

Electronic Supplementary Information

Ultra-fast Sensitization, Co-Sensitization and Tri-Sensitization of Dye-Sensitized Solar Cells with N719, SQ1 and Triarylamine Dyes

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This paper describes the synthesis of a new yellow triphenylamine dye (**6**) and the literature red (**5**)^{ESI-1} and the blue SQ1 dye^{ESI-1}. The performance of (**5**) and (**6**) in dye-sensitized solar cell (DSC) devices has been measured using I-V and EQE. This ESI contains characterisation data for (**5**) and SQ1. Details of the DSC devices prepared to illustrate the success of the method are also included along with an energy level diagram showing HOMO and Frank-Condon levels for (**6**) and N719 (ESI Fig. 2), EQE data for selected dyes (ESI Fig. 3), raw photo-acoustic data for (**6**) and N719 (ESI Fig. 4), UV-visible calibration data (ESI Fig. 5) and device photographs (ESI Fig. 6).

Experimental

Preparation of diphenyl(4-vinyl)-amine (**2**)^{ESI-1}

4-(*N,N*-Diphenylamino)-benzaldehyde (**1**) (7.5 g, 27.46 mmol) was dissolved in distilled THF (20 ml) under N₂ and added to a mixture of potassium *tert*-butoxide (4.62 g, 41.19 mmol) and methyl triphenyl phosphonium iodide (16.65 g, 41.19 mmol). This reaction mixture was stirred at RT for 24 h. The solution was then poured into distilled H₂O/CH₂Cl₂ (1:1, v/v) and the organic layer separated in a separating funnel, dried over anhydrous magnesium sulfate and the solvent removed *in vacuo*. The product was purified by column chromatography on silica gel in *n*-hexane/CH₂Cl₂

(95:5, v/v). The pure product was identified by TLC and precipitated in CH₂Cl₂/MeOH (1:20, v/v) to give a white solid. (Yield 5.40 g, 72.5%), mp 92-93 °C. Suitable but very small crystals for X-ray analysis were prepared by recrystallisation of **(2)** from CH₂Cl₂.

¹H NMR (500 MHz, DMSO-d₆) δ 5.15 (d, *J* = 11.0 Hz, 1H, H-CH=CH-), 5.69 (d, *J* = 17.6 Hz, 1H, H-CH=CH-), 6.66 (dd, *J* = 11.5, 10.7 Hz, 1H, CH₂=CH-), 6.92 (d, *J* = 8.5 Hz, 2H, =CH-*Ph*-N-), 7.00 (d, *J* = 8.5 Hz, 4H, -N-*Ph*₂), 7.04 (t, *J* = 7.55 Hz, 2H, -N-*Ph*₂), 7.29 (t, *J* = 7.8 Hz, 4H, -N-*Ph*₂), 7.37 (d, *J* = 8.2 Hz, 2H, =CH-*Ph*-N-). ¹³C NMR (500 MHz, DMSO-d₆) δ 112.60, 122.99, 123.16, 124.00, 127.24, 129.53, 131.47, 135.99, 146.91, 146.96. UV/vis (EtOH): λ_{max} 308 nm. KBr ν/cm⁻¹: ca. 3020, 2400, 1590, 1486, 1328. FTMS⁺-MS: (Accurate Mass), reference compound: NH₄OAc, calcd. for C₂₀H₁₇N 272.1437; found 272.1468 [M+H]⁺.

Preparation of 4-[2-(4-diphenylaminophenyl)vinyl]benzaldehyde (**3**)^{ESI-1}

Compound **(2)** (3 g, 11.06 mmol) was added to a mixture of 4-bromobenzaldehyde (0.93g, 5.02 mmol), sodium carbonate (1.33 g, 12.56 mmol), 2,6-di-*tert*-butylcresol (0.22 g, 1.00 mmol) and *trans*-di(μ-acetato)bis[*O*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (47.1 mg, 0.05 mmol) in anhydrous *N,N*-dimethylacetamide (DMAC) (20 ml) and the solution was stirred at 130 °C for 24 h. After cooling, the solution was poured into distilled H₂O/CH₂Cl₂ (1:1 v/v) and the mixture separated in a separating funnel. The organic layer was then dried over anhydrous magnesium sulfate, the solvent removed *in vacuo* and the product purified by column chromatography on silica gel with petroleum spirit/CH₂Cl₂ (95:5, v/v). The product was identified by TLC and the solvent removed *in vacuo* followed by precipitation in MeOH to give a yellow solid. Yield 2.0 g, 48%, mp 144-146°C. Suitable crystals for X-ray analysis were prepared by recrystallisation of **(3)** from CH₂Cl₂.

¹H NMR (500 MHz, DMSO-d₆) δ 6.95 (d, *J* = 8.5 Hz, 2H, -*Ph*-N-*Ph*₂), 7.05 (d, *J* = 8.2 Hz, 4H, -N-*Ph*₂), 7.08 (t, *J* = 8.2 Hz, 2H, -N-*Ph*₂), 7.19 (d, *J* = 16.4 Hz, 1H, -CH=CH-*Ph*-), 7.32 (t, *J* = 7.8 Hz, 4H, -N-*Ph*₂), 7.41 (d, *J* = 16.4 Hz, 1H, -CH=CH-*Ph*-), 7.55 (d, *J* = 8.5 Hz, 2H, -*Ph*-N-*Ph*₂), 7.77 (d, *J* = 8.2 Hz, CHO-*Ph*-CH=), 7.88 (d, *J* = 8.2 Hz, 2H, CHO-*Ph*-CH=), 9.97 (s, 1H, CHO-*Ph*-). ¹³C NMR (500 MHz, DMSO-d₆) δ 122.36, 123.54, 124.44, 125.40, 126.66, 128.13, 129.62, 130.00, 130.40, 131.51, 134.69, 143.47, 146.75, 147.44, 192.25. UV/vis (EtOH): λ_{max} 300 nm, 400 nm. FT-IR (KBr) ν/cm⁻¹ 2924, 2853, 1695, 1586, 1166. FTMS⁺-MS: m/z (Accurate Mass), reference compound: NH₄OAc, calcd. for C₂₇H₂₁NO 376.1696; found 376.1699 [M+H]⁺.

Preparation of 2-cyano-3-{4-[2-(4-diphenylaminophenyl)vinyl]phenyl}acrylic acid (**5**)^{ESI-1}

Compound **(3)** (0.5 g, 1.33 mmol) was dissolved in acetonitrile (20 ml) and cyanoacetic acid (2.27g, 26.63 mmol). Piperidine (1 ml) was added and the mixture was stirred at 90°C for 24 h under N₂.

After cooling, the solution was poured into a mixture of CH₂Cl₂/H₂O (pH was adjusted to 2 by addition of phosphoric acid). The mixture was separated using a separating funnel, and the organic layer removed *in vacuo* and subsequently dried over anhydrous sodium sulfate. The crude product was purified by column chromatography over silica gel using CHCl₃/MeOH (9.7:0.3, v/v) as eluent, followed by precipitation in methanol to give (**5**) as a red solid. Yield 0.35g, 60.3 %, mp 210-212°C.

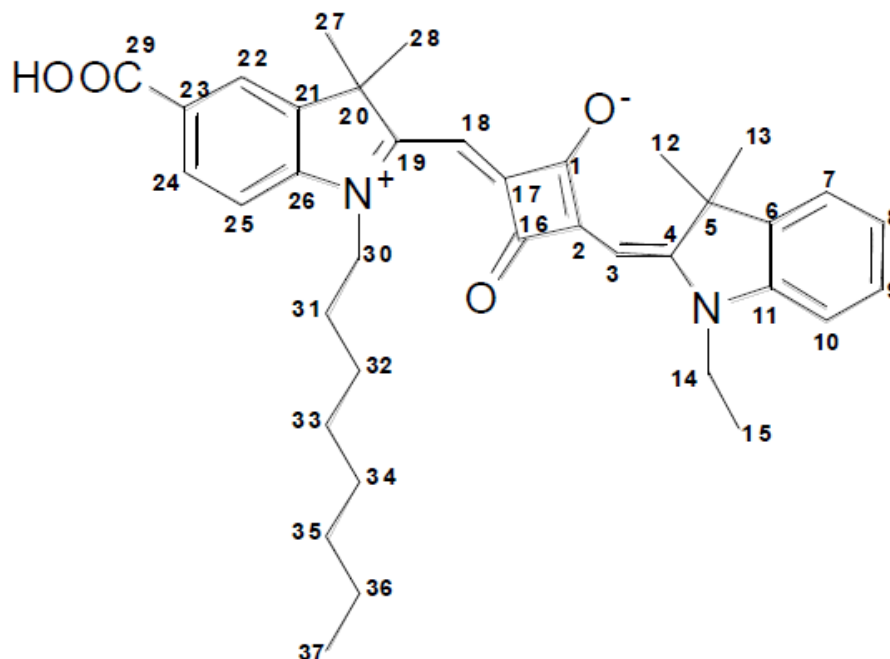
¹H NMR (500 MHz, DMSO-d₆) δ 6.96 (d, *J* = 8.5 Hz, 2H, -*Ph*-N-*Ph*₂), 7.06 (m, 6H), 7.22 (d, *J* = 16.4 Hz, 1H, -CH=CH-*Ph*-), 7.31 (t, *J* = 7.6 Hz, 4H, -N-*Ph*₂), 7.39 (d, *J* = 8.15 Hz, 1H, -CH=CH-*Ph*-), 7.51 (d, *J* = 8.5 Hz, 2H, -*Ph*-N-*Ph*₂), 7.76 (d, *J* = 8.5 Hz, 2H, =CH-*Ph*-CH=), 8.04 (d, *J* = 8.55 Hz, 2H, =CH-*Ph*-CH=), 8.28 (s, 1H, -C=CH-*Ph*). ¹³C NMR (500 MHz, DMSO-d₆) δ 118.54, 122.98, 123.25, 124.14, 124.47, 126.25, 126.50, 126.77, 127.62, 127.73, 129.55, 129.62, 131.26, 136.96, 138.48, 146.95, 165.00. UV/vis (EtOH): λ_{max}. 298 nm (ε = 25,000 M⁻¹cm⁻¹) and 370 nm (ε = 35,000 M⁻¹cm⁻¹), ε values are precise to ±0.5×10³ M⁻¹ cm⁻¹. FT-IR (KBr) ν/cm⁻¹ 3450, 3028, 2251, 1732, 1587, 1490, 1281, 1174. FTMS⁺-MS: *m/z* (Accurate Mass), reference compound: NH₄OAc, calcd for C₃₀H₂₂N₂O₂ 443.1754; found 443.1751 [M+H]⁺.

Preparation of SQ1; 5-Carboxy-2-[[3-[(1,3-dihydro-3,3-dimethyl-1-ethyl-2H-indol-2-ylidene)methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-3,3-trimethyl-1-octyl-3H-indolium^{ESI-2}

3-[(1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-4-hydroxy-cyclobutene-1,2-dione (4 g, 13 mmol) and 5-Carboxy-2, 3, 3-trimethyl-1-octyl-3H-indolium iodide (4.9 g, 15 mmol) were dissolved in a mixture of benzene (50 ml) and *n*-butanol (50 ml). The mixture was refluxed with a Dean-Stark apparatus for 18 h. The solvent was partly removed until the product precipitated. The crude product was filtered off and purified by column chromatography (methylene chloride:methanol = 97:3). 5.9 g (80 %); m.p. = 288 °C.

¹H NMR (500 MHz, Methanol-d₄) 0.88 (t, *J* = 13 Hz, 3H, H37), 1.32-1.19 (overlapping peaks, 8H, H-33+34+34+36), 1.43 (t, *J* = 15 Hz, 3H, H-15), 1.47 (m, 3H, H-32), 1.82-1.78 (overlapping peaks, 14H, H-12+13+27+28+31), 4.12 (m, 2H, H-30), 4.26 (q, *J* = 21 Hz, 2H, H-14), 5.99 (s, 1H, H-18); 6.08 (s, 1H, H-3), 7.23 (m, 1H, H-25), 7.28 (m, 1H, H-8), 7.33 (m, 1H, H-10), 7.42 (m, 1H, H-9), 7.51 (m, 1H, H-7), 8.04 (m, 1H, H-22), 8.05 (m, 1H, H-24). MS (FTMS +) [M + H]⁺ calculated = 581, [M + H]⁺ observed = 581, *m/e* Accurate Mass (FTMS +), reference compound: NH₄OAc, [M + H]⁺ calculated = 581.3374, M⁺ observed = 581.3362. Anal. Calcd for C₃₇H₄₄N₂O₄: C, 76.34; H, 7.64; N, 4.80; O, 11.02. Found: C, 76.17; H, 7.85; N, 4.63; O, 11.11.

UV-Visible λ_{max} 645 nm ($295000 \text{ M}^{-1}\text{cm}^{-1}$) in ethanol.



ESI Figure 1. Carbon labelling of SQ1 used for NMR assignments based on [ESI-2]

Device Examples

Device A - A titania photo-electrode was submersed in an ethanol solution containing **(6)** (0.1 mM) for a period of 18 hours. The electrode was then removed from the dye solution and the cell was constructed as described for passive dyeing.

Device B - A titania photo-electrode was submerged in an ethanol solution containing **(5)** (0.1 mM) for a period of 18 hours. The electrode was then removed from the dye solution and the cell was constructed as described for passive dyeing.

Device C - A titania photo-electrode was submersed in an acetonitrile:*tert*-butanol (1:1 v/v) solution containing N719 (0.5 mM) for a period of 18 hours. The electrode was then removed from the dye solution and the cell was constructed as described for passive dyeing.

Device D - 1.5 ml of **(6)** (2 mM) in ethanol was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C followed by electrolyte at ambient temperature.

Device E - 1.5 ml of **(5)** (2 mM) in ethanol was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C followed by electrolyte at ambient temperature.

Device F - 1.5 ml of a mixture of SQ1 (0.05 mM) and CDCA (5 mM) in ethanol was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C followed by electrolyte at ambient temperature.

Device G - 1.5 ml of N719 dye in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol (8.6 mM) was pumped through the DSC cell over a period of 5 minutes at a temperature of 50 °C followed by electrolyte at ambient temperature.

Device H - 1.5 ml of **(6)** (2 mM) in ethanol was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C followed by the addition of 1.5 ml of N719 dye in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol (8.6 mM), also pumped for 5 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

Device I - 1.5 ml of **(5)** (2 mM) in ethanol was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C followed by the addition of 1.5 ml of N719 dye in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol (8.6 mM), also pumped for 5 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

Device J - 1.5 ml of **(6)** (2 mM) in ethanol was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C followed by 1.5 ml of **(5)** (2 mM) in ethanol also pumped for 5 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

Device K - 1.5 ml of **(6)** (2 mM) in ethanol was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C followed by 1.5 ml of SQ1 (0.05 mM) and CDCA (5 mM) in ethanol also pumped for 5 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

Device L - 1.5 ml of **(6)** (2 mM) in ethanol was pumped through the DSC cell cavity followed by 1.5 ml of N719 dye in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol (8.6 mM) followed by 1.5 ml of SQ1 (0.05 mM) and CDCA (5 mM) in ethanol. Each dye solution was pumped for 5 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

Device M - 1.5 ml of **(6)** (2 mM) in ethanol was pumped through the DSC cell cavity followed by 1.5 ml of **(5)** (2 mM) followed by 1.5 ml of SQ1 (0.05 mM) and CDCA (5 mM) in ethanol. Each dye solution was pumped for 5 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

Calibration of UV-visible spectrometer to measure dye loadings

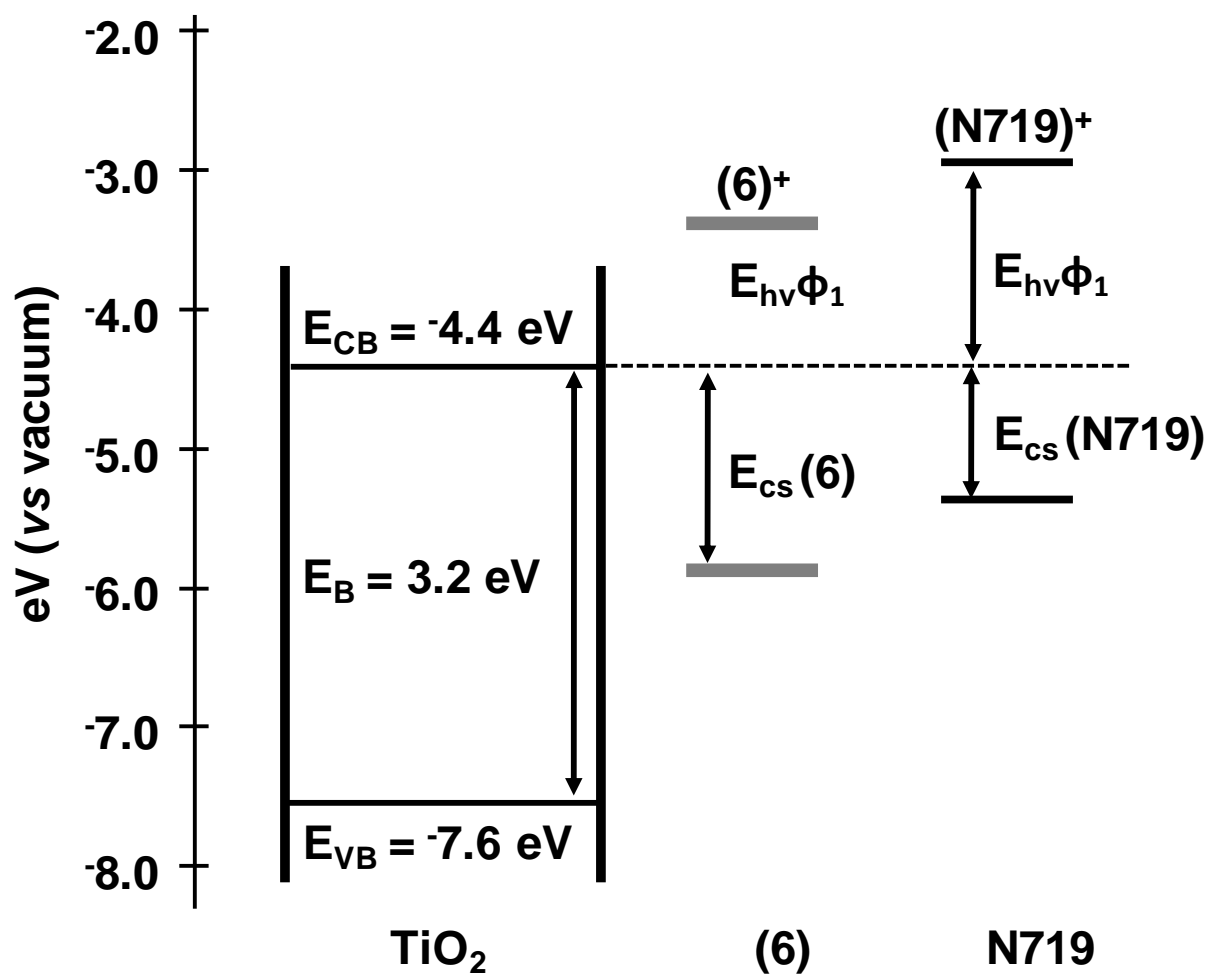
A calibration graph for **(6)** was created by dissolving **(6)** in ethanol and measuring the absorbance of the solution in quartz cuvettes (1 cm path-length) at $\lambda = 384$ nm on a Perkin Elmer 35 UV-visible spectrometer giving $\epsilon = 32,349 \text{ L cm}^{-1} \text{ mol}^{-1}$ (ESI Fig. 5a). A similar graph was created for N719 by measuring Absorbance at $\lambda_{\text{max}} = 520$ nm (ESI Fig. 5b) giving $\epsilon = 13,312 \text{ L cm}^{-1} \text{ mol}^{-1}$. However, a second graph for N719 was created using data at 384 nm (i.e. the λ_{max} of **(6)**) coincidentally giving the same ϵ value as for the data at 520 nm. This procedure was carried out because both N719 and **(6)** absorb at 384 nm; hence, for mixed solutions of **(6)** and N719 desorbed from co-sensitized devices, any absorbance from N719 could be subtracted from the data by first recording the N719 concentration at 520 nm, then calculating the value at 384 nm and subtracting this from the experimental value to give a more accurate concentration of **(6)**.

Acknowledgements

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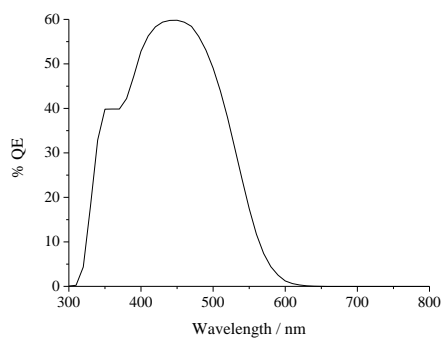
References

- [ESI-1] S. Hwang, J-H. Lee, Cha. Park, H. Lee, Cha. Kim, Chi. Park, M-H. Lee, W. Lee, J. Lee, K. Kim, Chu. Kim, *Chem. Commun.*, **2007**, 4887.
- [ESI-2] A. Burke, L. Schmidt-Mende, S. Ito and M. Grätzel, *Chem. Commun.*, 2007, 234.

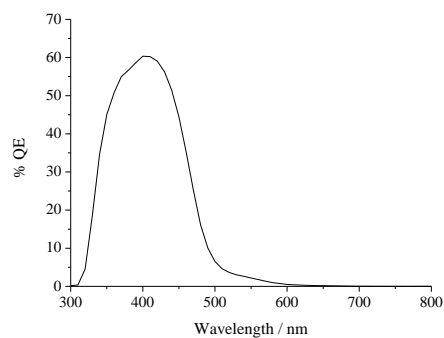


ESI Figure 2. Charge separation energies (E_{cs}), HOMO and Frank-Condon levels for **(6)** and N719

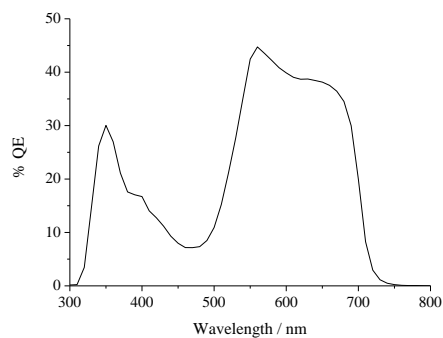
where E_{hv} is the laser energy ($\lambda = 495 \text{ nm}$) and ϕ_1 is the fraction of heat released



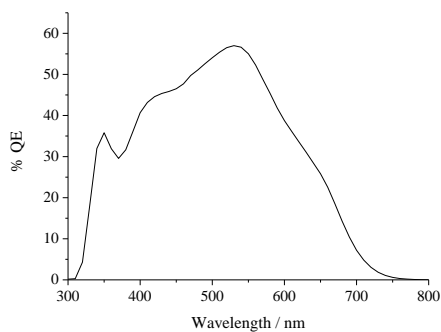
ESI Fig. 3a EQE of **(5)**



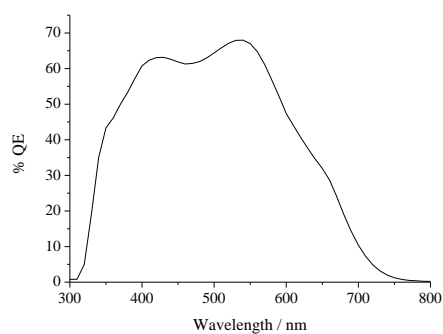
ESI Fig. 3b EQE of **(6)**



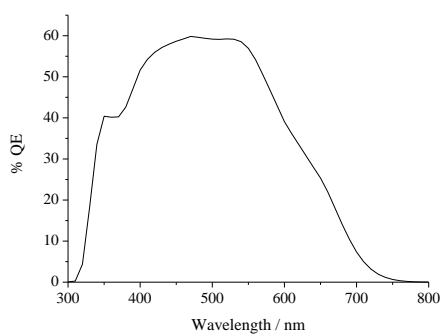
ESI Fig. 3c ESE of SQ1



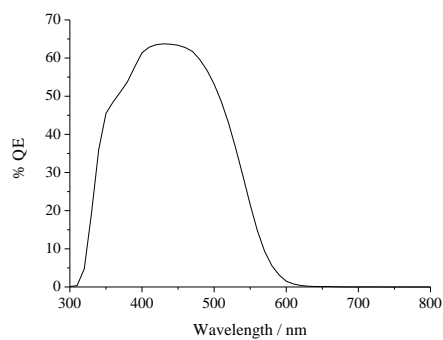
ESI Fig. 3d EQE of N719



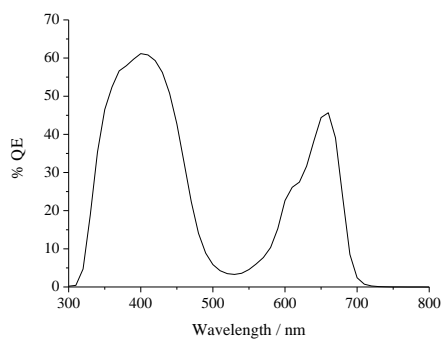
ESI Fig. 3e EQE for (6) + N719



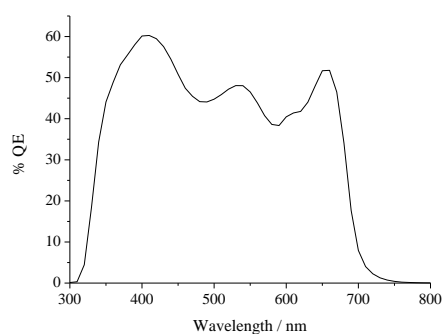
ESI Fig. 3f EQE for (5) + N719



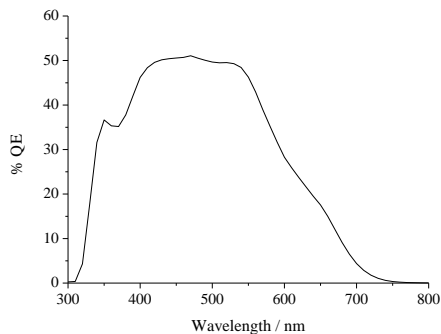
ESI Fig. 3g EQE for (5) + (6)



ESI Fig. 3h EQE for (6) + SQ1



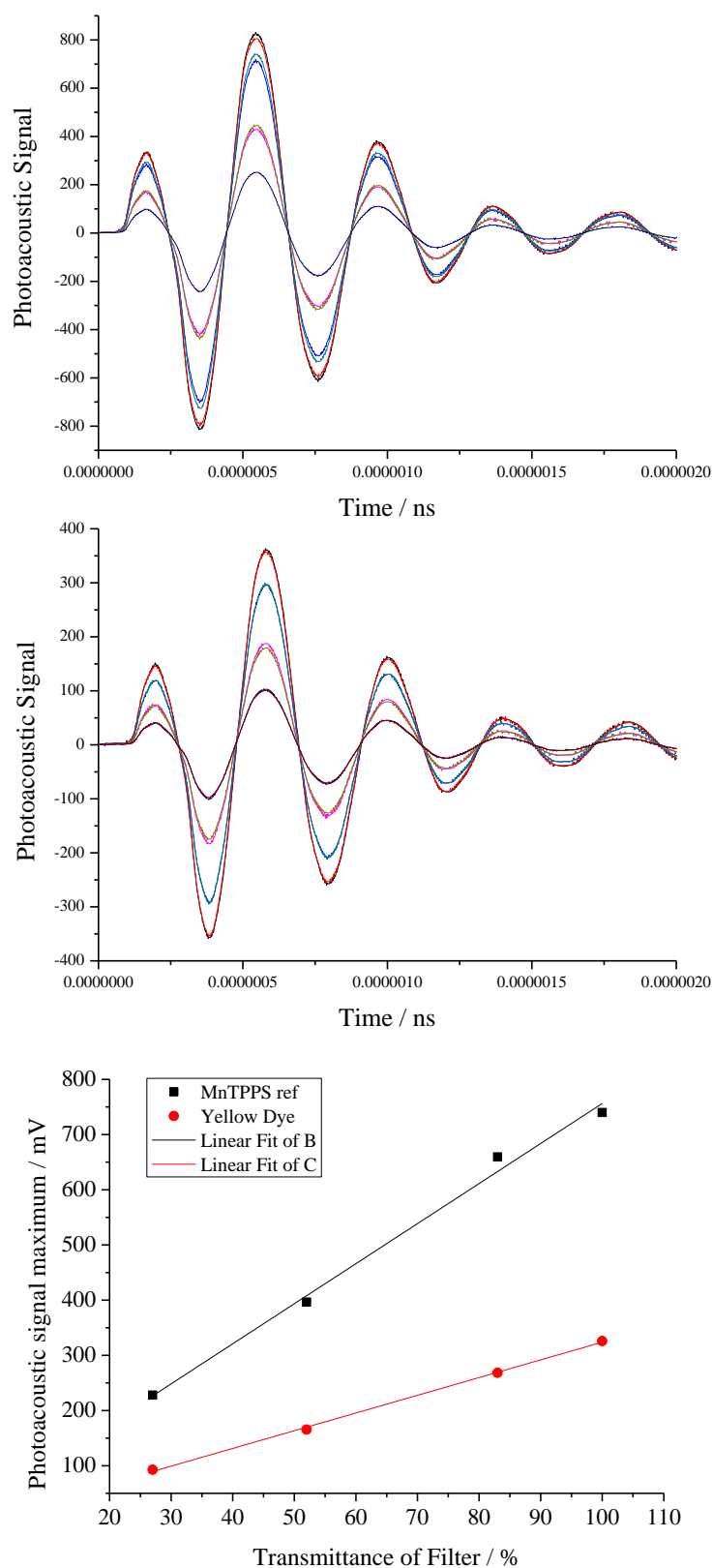
ESI Fig. 3i EQE for (6) + SQ1 + N719



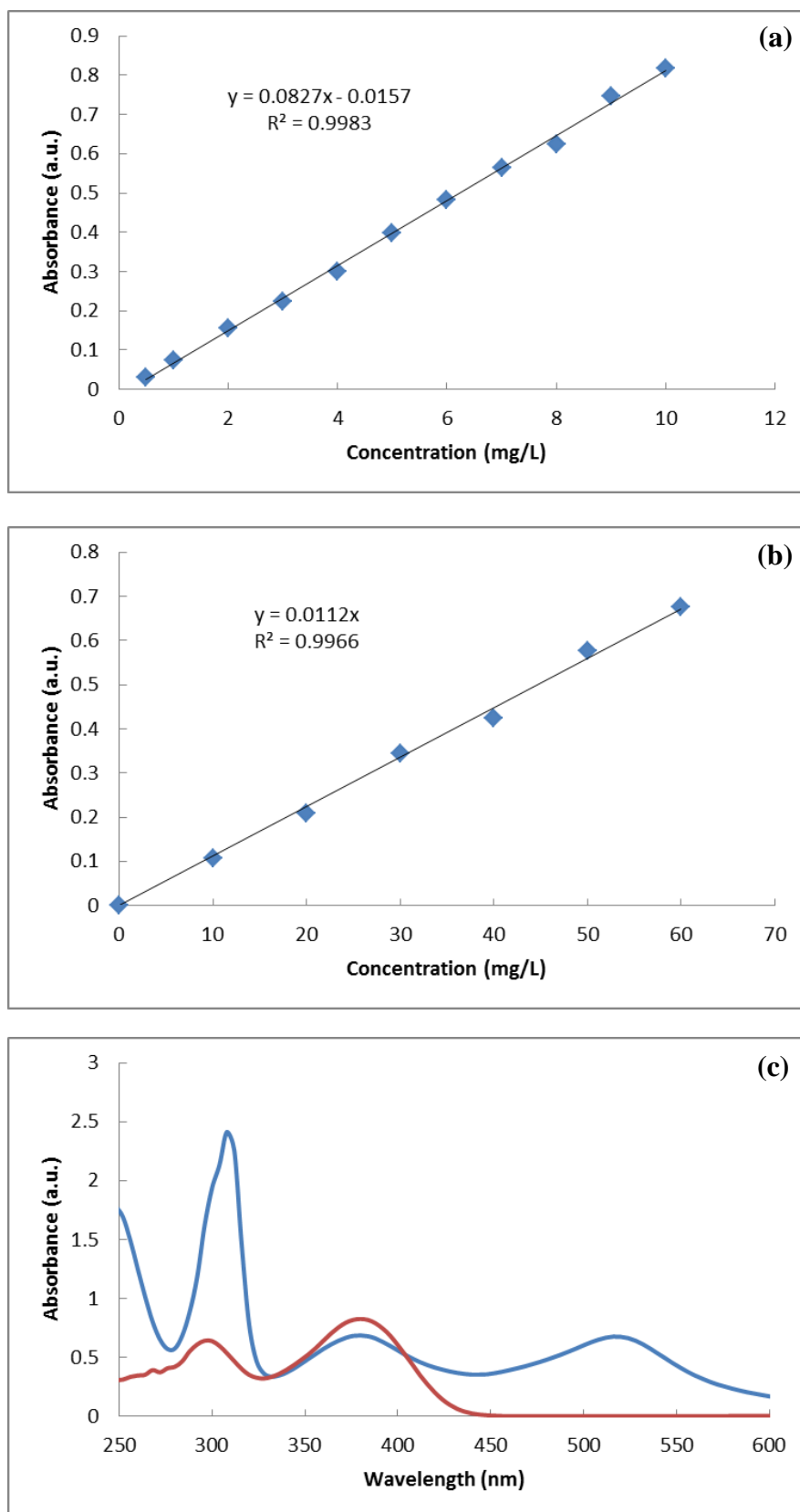
ESI Fig. 3j EQE for (6) + (5) + N719

ESI Figure 3. Spectral response of DSC devices

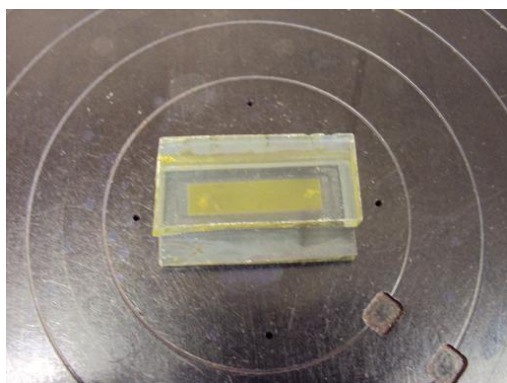
Raw Data from Photoacoustic Calorimetry (PAC) Measurements



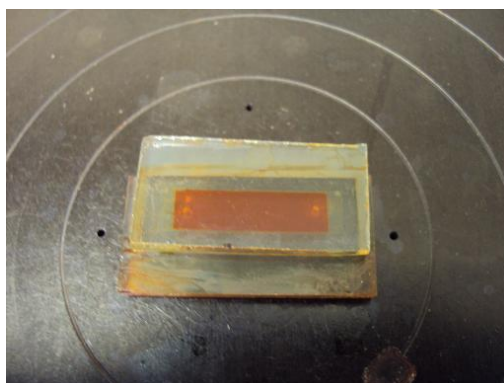
ESI Figure 4. Photoacoustic signals of glass-supported TiO_2 films dyed with (top) reference dye MnTPPS and (middle) (6) at different laser intensities, and (c) PAC signals plotted *versus* laser intensity as denoted by %T of filter.



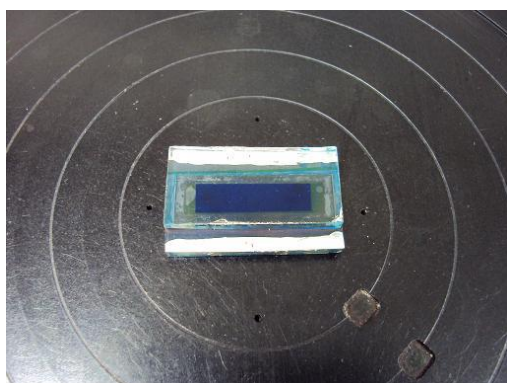
ESI Figure 5: Calibration graphs of (a) Absorbance at 384 nm *versus* concentration for **(6)** in ethanol giving a molar extinction coefficient for **(6)** of $32,349 \text{ L cm}^{-1} \text{ mol}^{-1}$ and (b) Absorbance at 520 nm *versus* concentration for N719 in ethanol giving a molar extinction coefficient for N719 of $13,312 \text{ L cm}^{-1} \text{ mol}^{-1}$ (an identical graph was plotted for N719 using data at $\lambda = 384 \text{ nm}$) and (c) UV-visible spectra of 10 mg/L of **(6)** - red line and 60 mg/L N719 - blue line.



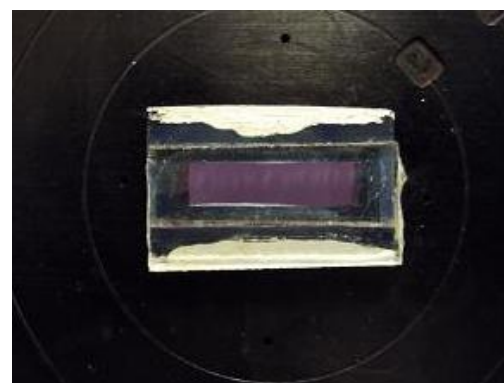
Device D dyed with (6)



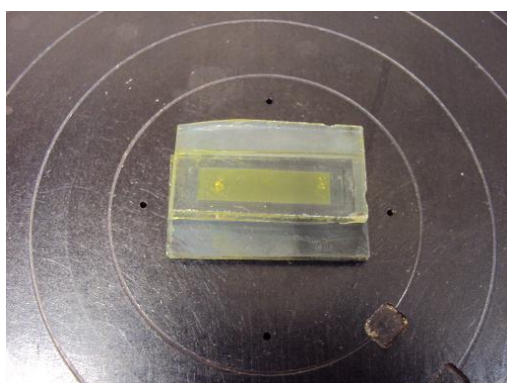
Device E dyed with (5)



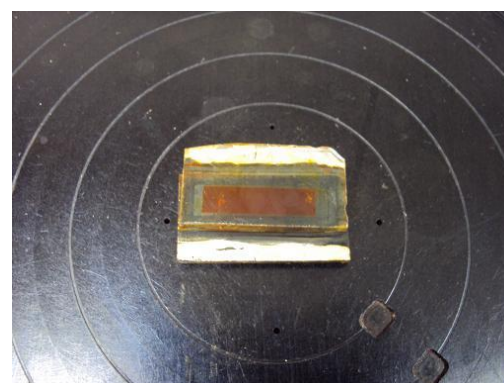
Device F dyed with SQ1



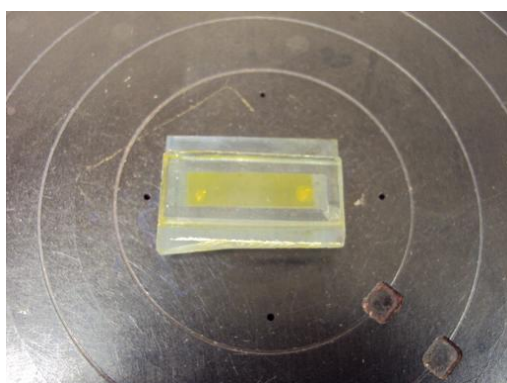
Device G dyed with N719



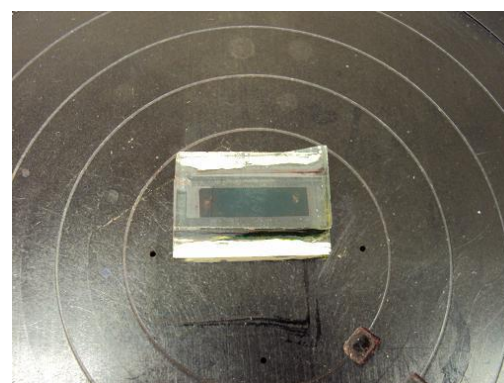
Device J dyed with (6)



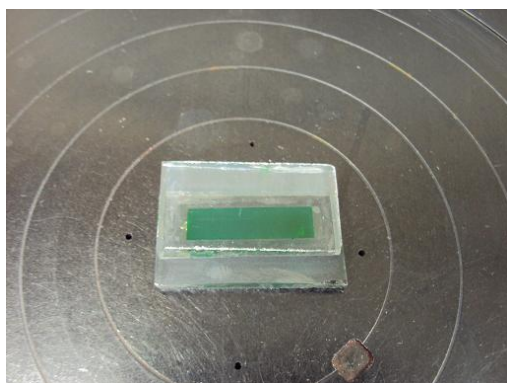
Device J after adding (5)



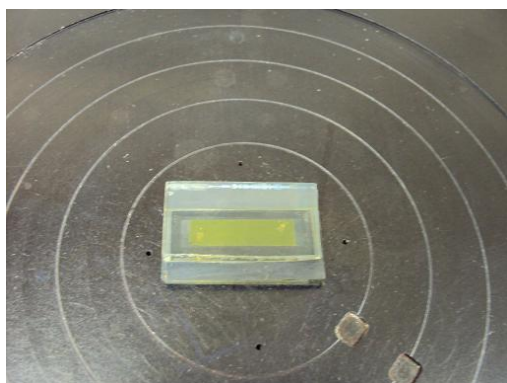
Device H1 dyed with (6)



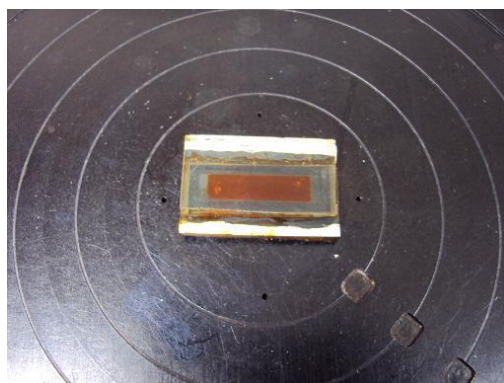
Device H1 after adding N719



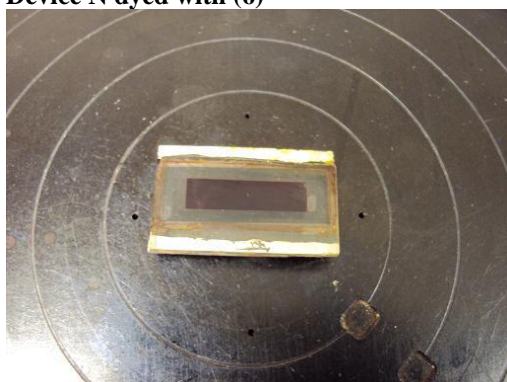
Device K dyed with mixture of (6) YD and SQ1



Device N dyed with (6)



Device N after adding (5)



Device N after adding N719

ESI Figure 6. Photographs of selected devices (2 x 0.5 cm)