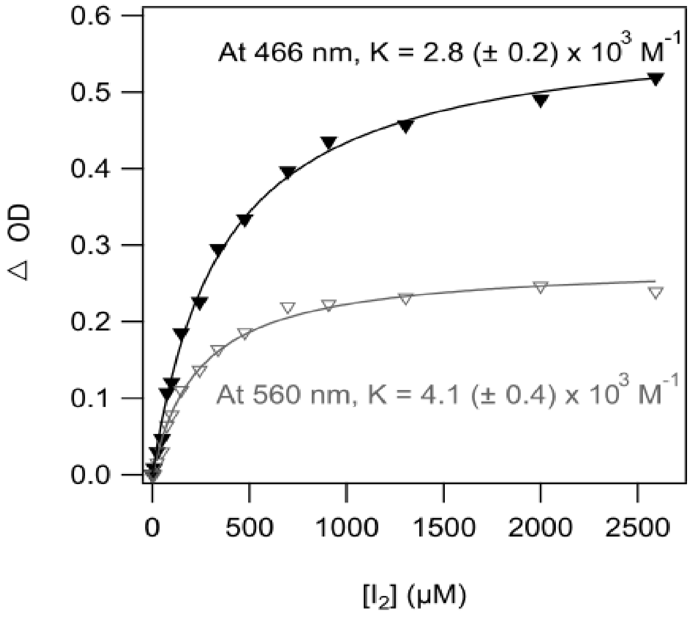


Figure S5 The maximum absorbance change *vs.* the iodine concentration for N719/TiO_2 film in DCM solution.

The change of optical density at 466 nm (charge transfer complex) and 560 nm *vs*. iodine concentration is plotted in Figure S6, and the binding constant is estimated to be 2.8 (± 0.2)×10^3 M^{-1} by fitting with Equation 2.

Iodine titration of N719 dissolved in ACN

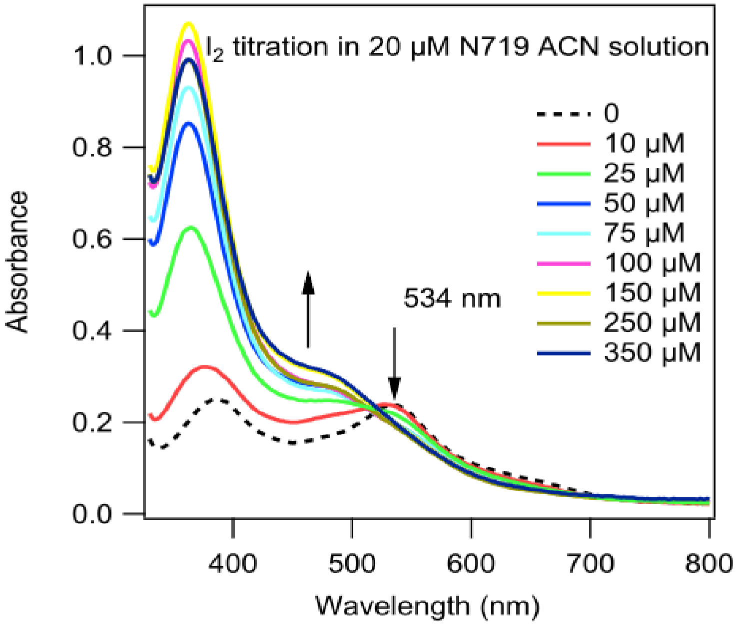


Figure S6 Absorption spectrum of during iodine titration of N719 in ACN solution. In this case the spectrum of the equivalent iodine solution in ACN without N719 has been subtracted.

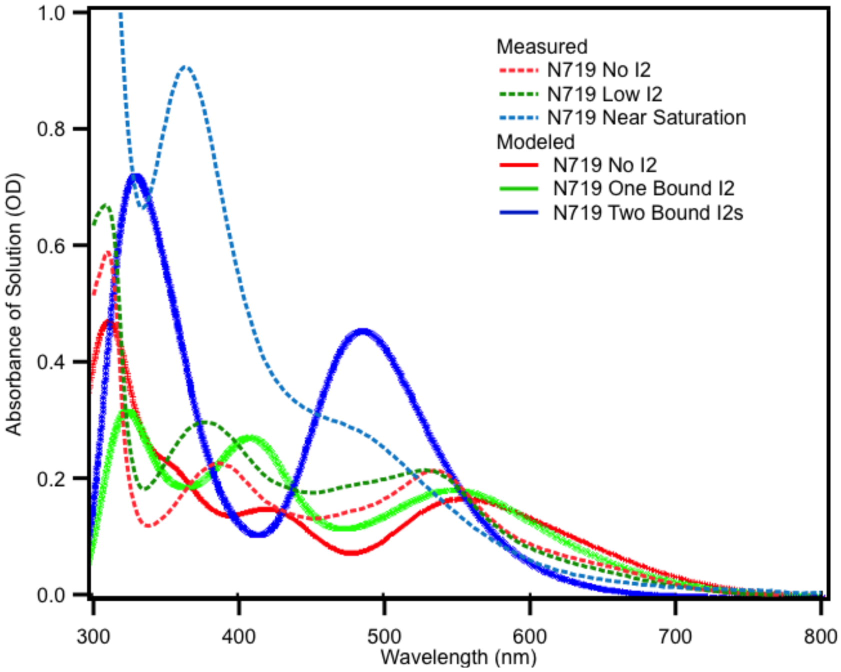


Figure S7 Comparison of modelled and measured absorption spectra in ACN solution.

The calculated spectrum with one iodine molecule matches quite well the spectra shifts measured at low iodine concentration, where the mono-iodine complex might dominate. The calculated spectrum with two iodine molecules bound matches some of the features of the measured spectrum near saturation. For example, it does mimic the blue shift and increase in intensity of the lowest MLCT. Measured 534 nm to ~478 nm (~0.27 eV) *vs.* modelled 557 nm to 485 nm (0.33 eV). The calculation appears to mimic the increase in height of the higher energy peak that occurs at 390 nm in the measured spectrum without iodine, while strongly overstating the degree of shift. However, the 360 nm peak in the measured spectrum contains an unknown amount of I_3^-, as discussed in the text. A much smaller increase in peak height is seen in Figure 4, where N719 is adsorbed on Al_2O_3, and the subtraction of the solution I_3^- can be done accurately.

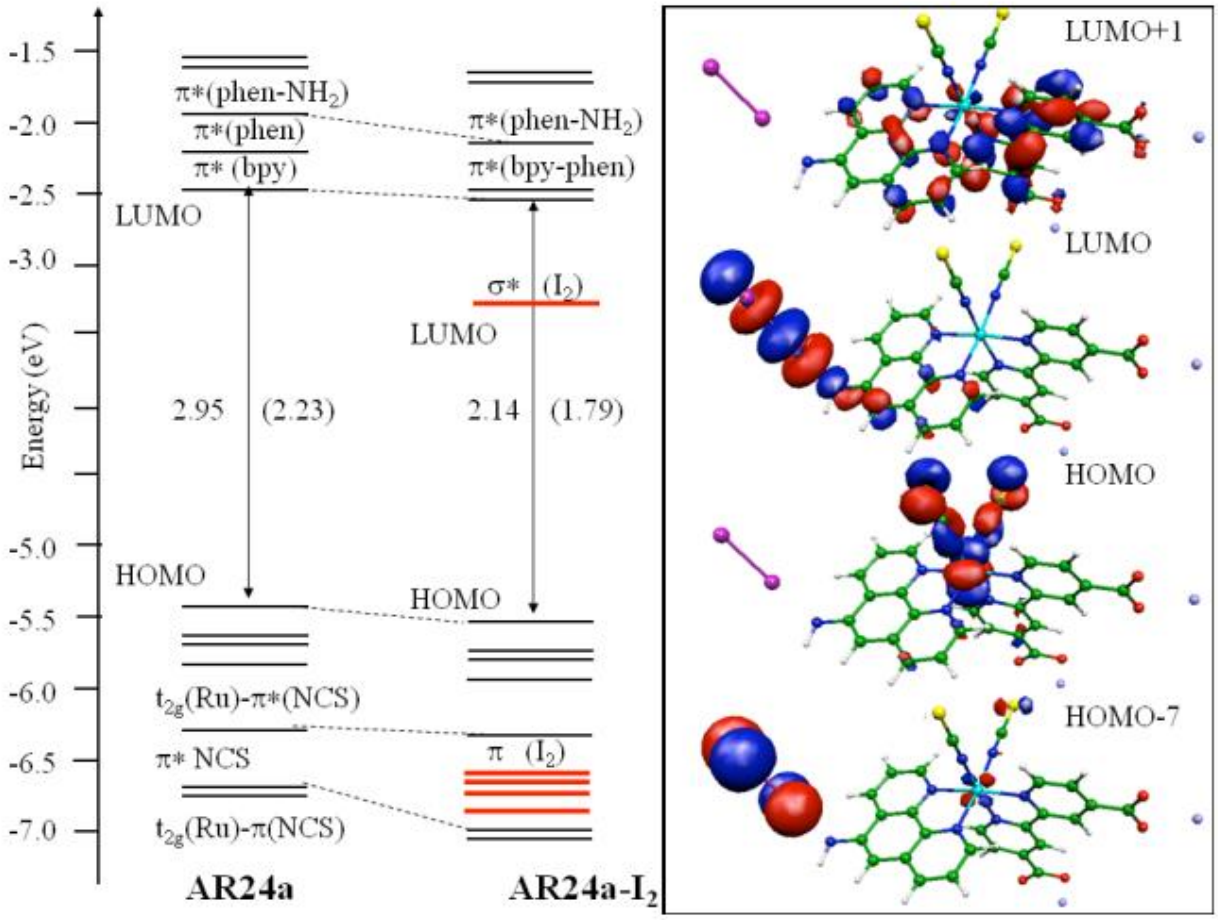


Figure S8 Schematic of the energy levels for AR24a and AR24a-I_2, along with isodensity plots of selected molecular orbitals for the latter. Levels in red are those mainly based on the I_2 moiety. Also indicated are the HOMO-LUMO gaps and the lowest TDDFT excitation energies (values in parentheses).

Solar cells' transient results

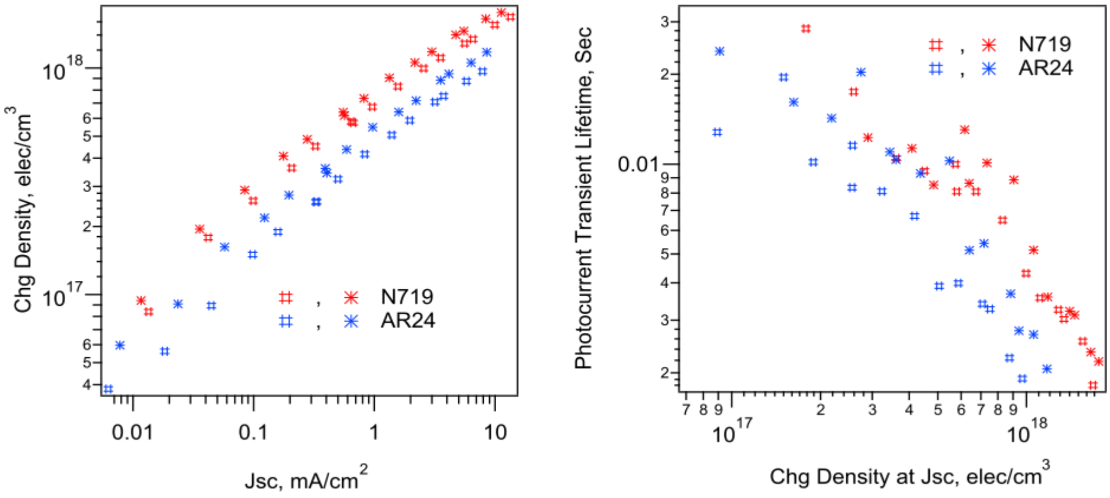


Figure S9 Additional transient results for the AR24 cells shown in figure 5 of main text. Left: charge density at short circuit conditions (by charge extraction) *vs.* short circuit photocurrent. Right: Photocurrent transient decay time *vs.* the charge density at short circuit.

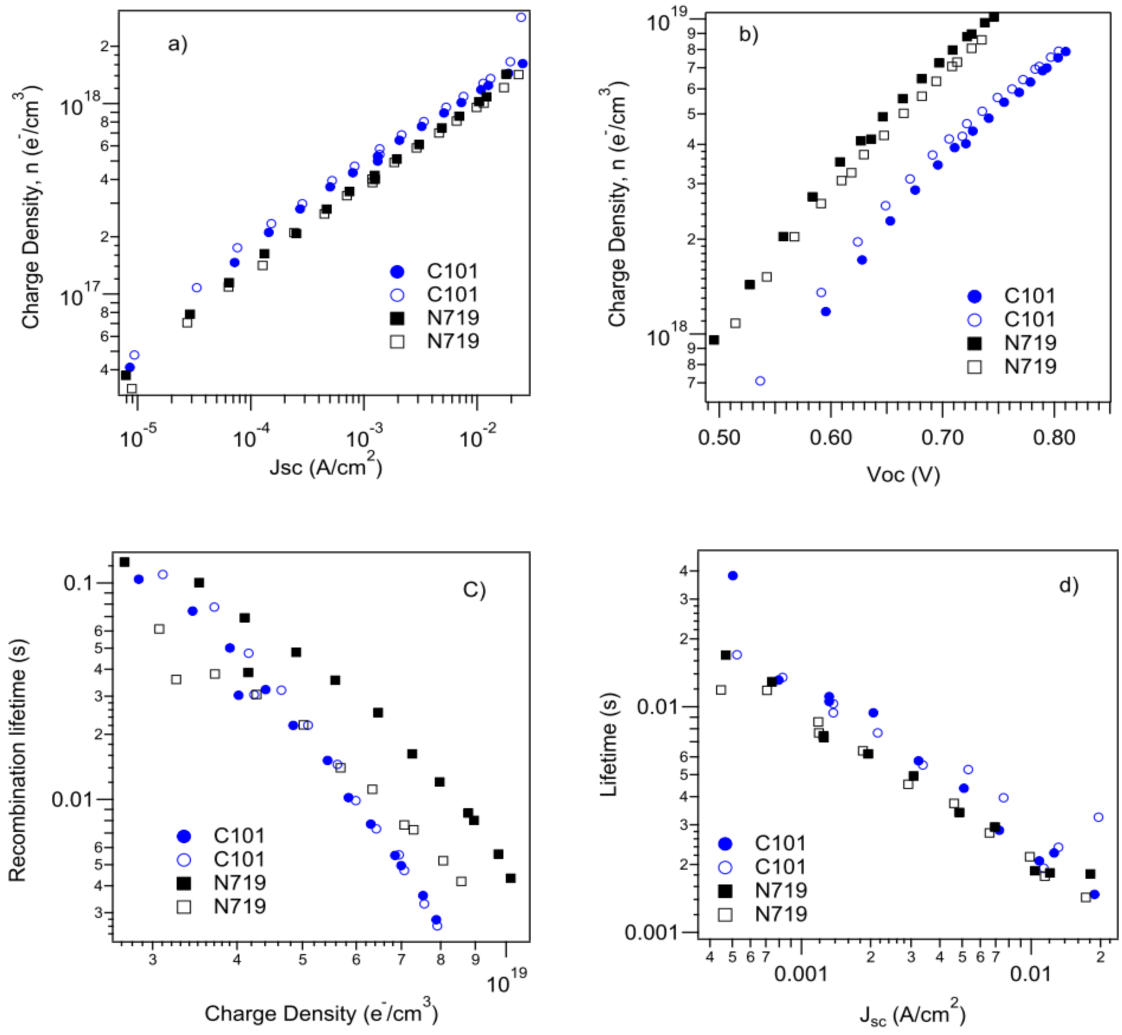


Figure S10 Charge in the cell plotted as a function of (a) J_{sc} and (b) V_{oc}, where the V_{oc} was varied by changing the bias light intensity, for N719 (black) and C101(blue); (c) electron lifetime (τ_n) for DSSCs with N719 and C101 dyes *vs.* charge density measured at V_{oc} and (d) electron transport time (τ_j) for DSSCs with N719 (black) and C101 (blue) dyes measured at short circuit plotted against J_{sc}. Electrolyte contained 0.8 M 1-methyl-3-propylimidazolium iodide (PMII), 0.05 M iodine (I_2), 0.05 M guanidinium thiocyanate (GuSCN), 0.025 M lithium iodide (LiI) and 0.28 M *tert*-butylpyridine (tBP) in 3-methoxypropionitrile (MPN).

In the case of the cells in Figure S9, the AR24 cells appear to have 30% less charge for a given current than the N719 cells. This could be interpreted as a lower trap density, as we have done in a previous paper (*Energy Environ. Sci.*, 2012, **5**, 7203). However, in this case we believe most of the difference comes from the lower collection efficiency at short circuit. As mentioned in the text, the transient diffusion length is only 12 µm. Taking into account the tendency of the transient method to overestimate the diffusion lengths, we would estimate the real diffusion length to be around 6 µm. This would give about 20% losses for a 6.5 µm film similar to the difference observed in the photocurrent at one sun. Thus we have made no adjustments for changes in trap density to any of the transients in Figure S9, or Figure 6. In the case of Figure 10a, the N719 cells show about 20% less charge *vs.* J_{sc}. This probably falls within the error in TiO_2 thickness and cell area.

Calculations of I_3^- created in various cases

Using 5.6×10^4 ($mol^{-1}cm^{-1}$) for the absorption coefficient of I_3^- in ACN at 360 nm, we find that at 350 µM iodine in 2 mL ACN the amount of triiodide generated in acetonitrile is 43 nmol. That is 6% of the 700 nmol iodine in the 2 mL solution, but since each I_3^- requires two I_2, about 12% of the iodine is consumed.

The extinction coefficient of triiodide were estimated to be 3.3×10^4 and 5.6×10^4 M^{-1} cm^{-1} in DCM and ACN respectively. Values are from UV-Vis measurements of iodine (0.23 mM) and mixture of iodine (0.23 mM) and iodide (4.5×10^{-5} M) in ACN and DCM and the Beer-Lambert law.

With bare TiO_2 film in ACN/I_2 91 nmol I_3^- is created, or 48 nm more than in the solution by itself. With the N719/TiO_2 film in ACN/I_2 108 nmol I_3^- is created when 93 nmol N719 are absorbed. At the same time, at 350 µM I_2, using a binding coefficient of 2×10^3, about 40% the dye has bound iodine meaning or 37 nmol. Thus the additional 17 nm I_3^- created is equivalent to about one half of the dyes which have bound iodine.

In 2 mL dye solution (40 nmol N719), after subtraction of the I_3^- created by the ACN/I_2 (Figure S10), there are ~23 nmol triiodide generated by dye-I_2 complexes. At 350 µM iodine in solution, virtually all the dissolved N719 has bound iodine(s), therefore the correspondence is again about 1:0.5.

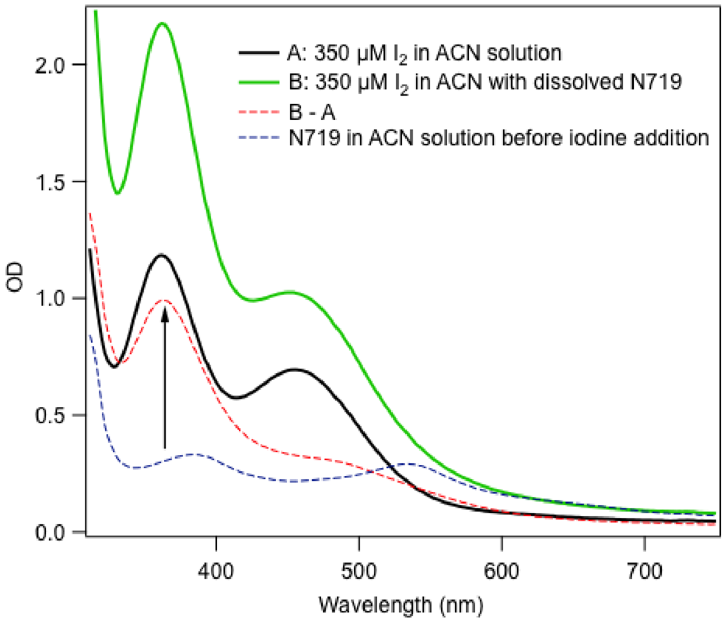


Figure S11 Absorption spectra of a 350 µM I_2 in ACN (black), 20 µM N719 and 350 µM I_2 in ACN (green), and 20 µM N719 alone in ACN (blue dot). The subtraction gives the spectrum of the N719 plus any changes in the iodine due to the N719. The arrow indicates the excess iodine tri-iodide (absorption at 360 nm) created when the dye is present.

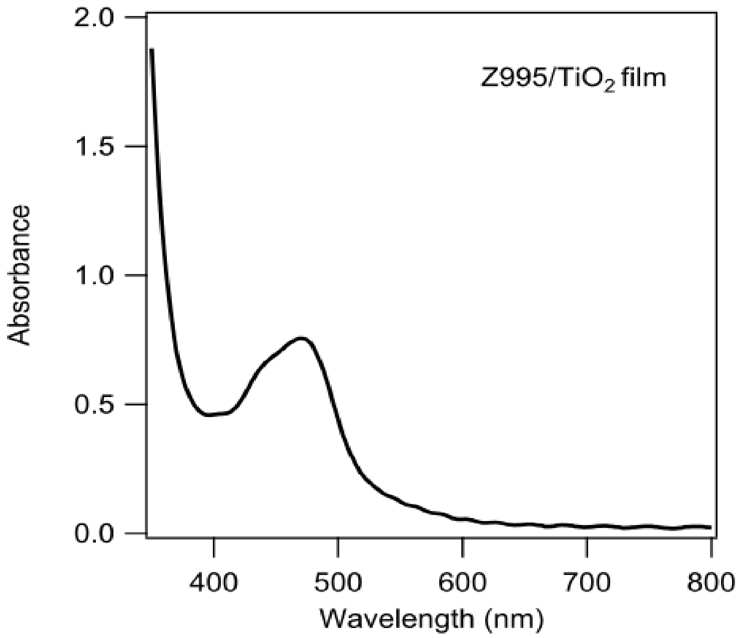


Figure S12 Absorption spectrum of Z995 absorbed onto a TiO_2 film.

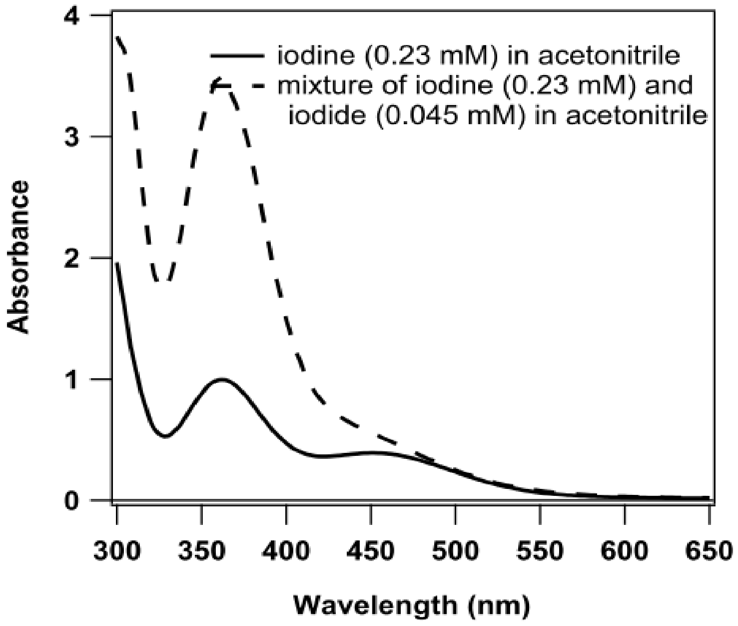


Figure S13 Absorption spectra of I_2 and I_3^- in acetonitrile.

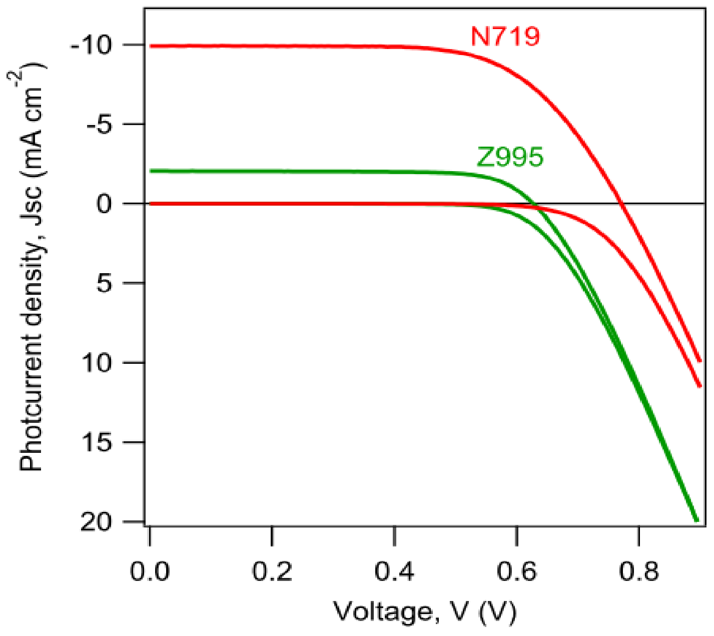


Figure S14 IV results for N719 and Z995 cells under 1 Sun and in dark. Electrolyte contained 0.8 M 1-methyl-3-propylimidazolium iodide (PMII), 0.05 M iodine (I_2), 0.05 M guanidinium thiocyanate (GuSCN), 0.3 M Benzimidazole in 3-methoxypropionitrile (MPN).

The J_{sc} and V_{oc} of the two dyes cannot be directly compared due to the difference in absorption spectrum, number of carboxylic acid groups and possibly regeneration kinetics. We emphasize that Z995 dye was chosen only to show that the spectral shifts in Figure 1 in the paper are in fact due to the thiocyanate groups. It is useful as a test of iodine binding and V_{oc}.