

## Electronic Supplementary Information

*In situ* monitoring and optimization of room temperature ultra-fast sensitization for dye-sensitized solar cells

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### Device manufacture

The working photoelectrode was prepared by doctor blading a thin film of commercial titania colloid (DSL-18NRT, Dyesol) onto TEC 15 glass (Pilkington) using two layers of Scotch tape (3M) as the spacer. Films were sintered at 450 °C for 30 minutes. A titanium oxide scattering layer (WER-40, Dyesol) was then deposited onto the working electrodes and the electrodes were again heated to a temperature of 450 °C for 30 minutes, after which the electrodes were immersed in TiCl<sub>4</sub>:THF<sub>2</sub> in deionised water (40 mM) at 70 °C for 30 mins, rinsed with de-ionised water, air-dried for 10 min and re-sintered at 450 °C for 30 mins. The final working electrodes prepared having a thickness of 17 μm as measured using stylus profilometry. To improve consistency of the doctor blade method the TiO<sub>2</sub> colloid was deposited on long strips of TEC glass, only after all the colloid layers had been deposited, sintered and treated was the glass cut to make individual cells.

Dye solutions containing N719, di-*tert* butyl pyridyl cis-bis(4,4'-dicarboxy-2,2'-bipyridine)dithiocyanato ruthenium(II), were prepared in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol at the stated concentrations. Dye solutions containing SQ1 (5 mM) and chenodeoxycholic acid (0.5 mM, Aldrich) were prepared in ethanol. N719 dye was used as purchased from Dyesol. SQ1 was prepared as described in the literature (A. Burke, L.

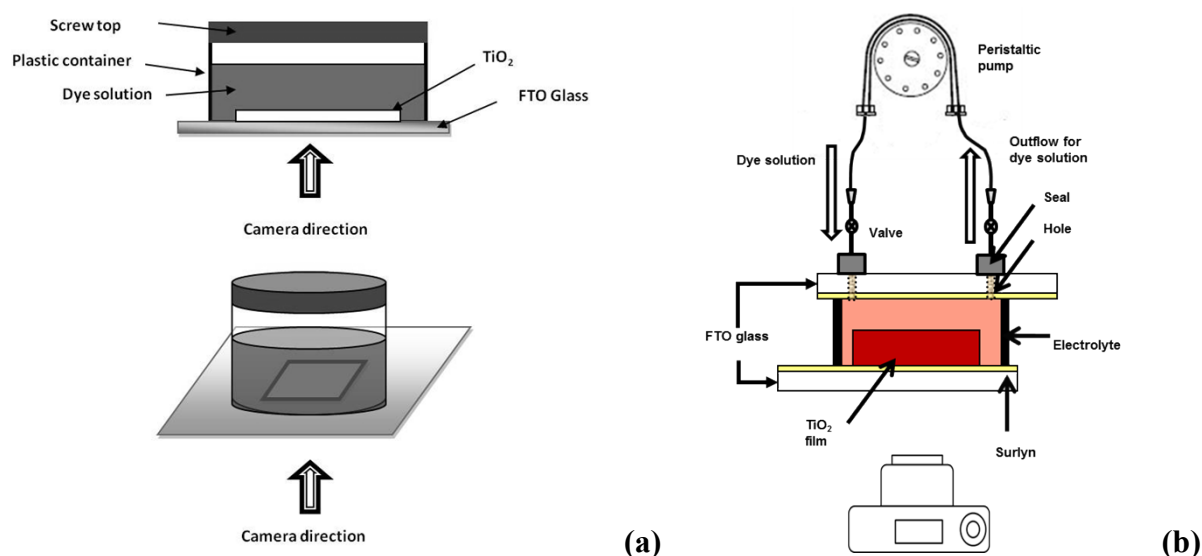
Schmidt-Mende, S. Ito and M. Grätzel, Chem. Commun., 2007, 234). For passively dyed devices, after dyeing, a Surlyn® (Du Pont) gasket was placed around the photo-electrode and a Pt-coated TEC 8 counter electrode which had been treated with Pt paste (PT1, Dyesol) and heated to 400 °C was placed on top and the two electrodes sealed together at 120 °C. For fast-dyed devices the working and counter electrodes were sealed together prior to dyeing as already described and the dye was pumped through the cavity. Electrolyte containing iodine/tri-iodide (I<sub>2</sub> 100 mM in acetonitrile) was added through a hole in the counter electrode which was then sealed using Surlyn®. For devices dyed with SQ1, the electrolyte described by Grätzel *et al.* (A. Burke, L. Schmidt-Mende, S. Ito and M. Grätzel, Chem. Commun., 2007, 234) was used.

### Time lapse measurements

For passive time lapse measurements electrodes were placed in *ca.* 50 ml of dye solution in a sealed container and images were captured from underneath the glass container (ESI Fig. 1a). Images were collected at 5 second intervals for the first 30 minutes and then at 30 second intervals thereafter over a total time period of 24 hours. Passive co-sensitisation was imaged in a 'one-pot' dye mixture.

For fast-dyeing time-lapse measurements, dye solutions were pumped through a sealed photoelectrode cavity using a Masterflex® peristaltic pump (ESI Fig. 1b) at a flow rate of 4 ml/min and digital images were collected at 5 second intervals over a period of an hour. Co-sensitization was achieved by pumping mixtures of dyes through the photoelectrode together. The N719/SQ1/CDCA mixtures were 0.5 mM N719/1.0 μM SQ1, 1.5 mM/4.0 μM SQ1 and 4.5 mM/10.0 μM SQ1 with a CDCA concentration of 1.67 mM in all cases.

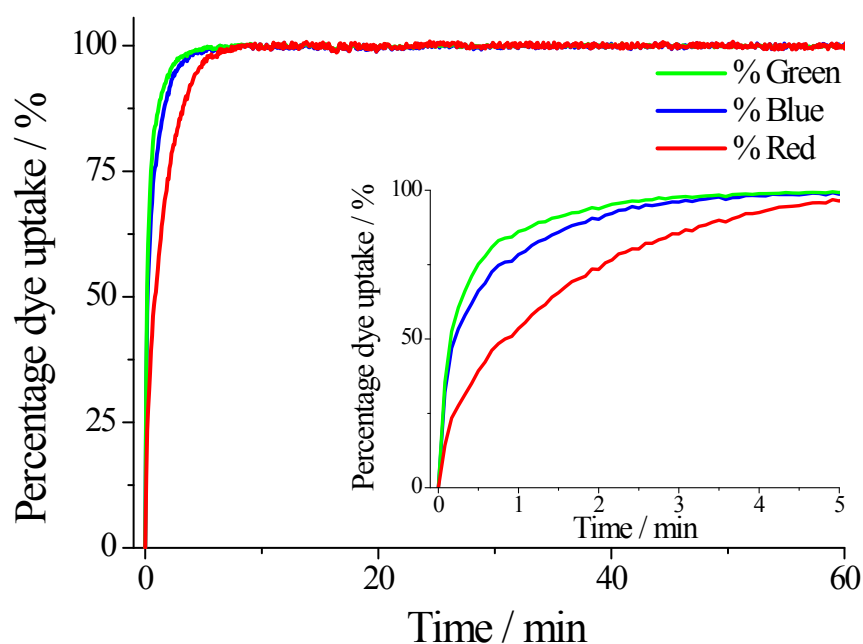
Digital images were collected using a Canon Powershot G10 digital camera from approximately 5 cm below the sample. Consistent light was provided by a UV-filtered tungsten halogen lamp to reduce any dye photo-degradation. Image analysis was carried out using a software package (Sigma Scan Pro) and the data recorded in RGB format with colour intensity graded from 0 to 256 (dark to light) so numbers dropped as dyeing proceeded. Average RGB values from selected regions of the TiO<sub>2</sub> were then plotted against time.



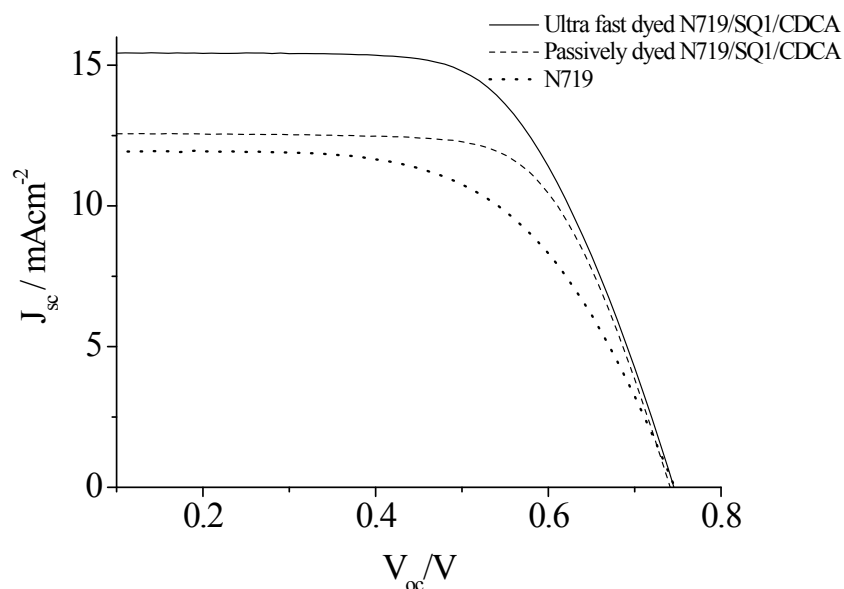
**ESI Fig. 1** Schematic of the experimental set-up for time-lapse monitoring of (a) passive and (b) ultra-fast dyeing.

### Device characterisation

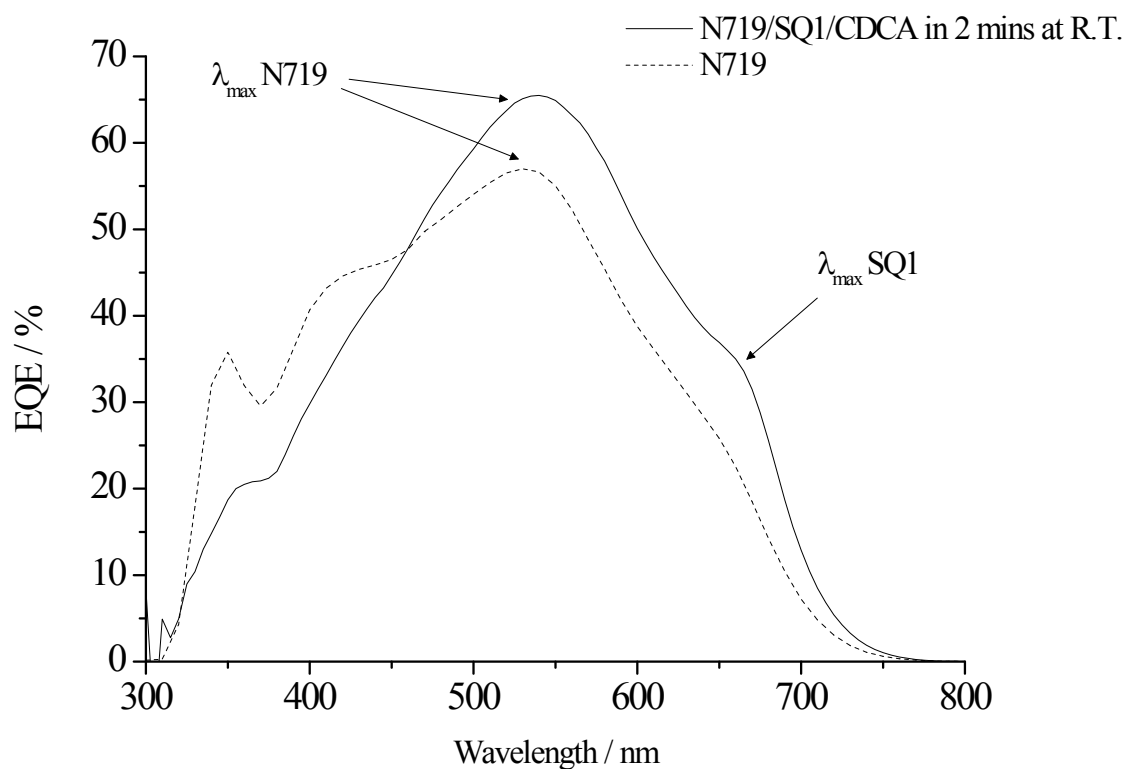
Current-voltage characteristics were measured using a Oriel Sol3A (94023A) utilising a Xenon arc lamp (150 W), an AM1.5 filter and a Keithley 2400 source meter. A certified (Oriel 91150V) monocrystalline silicon reference cell traceable to the National Renewable Energy Laboratory (NREL) was used to adjust the solar simulator to one sun ( $100 \text{ mW cm}^{-2}$ ). Diffuse reflectance UV-vis spectroscopy was measured with a Perkin Elmer Lambda 750S with 60 mm inte- grating sphere. Samples were placed against the reflectance opening of the integrating sphere so that only the TiO<sub>2</sub> film was in the beam path. Spectra were recorded between 250 and 800 nm at pre-determined intervals. Spectral response measurements were made from 300–800 nm on a QEX10 Quantum Efficiency Measurement System in DC mode at a resolution of 5 nm.



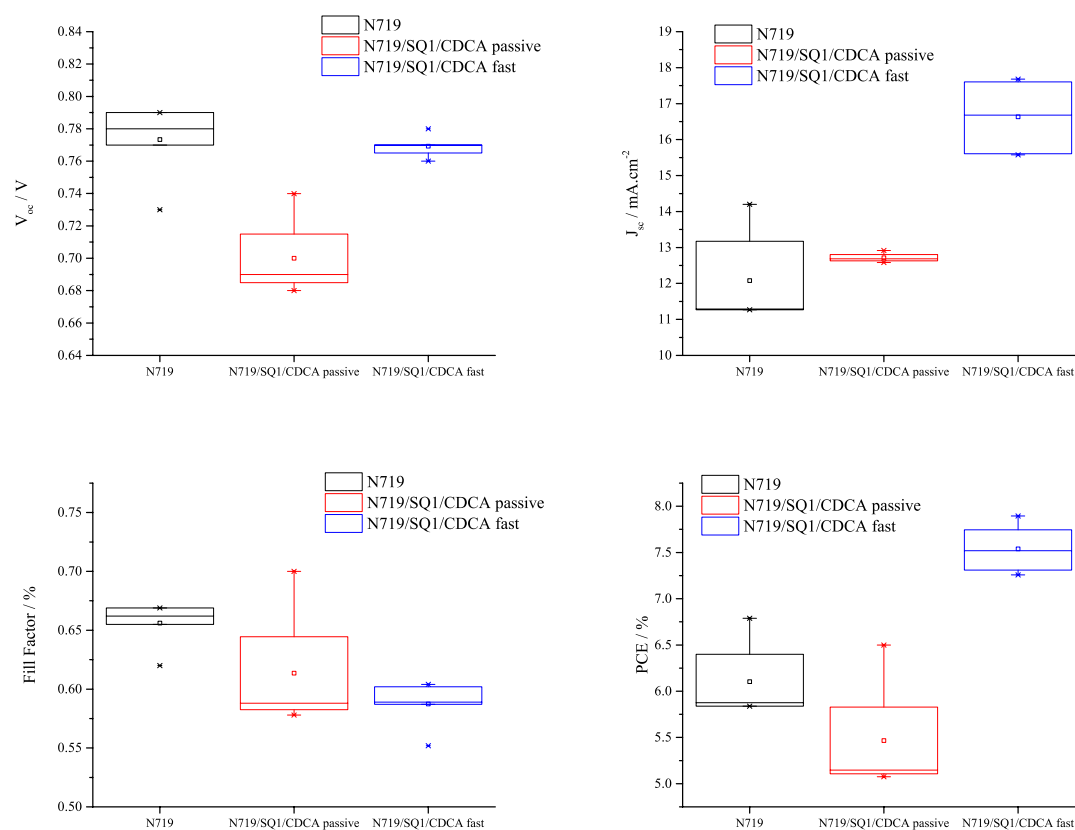
**ESI Fig. 2** Percentage dye uptake for N719 (4.5 mM) over 60 min. Red (R), green (G) and blue (B) colour data extracted from images taken every 5s. Inset is the same data over the first 5 min.



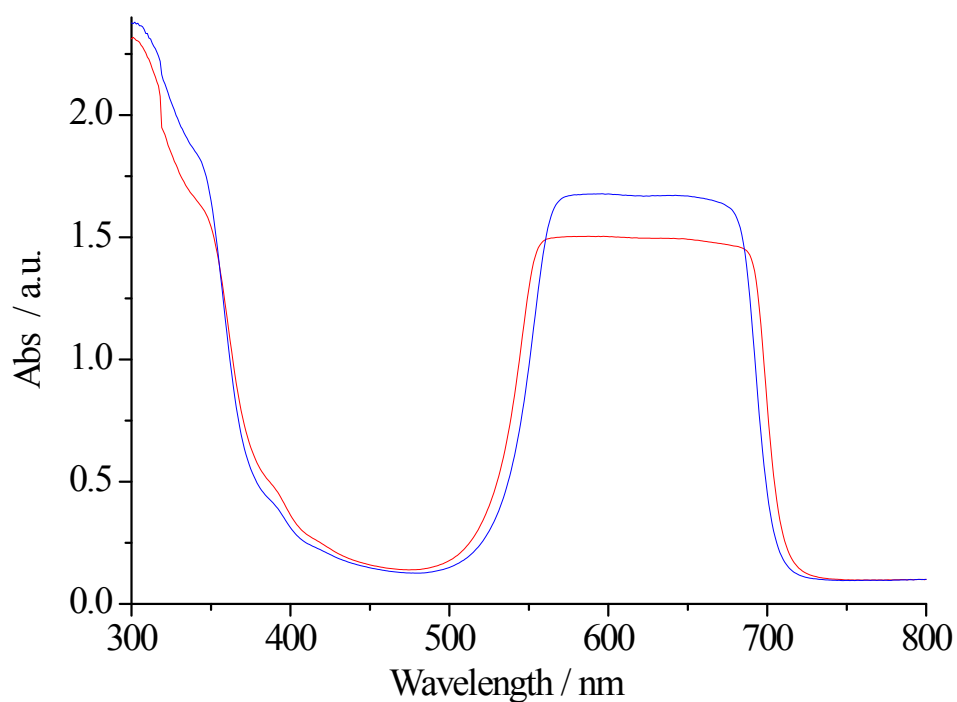
**ESI Fig. 3** IV data of a passively dyed N719 device (dotted line), passive N719/SQ1/CDCA device (dashed line) and an ultra-fast dyed device in 2 minutes at room temperature with a dye mix of N719/SQ1/CDCA (solid line). The dye concentrations are 4.5 mM N719/ 11.3  $\mu\text{M}$  SQ1/ 1.67 mM CDCA for the cocktail mixture and 4.5 mM N719.



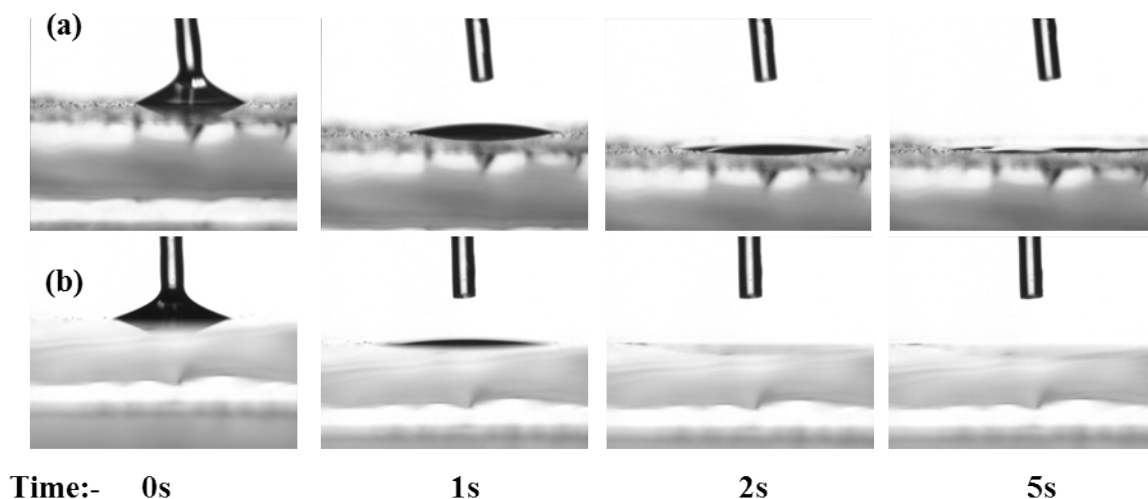
**ESI Fig. 4** External quantum efficiency of a passively dyed 4.5 mM N719 device (dashed line) and an ultra-fast dyed device dyed in 2 minutes at room temperature with a dye mix of N719/SQ1/CDCA at concentrations of 4.5 mM N719/ 11.3  $\mu$ M SQ1/ 1.67 mM CDCA.



**ESI Fig. 5** Box plots indicating the spread of data obtained from the systems studied. Fast, pump dyed and passively dyed N719/SQ1/CDCA systems are compared to N719 dyed passively. The graph shows the clear advantage of dyeing with N719/SQ1/CDCA via a fast pump method resulting in much higher and more consistent device efficiencies (PCEs). The dye concentrations used are 4.5 mM N719/ 11.3  $\mu\text{M}$  SQ1/ 1.67 mM CDCA (for both the passive and fast dyed devices) and for N719 only the concentration used was 4.5 mM.

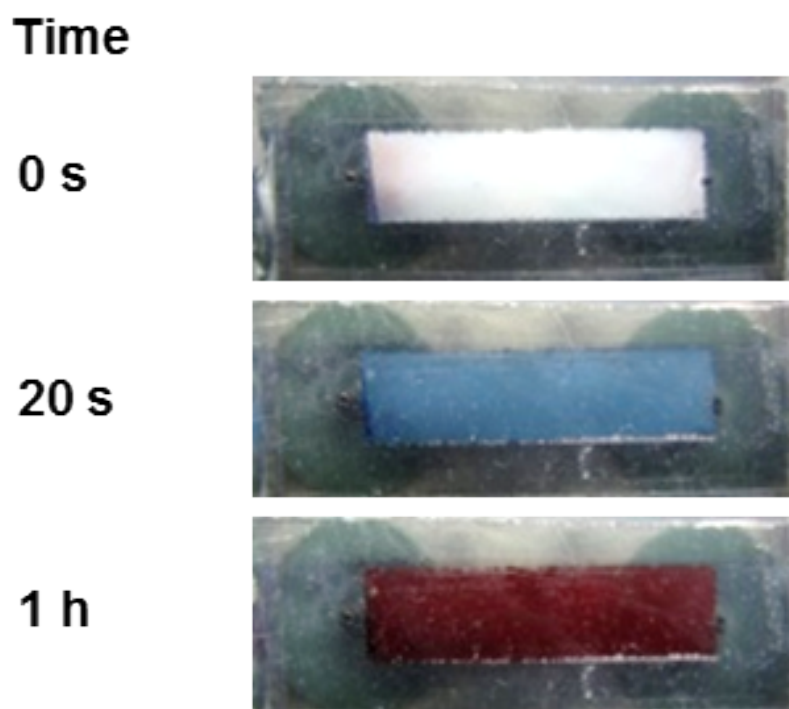


**ESI Fig.6** Diffuse reflectance UV of saturated TiO<sub>2</sub> films with SQ1 (red line) and SQ1/CDCA (blue line). The decrease of aggregation of the SQ1 due to the presence of CDCA is indicated by a narrower and higher absorbance.



**ESI Fig. 7** Contact angle pictures (from video) of N719 contacted with a TiO<sub>2</sub> film (a), and with a TiO<sub>2</sub> film dyed with SQ1/CDCA (b). The pictures show the difference in N719 wetting when the film is dyed with SQ1/CDCA (bottom) where the dye almost instantaneously

impregnates the film, whereas with bare TiO<sub>2</sub> (top) the dye sits on the surface for a longer time.



**ESI Fig. 8** Digital images of TiO<sub>2</sub> photo-electrode dyed with a mixture of N719 and SQ1 dyes at the times shown.

### **Acknowledgements**

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