Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

SUPPORTING INFORMATION

Multiple linker Half-squarylium Dyes for Dye-Sensitized Solar Cells; Are Two Linkers Better than One?

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Experimental

3,4-Diethoxy-3-cyclobutene-1,2-dione (1) [ESI-1]

Squaric acid (5 g, 44 mmol) was suspended in ethanol (50 ml) and refluxed for 3 h. The reaction was cooled to RT and the solvent was removed *in vacuo*. The white solid material obtained from the reaction was dissolved in ethanol (50 ml), the mixture was heated under reflux for 30 min and the solvent was removed *in vacuo*. This step was repeated three times. The product was used without any further purification (Yield 7.48 g, quantitative).

^{1}H NMR spectrum (500 MHz, DMSO-d$_6$): δ 1.38 (t, J=14.2 Hz, 3H, CH_3-CH$_2$-O-); 4.65 (q, J=20.2 Hz, 2H, CH$_3$-CH_2-O-).
^{13}C NMR (101 MHz, DMSO-d$_6$): δ 15.1; 70.1; 183.6; 189.0.
MS (FTMS +) M$^+$ calculated = 171, M$^+$ observed = 171, *m/e* Accurate Mass (FTMS +), reference compound: NH$_4$OAc, M$^+$ calculated = 171.0652, M$^+$ observed = 171.0650.

3-(2-Carboxyethyl)-1,1,2-trimethyl-1H-benzo[e]indolium iodide (2) [ESI-2]

A mixture of 1,1,2-trimethyl-1H-benzo[e]indole (2 g, 9.5 mmol) and 3-iodopropionic acid (3 g, 15 mmol) was heated under reflux overnight under nitrogen in anhydrous acetonitrile (80 ml).

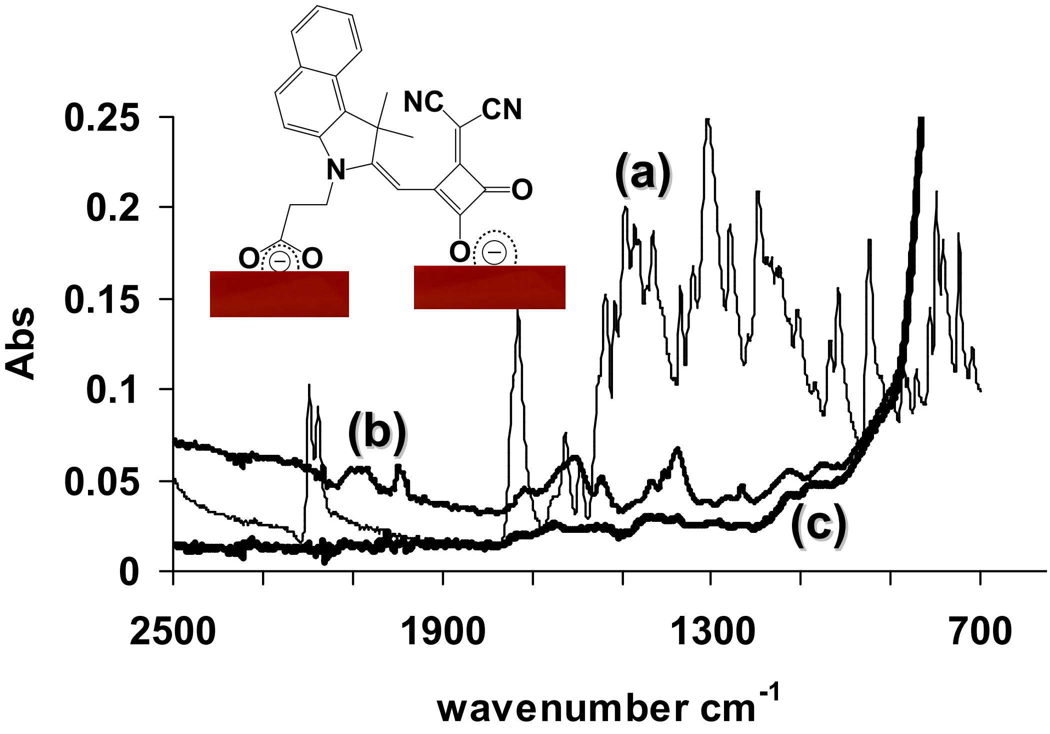
After cooling, the solvent was removed *in vacuo* and the product was re-crystallized from methanol to give a tan solid. (Yield 2.42 g, 90%).

^{1}H NMR (400 MHz, DMSO) δ 1.62 (s, 2H), 1.76 (s, 13H), 2.51 (d, J = 1.6 Hz, 2H), 2.61 (s, 1H), 2.99 (s, 6H), 3.06 (t, J = 6.9 Hz, 5H), 4.79 (t, J = 6.9 Hz, 5H), 7.63 – 7.85 (m, 5H), 8.14 – 8.33 (m, 7H), 8.38 (d, J = 8.3 Hz, 2H).
^{13}C NMR (101 MHz, DMSO) δ 14.8, 15.4, 21.9, 22.3, 31.8, 44.3, 55.7, 56.1, 113.9, 117.3, 123.4, 123.9, 126.2, 127.7 (2 signals), 127.9, 128.4, 128.9, 130.1 (2 signals), 130.2, 131.1, 132.8, 133.5, 137.3, 138.5, 138.8, 172.0, 198.2.
MS (FTMS +) $[M + H]^+$ calculated = 283, $[M + H]^+$ observed = 283, *m/e* Accurate Mass (FTMS +), reference compound: NH_4OAc, $[M + H]^+$ calculated = 282.1489, $[M + H]^+$ observed = 282.1490

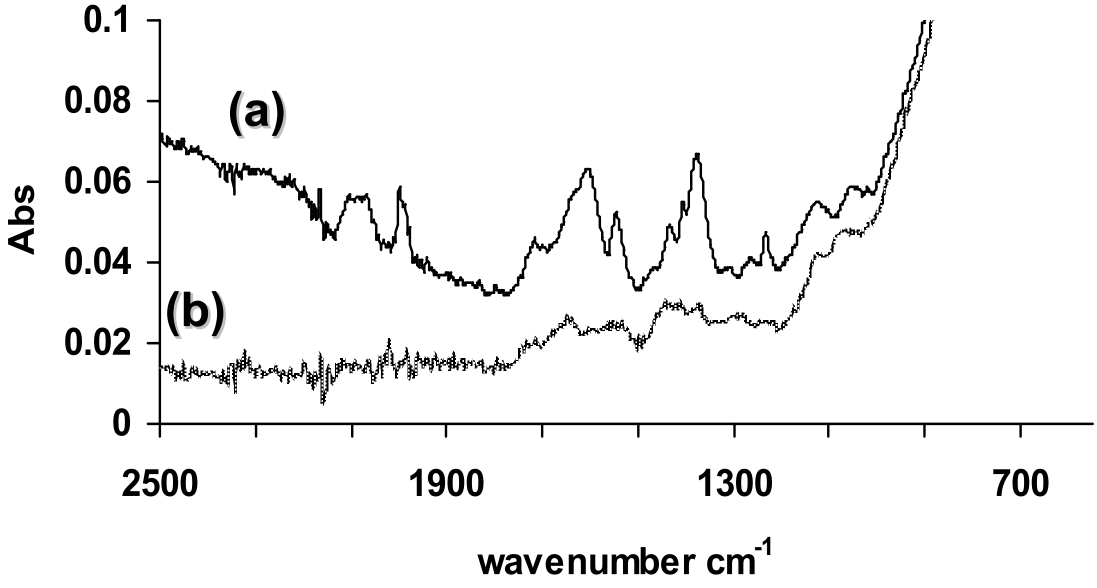
Preparation of 3-Ethoxy-(1-Carboxyethyl)-1,1,2-trimethyl-1H-benzo[e]indolium iodide -2-ylidene)methyl]-3-cyclobutene-1,2-dione (3) $^{\mathbf{ESI\text{-}3}}$

Compounds (**3**), (**7**) and **(10)** were prepared using (**2**), (**6**) and **(9)** respectively. In addition, (**6a**) and (**6b**) were prepared using (**5a**) and (**5b**). A typical procedure is described for the preparation of **(3)**. A mixture of 3,4-diethoxy-3-cyclobutene-1,2-dione (**1**) (1.8 g, 11 mmol), 3-(2-Carboxyethyl)-1,1,2-trimethyl-1H-benzo[e]indolium iodide (3.1 g, 11 mmol) and triethylamine (1.5 ml, 11.5 mmol) was heated under reflux in ethanol (30 ml) for 30 min. The solvent was removed *in vacuo* and the product was obtained as an orange solid after purification by column chromatography (SiO_2) with ethyl acetate and petrol as eluent.
(3 g, 70 %)
^{1}H NMR (400 MHz, THF) δ 1.42 (t, J = 7.3 Hz, 8H), 1.47 – 1.89 (m, 38H), 1.94 (s, 13H), 2.08 (s, 1H), 2.76 (t, J = 7.3 Hz, 5H), 3.16 (q, J = 7.3 Hz, 6H), 3.30 (s, 1H), 3.62 (s, 23H), 4.32 (t, J = 7.3 Hz, 5H), 4.90 (q, J = 7.1 Hz, 5H), 5.53 (s, 2H), 7.35 (t, J = 7.5 Hz, 3H), 7.46 – 7.58 (m, 5H), 7.89 (dd, J = 8.3 Hz, 5.7, 5H), 8.22 (d, J = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, THF) δ 5.83, 13.37, 24.18, 28.53, 36.63, 43.61, 47.56, 67.60, 79.00, 108.23, 120.23, 121.28, 124.79, 126.79, 127.34, 127.59, 129.09, 129.82, 138.01, 166.88, 169.68, 171.21, 185.32, 186.53, 189.90. MS (FTMS +) $[M + H]^+$ calculated = 406, $[M + H]^+$ observed = 406, *m/e* Accurate Mass (FTMS +), reference compound: NH_4OAc, $[M + H]^+$ calculated = 406.1649, $[M + H]^+$ observed = 406.1647. FT-IR (ATR) ν/cm^{-1} 3543-3060 (s), 2978 (w), 1738 (s), 1707 (s). UV-Visible $\lambda_{max.}$ 440 nm (116000 $M^{-1}cm^{-1}$) in ethanol.

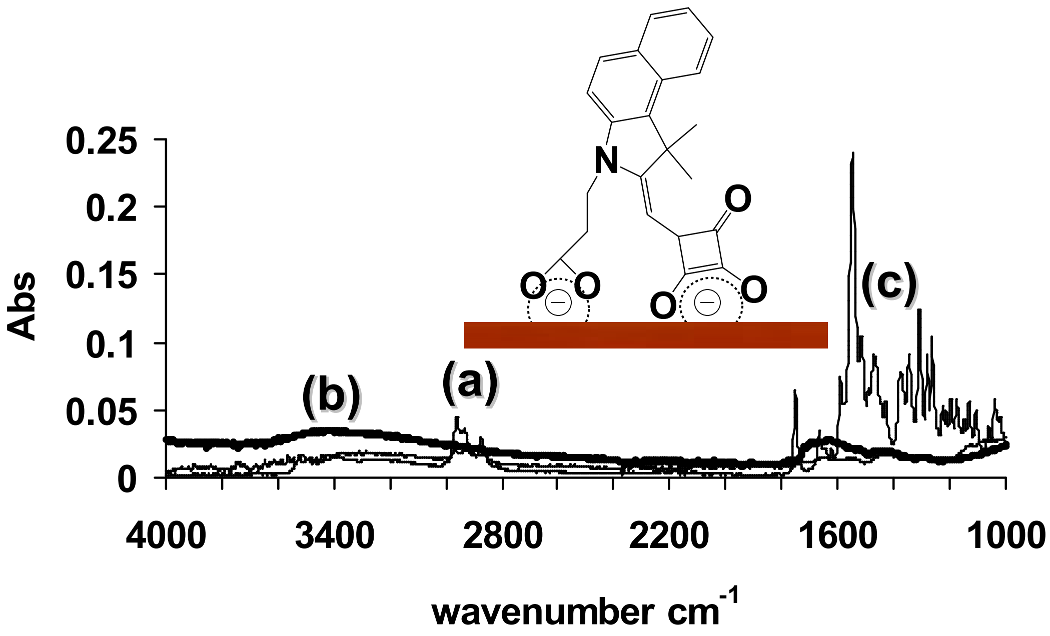
ATR Spectroscopy of Multiple Linker HfSQ Dyes



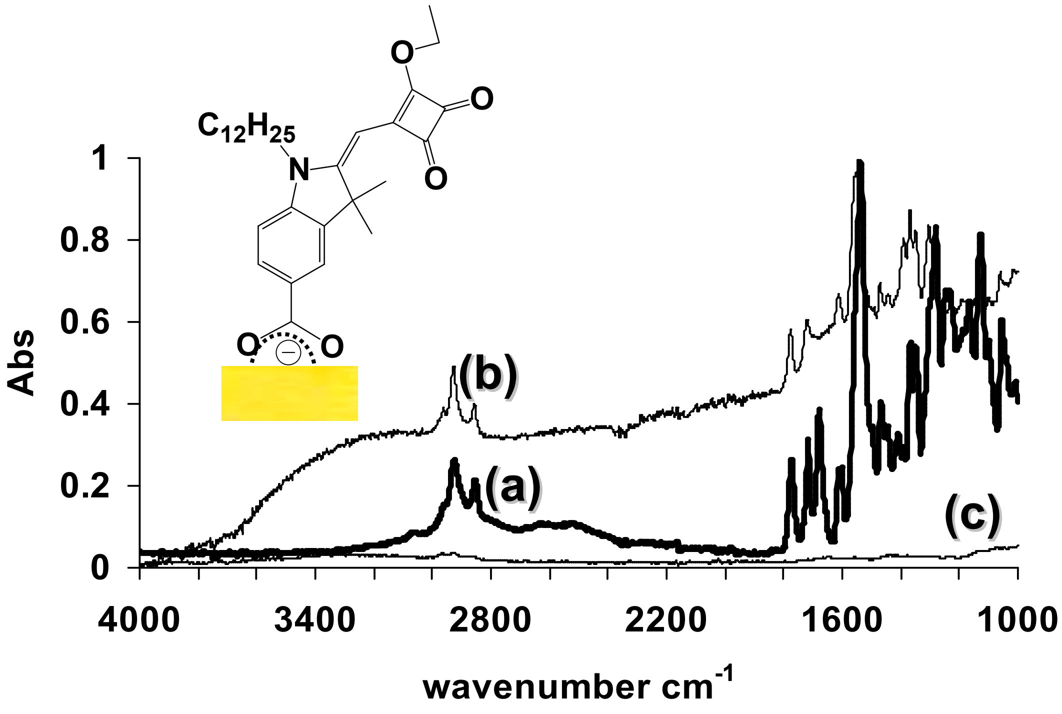
ESI Fig. 1. Infrared spectra of (**4**) (a) as powder, (b) adsorbed to a TiO_2 titania film and (c) an un-dyed TiO_2 film



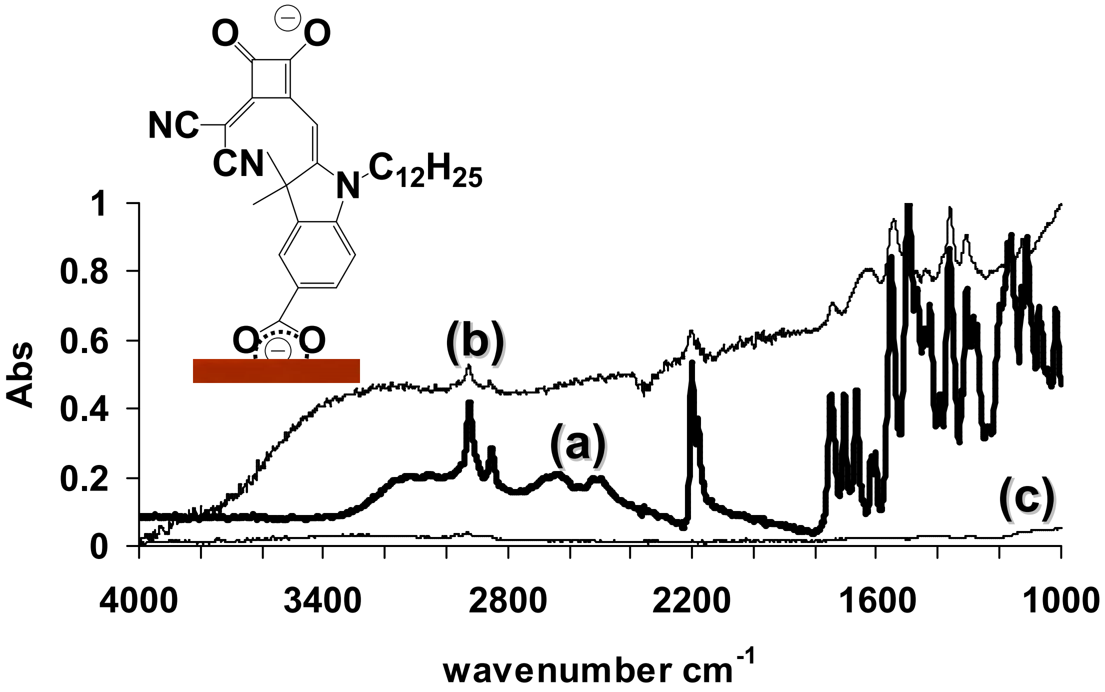
ESI Fig. 2. Expanded section of IR spectra of (**4**) (a) adsorbed to a TiO_2 film and (b) an un-dyed TiO_2 film



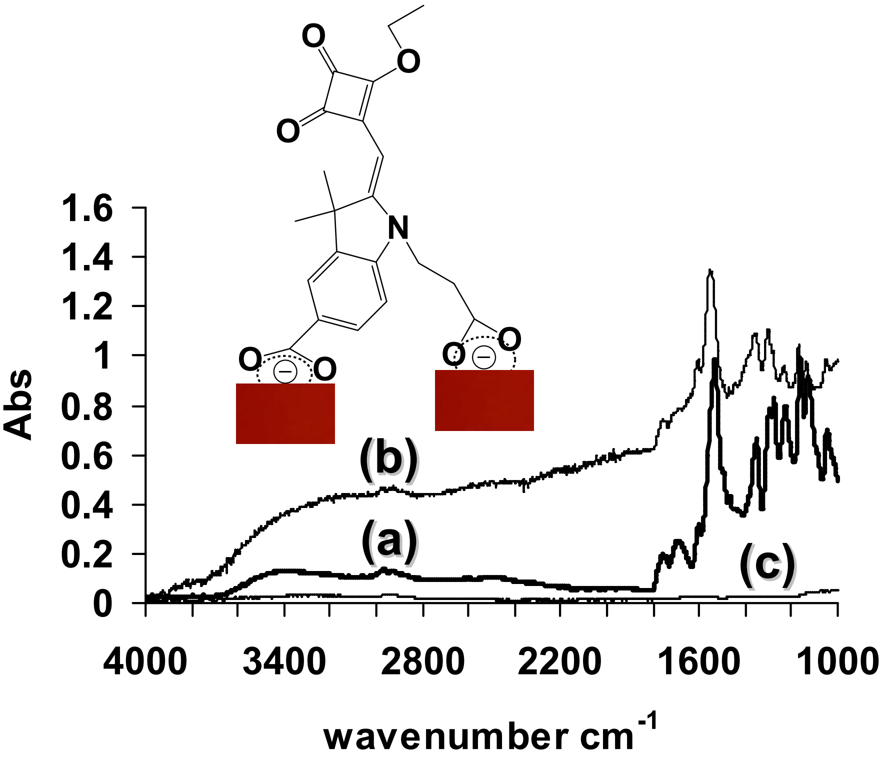
ESI Fig. 3. Infrared spectra of (**5**) (a) as powder, (b) adsorbed to a TiO_2 film and (c) an un-dyed TiO_2 film



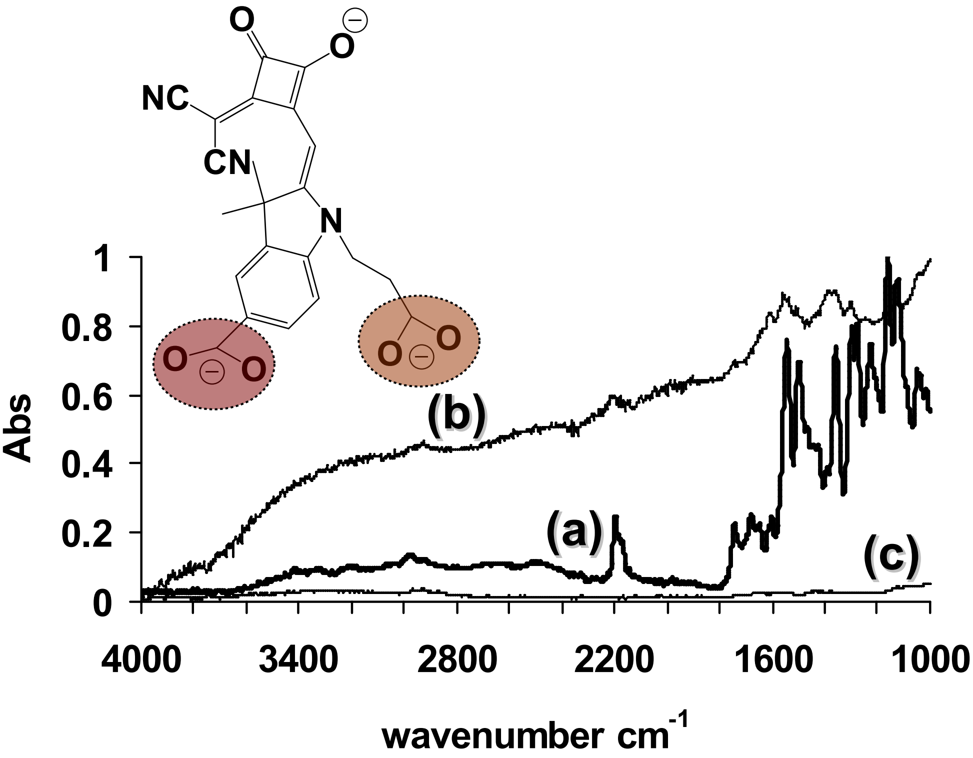
ESI Fig. 4. Infrared spectra of (7) (a) as powder, (b) adsorbed to a TiO_2 film and (c) an un-dyed TiO_2 film



ESI Fig. 5. Infrared spectra of (**8**) (a) as powder, (b) adsorbed to a TiO_2 film and (c) an un-dyed TiO_2 film

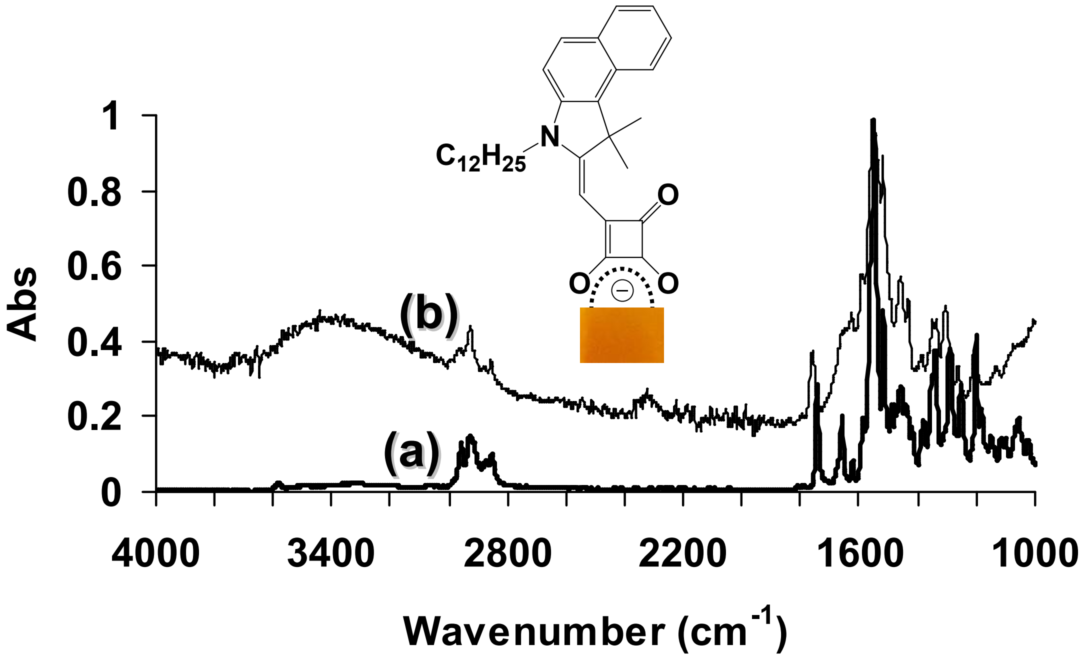


ESI Fig. 6. Infrared spectra of (**10**) (a) as powder sample, (b) adsorbed to a TiO_2 film and (c) an un-dyed TiO_2 film

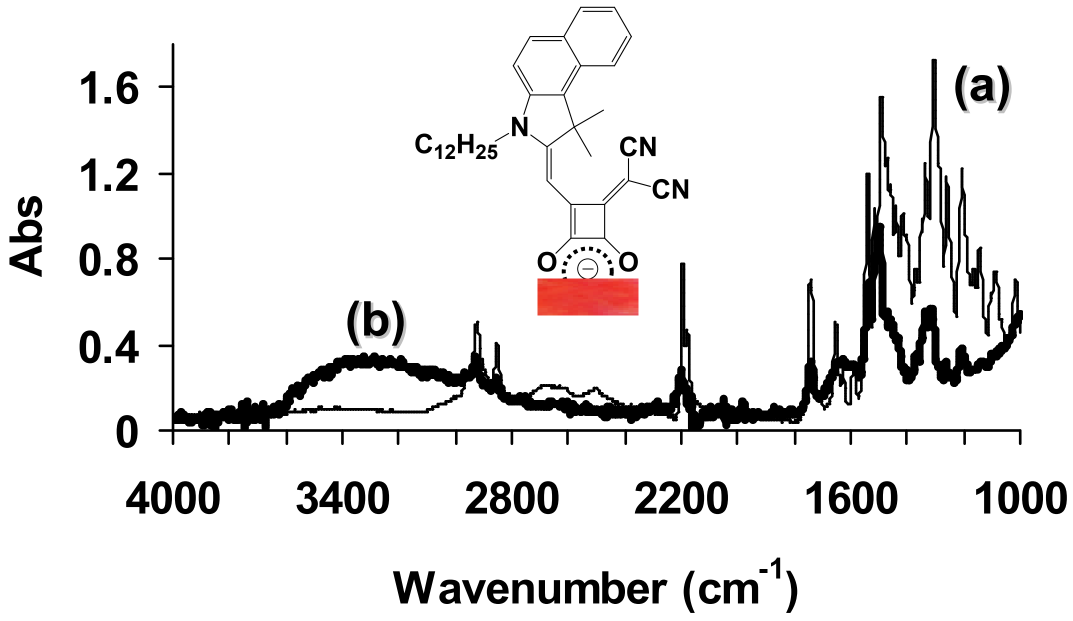


ESI Fig. 7. Infrared spectra of (**11**) (a) as powder, (b) adsorbed to a TiO_2 film and (c) an undyed TiO_2 film

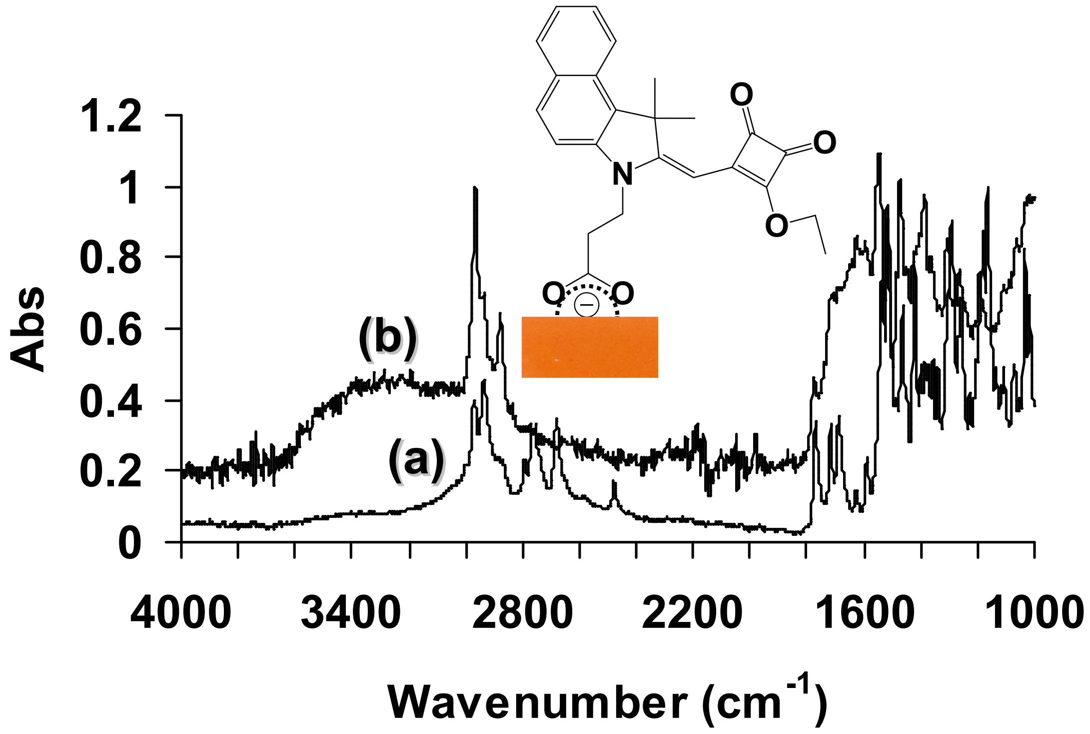
ATR Infrared Spectroscopy of HfSQ dyes from^{ESI-4}



ESI Fig. 8. Infrared spectra of (**7b'**) from^{ESI-4} (a) as powder and (b) adsorbed to a TiO_2 film



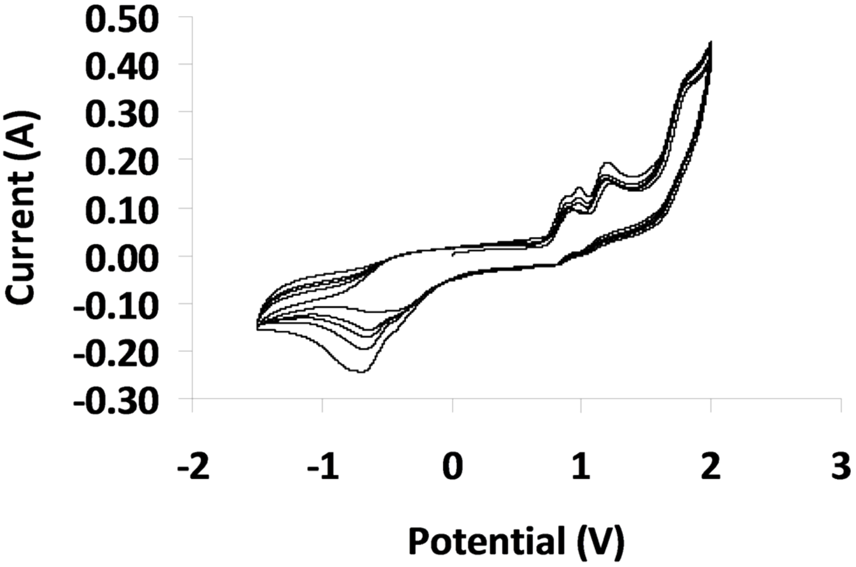
ESI Fig. 9. Infrared spectra of (**8'**) from^{ESI-4} (a) as powder and (b) adsorbed to a TiO_2 film



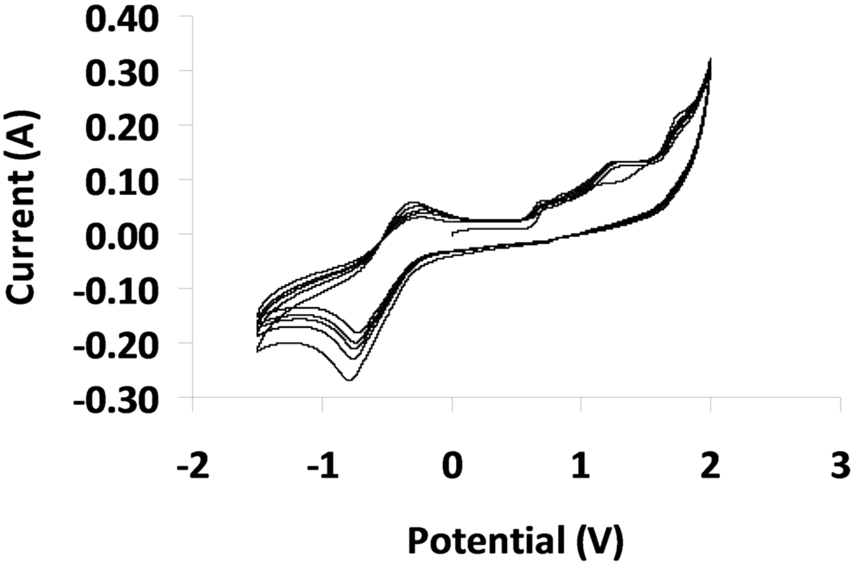
ESI

Fig. 10. Infrared spectra of (**10'**) from[ESI-4] (a) as powder and (b) adsorbed to a TiO_2 film

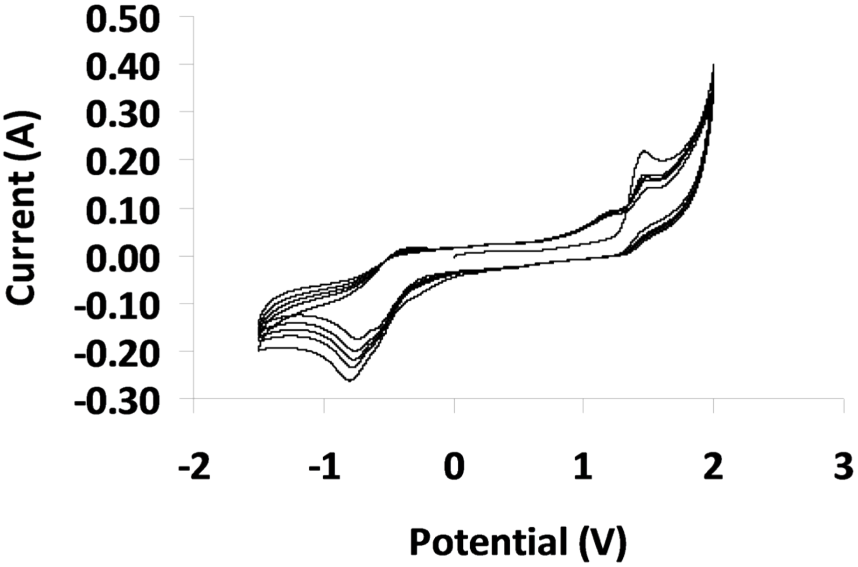
Cyclic Voltametry



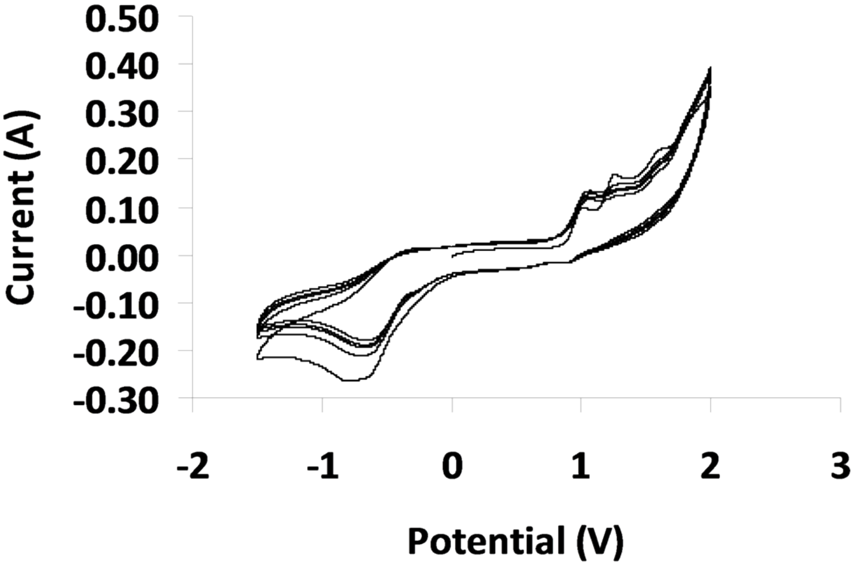
ESI Fig. 11. Cyclic Voltammetry of (**4**) 10 mM in degassed DMF *vs.* Ag/AgCl



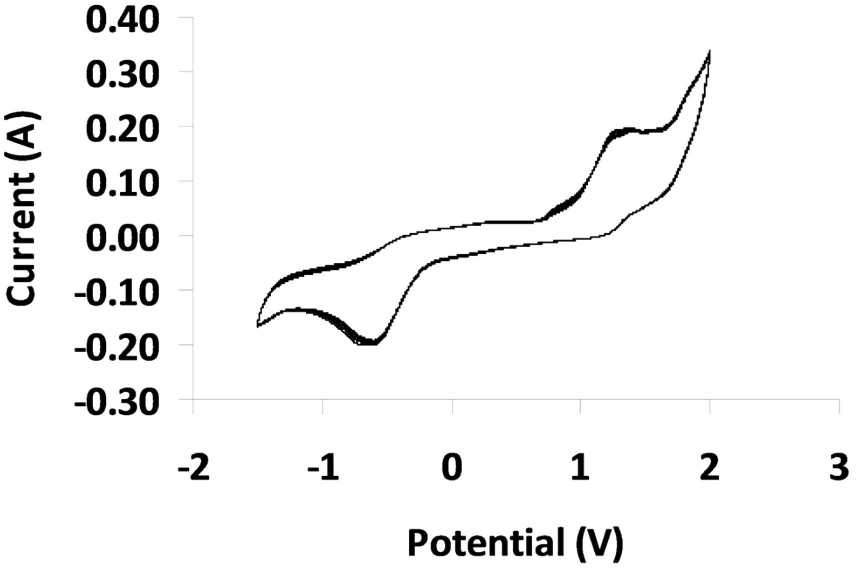
ESI Fig. 12. Cyclic Voltammetry of (**5**) 10 mM in degassed DMF vs. Ag/AgCl



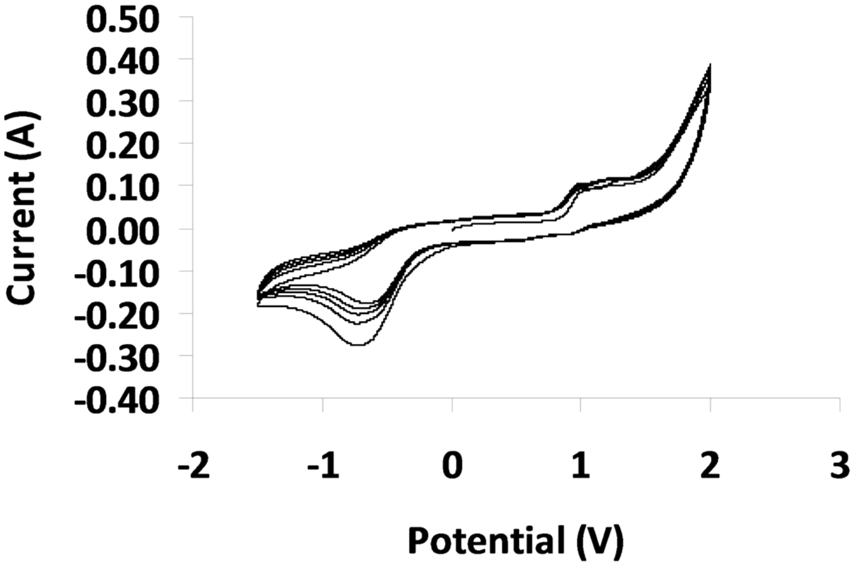
ESI Fig. 13. Cyclic Voltammetry of (**7**) 10 mM in degassed DMF vs. Ag/AgCl



ESI Fig. 14. Cyclic Voltammetry of (**8**) 10 mM in degassed DMF vs. Ag/AgCl

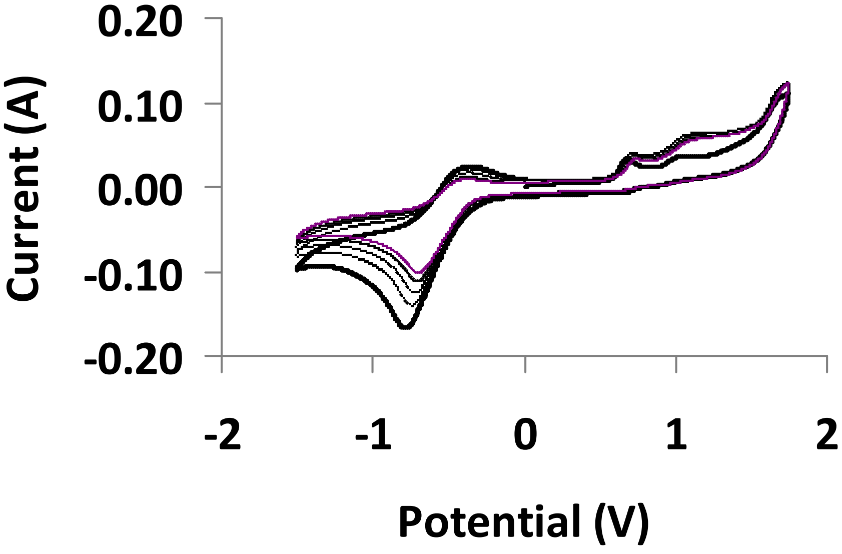


ESI Fig. 15. Cyclic Voltammetry of (**10**) 10 mM in degassed DMF vs. Ag/AgCl

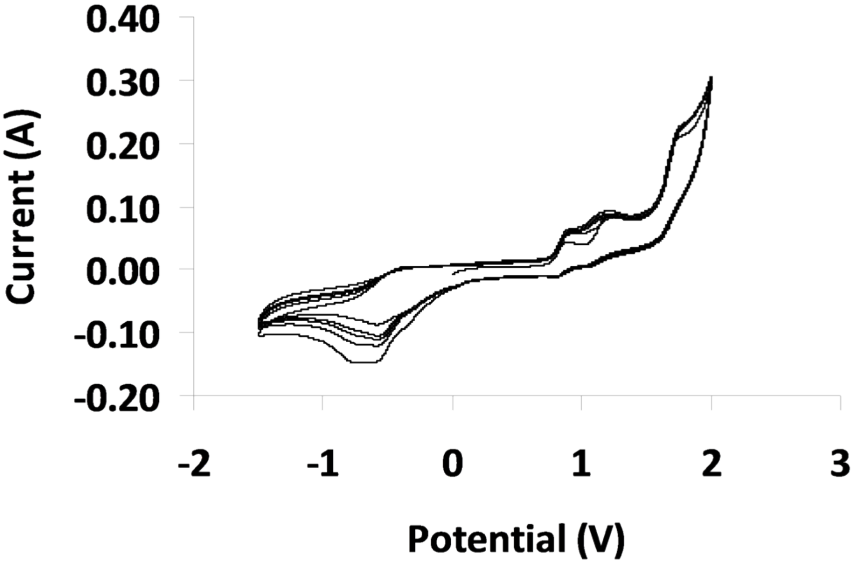


ESI Fig. 16 Cyclic Voltammetry of (**11**) 10 mM in degassed DMF vs. Ag/AgCl

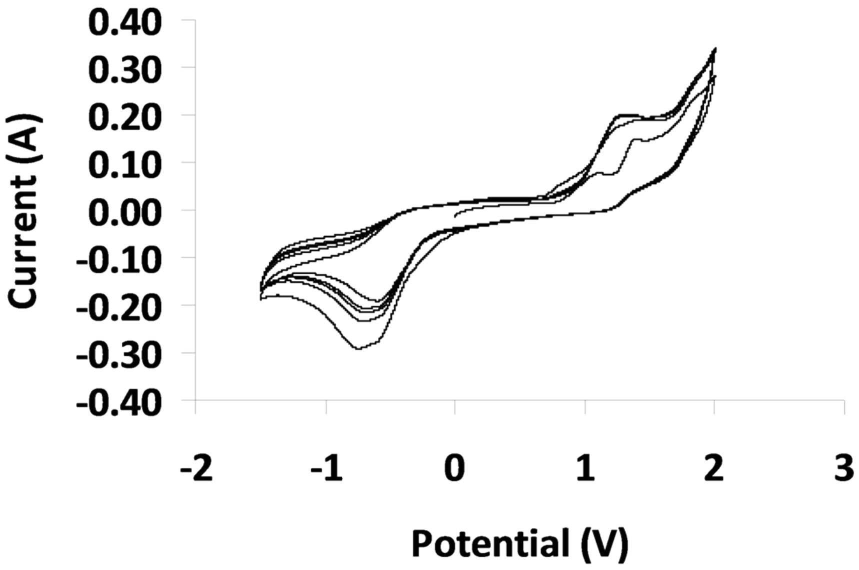
Cyclic Voltammetry of Selected HfSQ Dyes from [ESI-4]



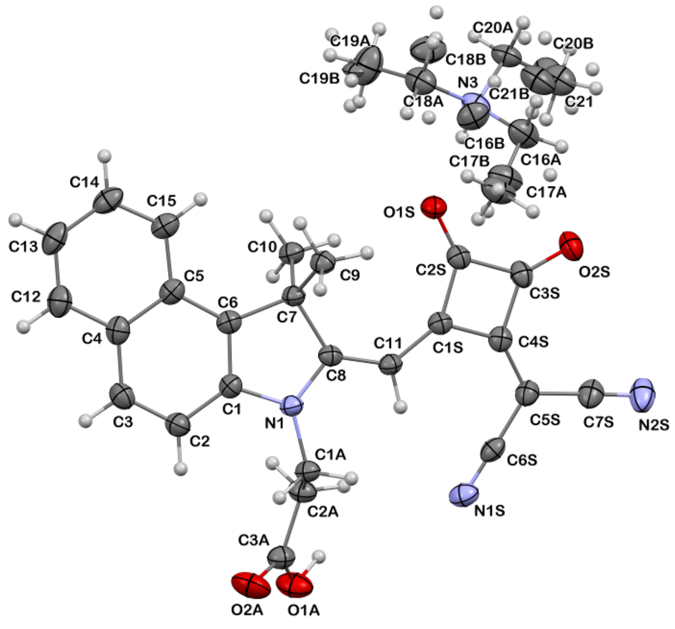
ESI Fig. 17. Cyclic Voltammetry of (**7b'**) 10 mM in degassed DMF vs. Ag/AgCl [ESI-4]



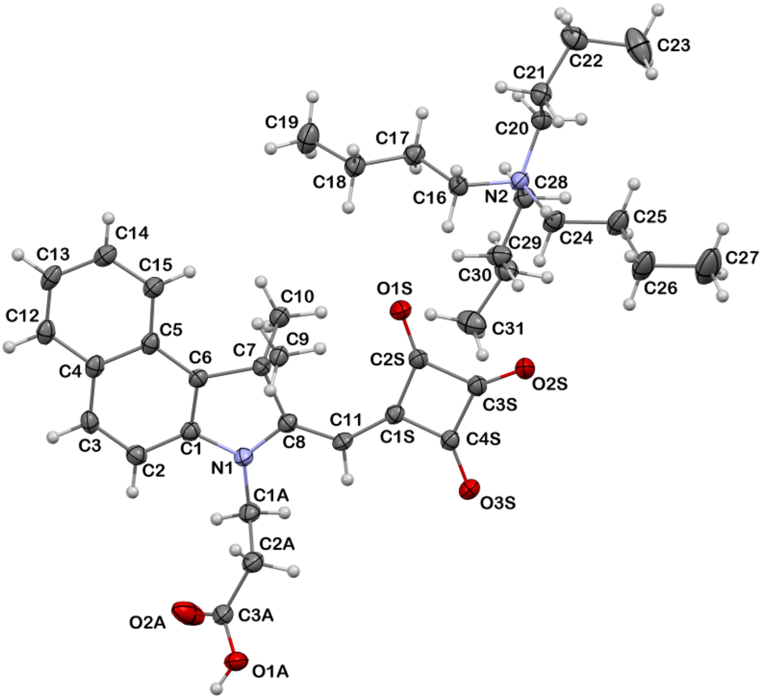
ESI Fig. 18. Cyclic Voltammetry of (**8'**) 10 mM in degassed DMF vs. Ag/AgCl [ESI-4]



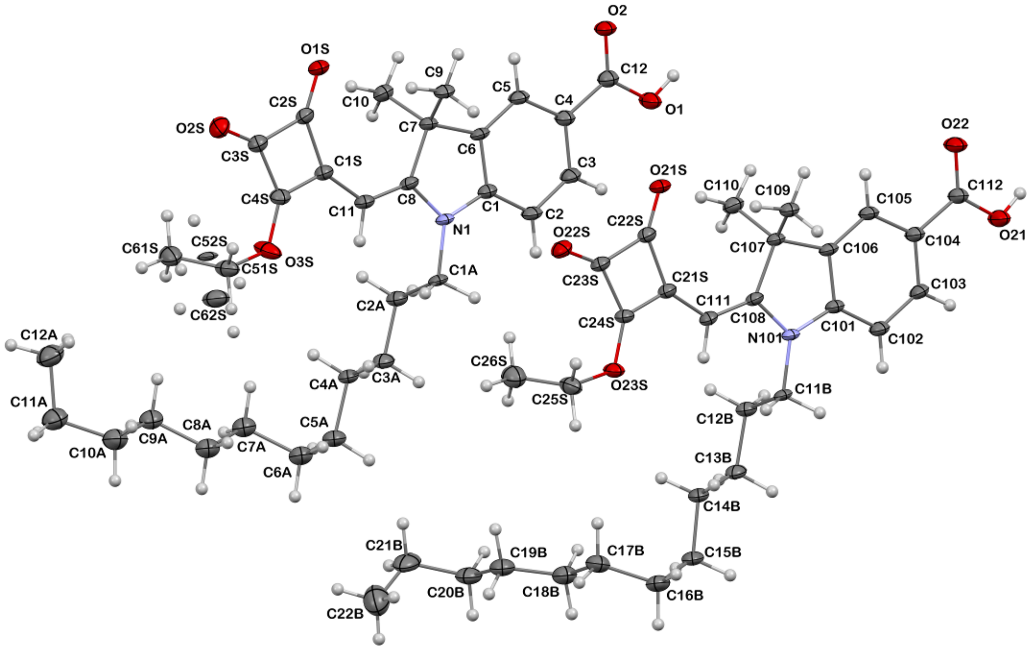
ESI Fig. 19. Cyclic Voltammetry of (**10'**) 10 mM in degassed DMF vs. Ag/AgCl [ESI-4]



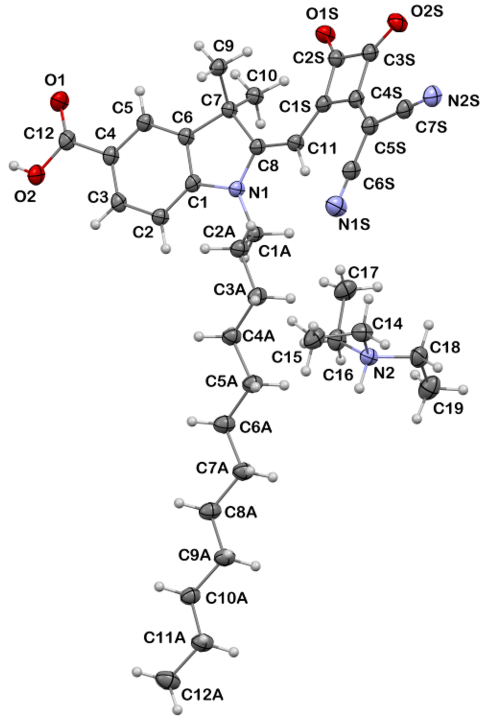
ESI Fig. 20. Crystal structure of (**4**) with atom labelling scheme. Both components of positional disorder are shown. Displacement ellipsoids – 50% probability.



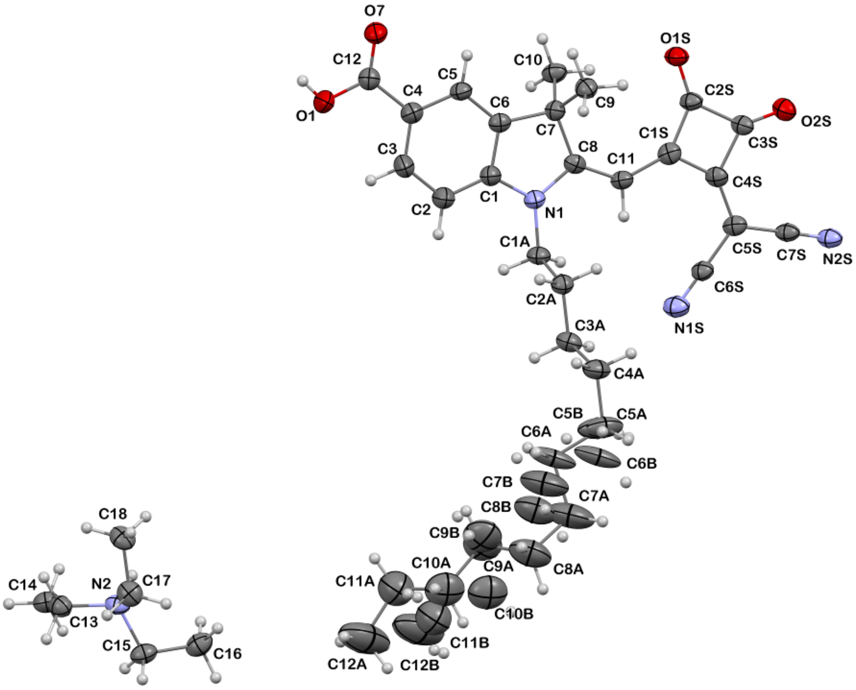
ESI Fig. 21. Crystal structure of (**5**) with atom labelling scheme. Displacement ellipsoids – 50% probability.



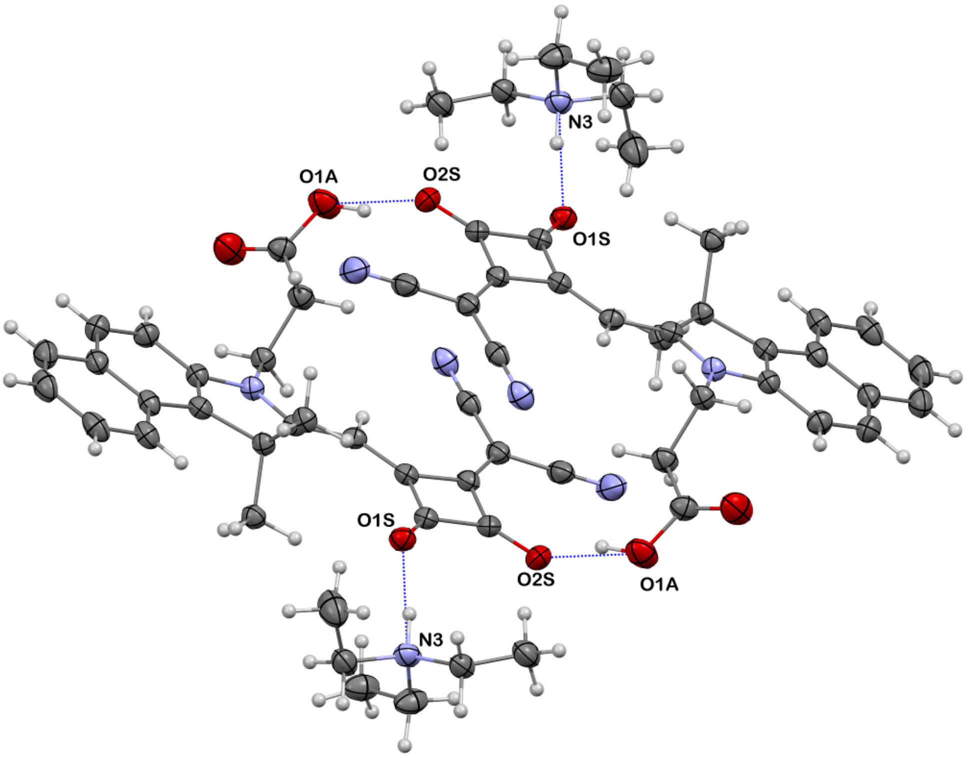
ESI Fig. 22. Crystal structure of (7) with atom labelling scheme. Two independent molecules present in the asymmetric part of the unit cell are shown (Z’=2). Displacement ellipsoids – 50% probability.



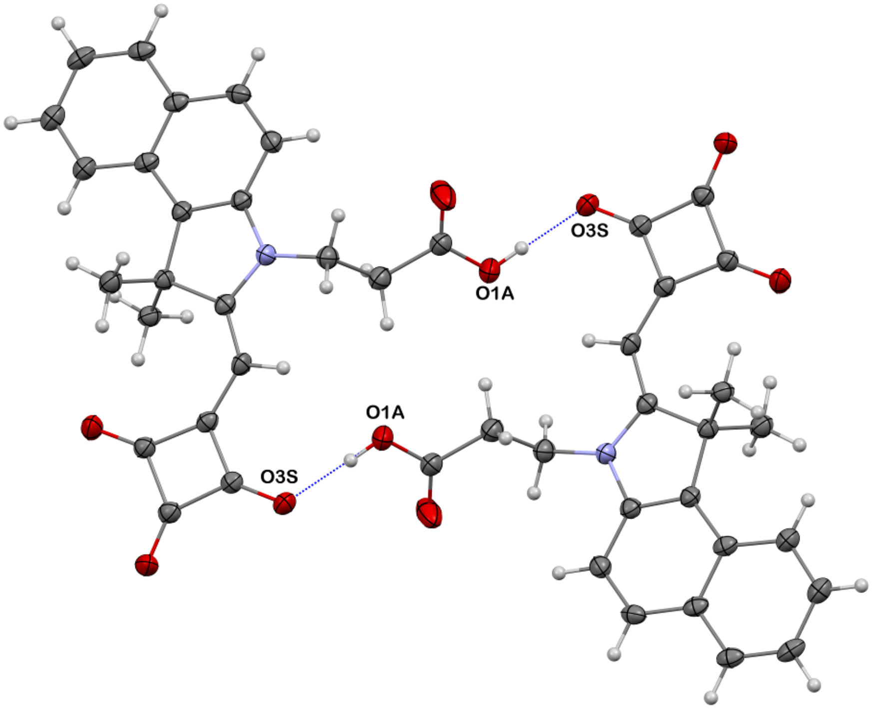
ESI Fig. 23. Crystal structure of (**8**) (**polymorph 1**) with atom labelling scheme. Displacement ellipsoids – 50% probability.



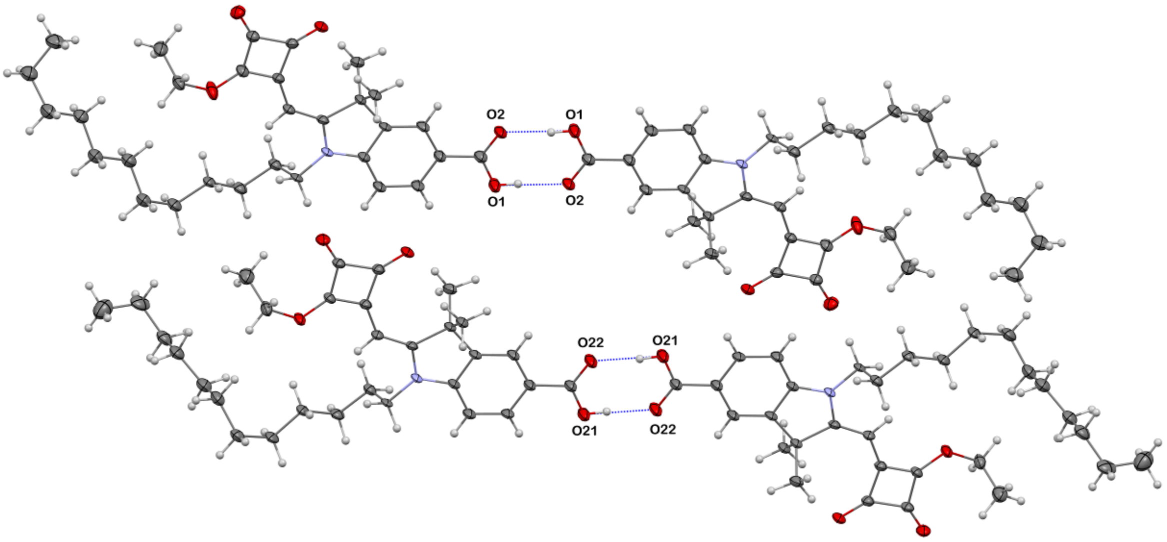
ESI Fig. 24. Crystal structure of (**8**) (**polymorph 2**) with atom labelling scheme. Displacement ellipsoids – 50% probability.



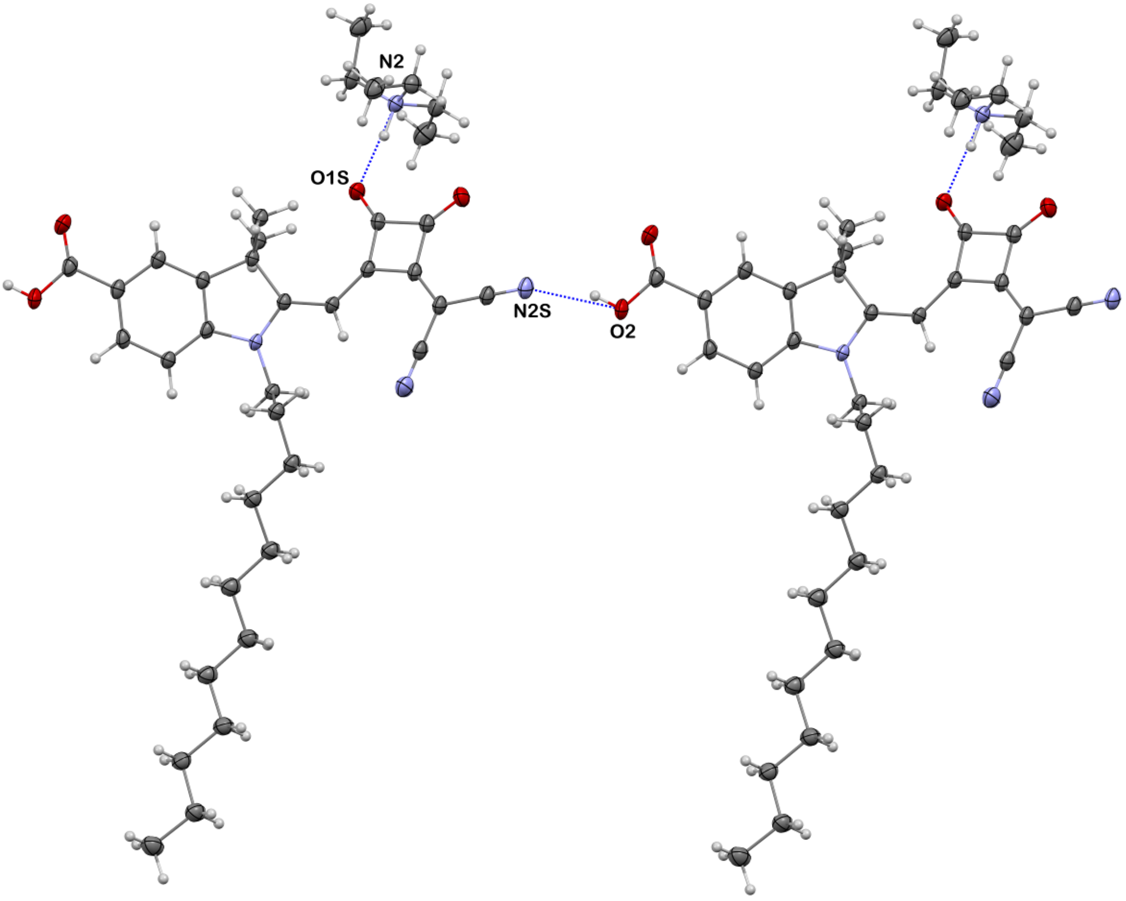
ESI Fig. 25. Hydrogen bond network in crystal structure of (**4**).



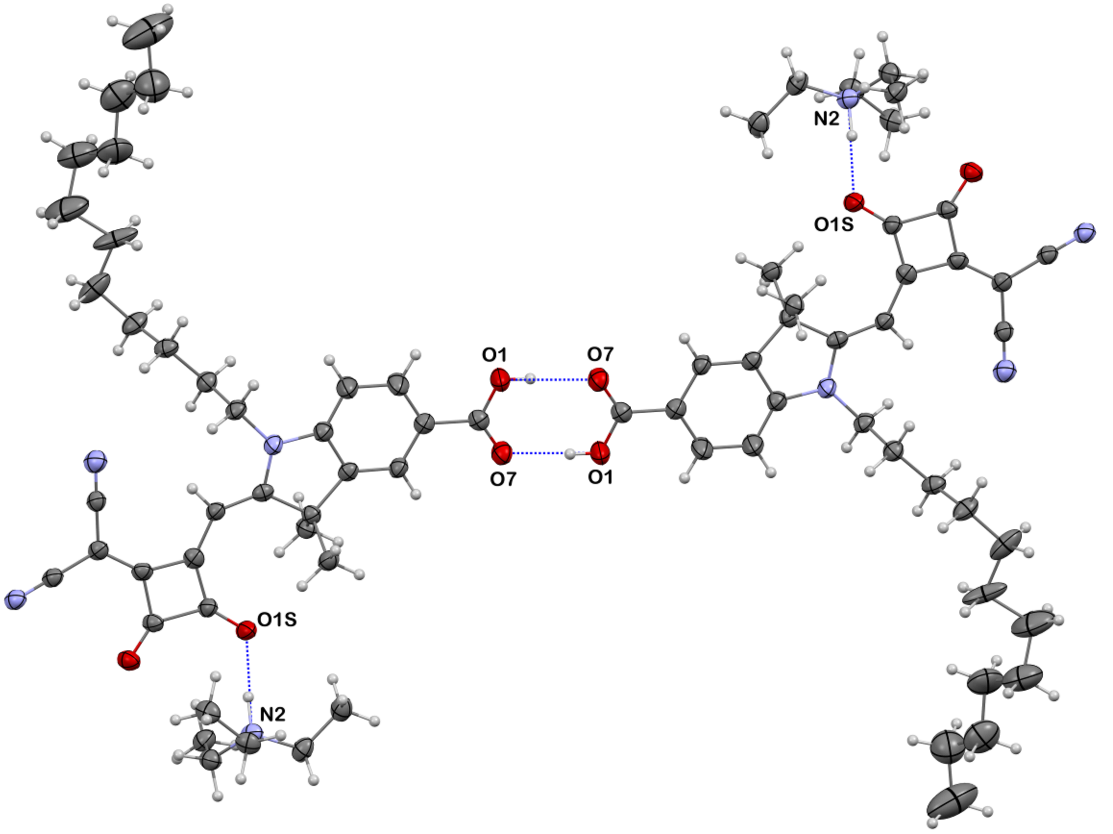
ESI Fig. 26. Hydrogen bond network in crystal structure of (**5**).



ESI Fig. 27. Hydrogen bond network in crystal structure of (**7**). Two independent molecules are shown.



ESI Fig. 28. Hydrogen bond network in crystal structure of (**8**) (**polymorph 1**).

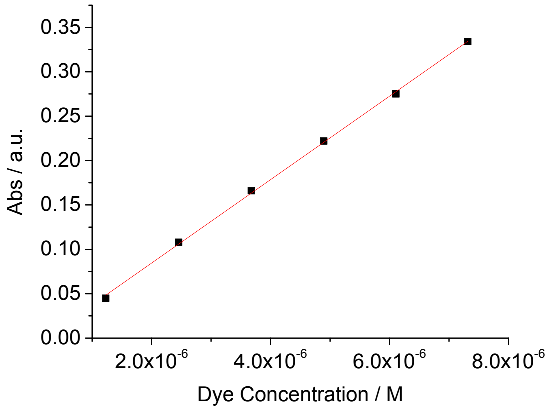


ESI Fig. 29. Hydrogen bond network in crystal structure of (**8**) (polymorph **2**).

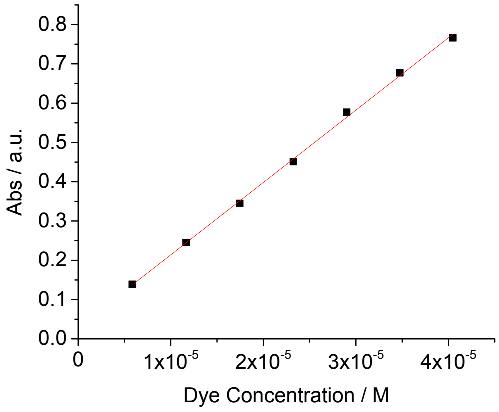
ESI Table 1. UV-visible spectroscopic data of selected dyes

Dye	**λ_{max} / nm**	**ε / x 10^4 $M^{-1}cm^{-1}$**	**Error in ε / x 10^4**
(**4**)	467	4.70	0.05
(**5**)	443	1.84	0.02
(**7**)	428	7.80	0.07
(**8**)	466	5.50	0.06
(**10**)	425	1.60	0.04
(**11**)	459	0.25	0.006

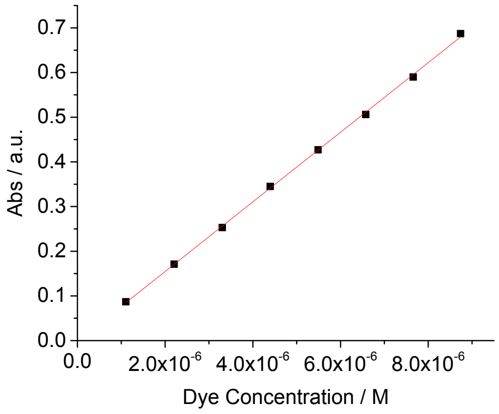
Dye (4)



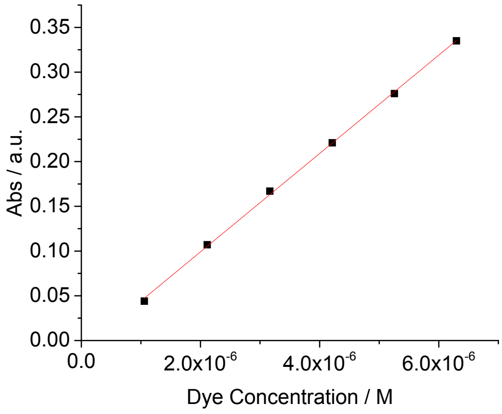
Dye (5)



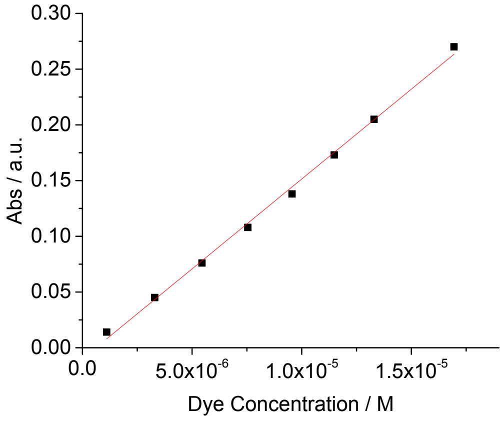
Dye (7)



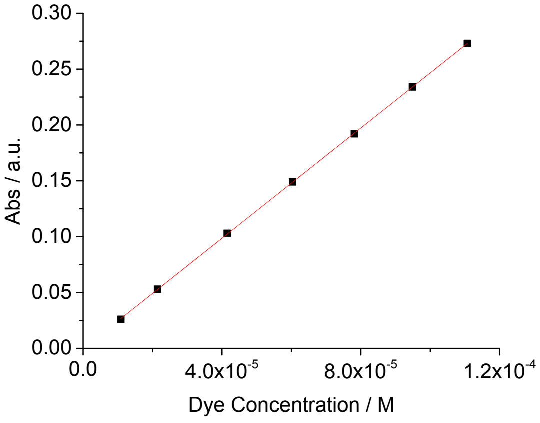
Dye (8)



Dye (10)



Dye (11)



ESI Fig. 30 Calibration graphs of (**4**), (**5**), (**7**), (**8**), (**10**) and (**11**)

ESI References

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