SUPPORTING INFORMATION

A Study of Dye Anchoring Points in Half-squarylium Dyes for Dye-Sensitized Solar Cells

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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).

1H NMR spectrum (500 MHz, DMSO-d6): δ 1.38 (t, J=14.2 Hz, 3H, CH3-CH2-O-); 4.65 (q, J=20.2 Hz, 2H, CH3-C=H2-O-).

13C NMR (101 MHz, DMSO-d6): δ 15.1; 70.1; 183.6; 189.0.

MS (FTMS +) M+ calculated = 171, M+ observed = 171, m/e Accurate Mass (FTMS +), reference compound: NH4OAc, M+ calculated = 171.0652, M+ observed = 171.0650.
2,3,3-Trimethyl-1-methyl-3H-indole (2a) ESI-2

A mixture of 2,3,3-trimethyl-3H-indole (8 g, 50 mmol) and methyl iodide (27.6 g, 200 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 ethyl acetate to give a red solid. (Yield 7.8 g, 91%). A suitable crystal for X-ray analysis was prepared by slow evaporation from ethyl acetate.

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 1.54 (s, 6H, -C-(CH$_3$)$_2$); 2.78 (s, 3H, -N=C-CH$_3$); 3.98 (s, 3H, -N-C$_2$H$_5$); 7.64 (m, 2H, Ar-H); 7.84 (d, J = 8.0 Hz, 1H, Ar-H); 7.92 (d, J = 8.0 Hz, 1H, Ar-H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$): δ 14.2; 21.7; 34.76; 39.0; 53.9; 115.1; 123.3; 128.8; 129.3; 141.6; 142.1; 196.0.

MS (FTMS +) M$^+$ calculated = 174, M$^+$ observed = 174.

2,3,3-Trimethyl-1-ethyl-3H-indole (2b) ESI-3

A mixture of 2,3,3-trimethyl-3H-indole (8 g, 50 mmol) and ethyl iodide (31 g, 200 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 ethyl acetate to give a red solid. (Yield 9.4 g, 90%). A suitable crystal for X-ray analysis was prepared by slow evaporation from ethyl acetate.

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 1.45 (t, J = 13.0 Hz, 3H, -N-CH$_2$-CH$_3$); 1.54 (s, 6H, -C-(CH$_3$)$_2$); 2.85 (s, 3H, -N=C-CH$_3$); 4.50 (q, J=20 Hz, 2H, -N-CH$_2$-CH$_3$); 7.63 (m, 2H, Ar-H); 7.85 (d, J = 9.0 Hz, 1H, Ar-H); 7.98 (d, J = 8.0 Hz, 1H, Ar-H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$): δ 12.7; 13.9; 21.9; 43.1; 54.1; 115.3; 123.6; 128.9; 129.4; 140.7; 142.0; 196.1.

MS (FTMS +) M$^+$ calculated = 188, M$^+$ observed = 188.

2,3,3-Trimethyl-1-hexadecyl-3H-indole (2c) ESI-4

A mixture of 2,3,3-trimethyl-3H-indole (8 g, 50 mmol) and hexadecyl iodide (70 g, 200 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 ethyl acetate to give a red solid. (Yield 16 g, 90%). A suitable crystal for X-ray analysis was prepared by slow evaporation from ethyl acetate.

$^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 0.84(5) (m, J = 19.0 Hz, 3H, -N-(CH$_2$)$_{15}$-CH$_3$); 1.44-1.23 (m, 20H, -N-(CH$_2$)$_{15}$-CH$_3$); 1.56 (s, 6H, -C-(CH$_3$)$_2$); 1.72 (m, J = 22.0 Hz, 2H, -N-(CH$_2$)$_{15}$-CH$_3$); 1.85 (m, J = 25.0 Hz, -N-(CH$_2$)$_{15}$-CH$_3$); 2.89 (s, 3H, -N=C-CH$_3$); 3.24 (m, J = 14.0 Hz, -N-(CH$_2$)$_{15}$-CH$_3$); 4.48 (m, J = 15.0 Hz, -N-(CH$_2$)$_{15}$-CH$_3$); 7.61(5) (dd, J = 8.0 Hz, 2H, Ar-H); 7.87 (d, J = 8.0 Hz, 1H, Ar-H); 8.02 (d, J = 8.0 Hz, 1H, Ar-H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$): $\delta$ 9.1; 13.8; 13.9; 14.5; 26.9; 27.3 (2 signals); 29.1; 29.5; 30.1; 30.4; 30.7 (2 signals); 31.2; 32.5; 32.8; 47.8; 54.2; 60.7; 115.5; 123.55; 127.7; 128.9; 129.4; 141.0; 141.8; 196.3.

MS (FTMS +) $M^+$ calculated = 384, $M^+$ observed = 384, m/e Accurate Mass (FTMS +), $M^+$ calculated = 384.3625, $M^+$ observed = 384.3622.

3-Ethoxy-4-[(1-methyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-3-cyclobutene-1,2-dione (3a) ESI-5

Compounds (3a) to (3c) were prepared using (2a) to (2c) respectively. In addition, (6a) and (6b) were prepared using (5a) and (5b). Compounds (10) and (12) were prepared from compounds (9) and (11) respectively. A typical procedure is described for the preparation of 3-ethoxy-4-[(1-methyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-3-cyclobutene-1,2-dione using 2,3,3-trimethyl-1-methyl-3H-indolium iodide. A mixture of 3,4-diethoxy-3-cyclobutene-1,2-dione (1) (3.15 g, 18.5 mmol), 2,3,3-trimethyl-1-methyl-3H-indolium iodide (7 g, 23.3 mmol) and triethylamine (3 ml, 23 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. (Yield 4.15 g, 75%).

$^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 1.45 (t, J = 15.0 Hz, 3H, -O-CH$_2$-CH$_3$); 1.55 (s, 6H, -C-(CH$_3$)$_2$); 3.33 (s, 3H, -N=C-CH$_3$); 3.34 (s, 3H, -N-CH$_3$); 4.81(5) (q, J = 22.0 Hz, 2H, -O-CH$_2$-CH$_3$); 5.31 (s, 1H, -C=CH-C-); 7.07 (m, J = 15.0 Hz, 1H, Ar-H); 7.18(5) (d, J = 8.0 Hz, 1H, Ar-H); 7.29 (m, J = 15.0 Hz, 1H, Ar-H); 7.42(5) (d, J = 8.0 Hz, 1H, Ar-H).
$^{13}$C NMR (101 MHz, DMSO-d$_6$): $\delta$ 15.6; 26.4; 33.7; 47.3; 69.6; 69.7; 80.90; 109.0; 121.8; 122.8; 127.8; 140.3; 142.9; 168.5; 172.6; 186.4; 187.9; 192.1.

MS (FTMS +) $M^+$ calculated = 298, $M^+$ observed = 298, $m/e$ Accurate Mass (FTMS +), reference compound: NH$_4$OAc, $M^+$ observed = 298.1438, $M^+$ found = 298.1441.

FT-IR (KBr) $\nu$/cm$^{-1}$ 2930 (w), 1755 (m), 1712 (s).

3-Ethoxy-4-[(1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-3-cyclobutene-1,2-dione (3b) $^{ESI-3}$

(Yield 4.11 g, 71%).

$^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 1.20 (t, J = 13.0 Hz, 3H, -N-CH$_2$-C$_3$H$_3$); 1.44 (t, J = 14.0 Hz, 3H, -O-CH$_2$-CH$_3$); 1.54 (s, 6H, -C-(C$_3$H$_3$)$_2$); 3.35 (s, 3H, -N=C-C$_3$H$_3$); 3.95 (q, J = 21.0 Hz, 2H, -O-C$_2$H$_2$-CH$_3$); 5.35 (s, 1H, -C=CH-C); 7.07 (m, J = 13.0 Hz, 1H, Ar-H); 7.18 (5) (d, J = 8.0 Hz, 1H, Ar-H); 7.29 (m, J = 16.0 Hz, 1H, Ar-H); 7.45 (d, J = 9.0 Hz, 1H, Ar-H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$): $\delta$ 11.0; 15.7; 26.4; 30.7; 37.1; 39.0; 47.4; 69.7; 80.3; 109.0; 122.0; 122.5; 127.9; 140.5; 141.8; 167.3; 172.6; 186.2; 187.7; 192.1.

MS (FTMS +) $M^+$ calculated = 312, $M^+$ observed = 312, $m/e$ Accurate Mass (FTMS +), reference compound: NH$_4$OAc, $M^+$ observed = 313.1628, $M^+$ found = 313.1630.

FT-IR (KBr) $\nu$/cm$^{-1}$ 2950 (w), 1775 (m), 1702 (s).

3-Ethoxy-4-[(1-hexadecyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-3-cyclobutene-1,2-dione (3c) $^{ESI-6}$

(Yield 6.3 g, 66%), 280-285°C

$^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 0.88 (m, J = 13.0 Hz, 3H, -N-(CH$_2$)$_{15}$-CH$_3$); 1.44-1.23 (m, 25H, -N-(CH$_2$)$_{15}$-CH$_3$) overlapping $\approx$ 1.44 (t, 3H, -O-CH$_2$-CH$_3$); 1.54 (m, J = 14.0 Hz, 2H, -N-(CH$_2$)$_{15}$-CH$_3$); 1.63 (s, 6H, -C-(CH$_3$)$_2$); 1.75 (m, J = 14.0 Hz, 2H, -N-(CH$_2$)$_{15}$-CH$_3$); 3.81 (m, J = 15.0 Hz, 2H, -N-(CH$_2$)$_{15}$-CH$_3$); 4.91(5) (q, J = 22.0 Hz, 2H, -O-CH$_2$-CH$_3$); 5.41 (s, 1H, -C=CH-C-); 6.89(5) (d, J = 8.0 Hz, 2H, Ar-H); 7.08 (d, J = 8.0 Hz, 1H, Ar-H); 7.27 (m, J = 13.0 Hz, 1H, Ar-H).
\[ ^{13}\text{C NMR} \ (101 \text{ MHz, DMSO-d}_6): \delta \ 15.9; \ 22.7; \ 26.4; \ 27.0 \ (2 \text{ signals}); \ 29.3; \ 29.3; \ 29.5; \ 29.6 \ (2 \text{ signals}); \ 29.7; \ 31.9; \ 43.0; \ 48.0; \ 69.9; \ 81.3; \ 108.4; \ 122.0; \ 122.7 \ (2 \text{ signals}); \ 141.0; \ 142.7; \ 168.4; \ 173.8; \ 187.4; \ 192.5. \]

FT-IR (KBr) \( \nu/cm^{-1} \): 2990 (w), 1795 (m), 1732 (s).

**3-[(1-Methyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-4-hydroxy-cyclobutene-1,2-dione (4a) **ESI-6, ESI-7

Compounds (4a) to (4c) were prepared using (3a) to (3c), respectively. In addition, (7a) and (7b) were prepared from (6a) and (6b). A typical procedure is described for the preparation of 3-[(1-methyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-4-hydroxy-cyclobutene-1,2-dione (4a) from 3-ethoxy-4-[(1-methyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-3-cyclobutene-1,2-dione (3a). 3-ethoxy-4-[(1-methyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-3-cyclobutene-1,2-dione (4g, 13.5 mmol) was dissolved in ethanol (40 ml) and heated under reflux. NaOH (3 ml, 40 %) was added and the solution was refluxed for 10 min. The mixture was concentrated and 15 ml of cold ethanol was added. The yellow product crystallized and was washed with ethanol three times. Yield 2.90 g (80 %).

\[ {^1}\text{H NMR} \ (500 \text{ MHz, DMSO-d}_6): \delta \ 1.56 \ (s, 6H, \ -C-(CH}_3)_2); \ 3.19 \ (s, 3H, \ -N=C=CH}_3); \ 5.35 \ (s, \ 1H, \ -C=CH-C-); \ 6.81-6.87 \ (m, \ 2H, \ Ar-H); \ 7.13 \ (d, \ J = 8.0 \text{ Hz,} \ 1H, \ Ar-H); \ 7.23 \ (m, \ J = 6.0 \text{ Hz,} \ 1H, \ Ar-H). \]

\[ {^{13}}\text{C NMR} \ (101 \text{ MHz, DMSO-d}_6): \delta \ 18.5; \ 27.6; \ 29.0; \ 45.6; \ 56.0; \ 84.5; \ 106.5; \ 119.4; \ 121.5; \ 127.2; \ 139.8; \ 144.4; \ 158.5; \ 178.7; \ 186.2; \ 195.1; \ 210.2. \]

MS (FTMS +) \( \text{M}^+ \) calculated = 270, \( \text{M}^+ \) observed = 270, \( m/e \) Accurate Mass (FTMS +), reference compound: NH$_4$OAc, \( \text{M}^+ \) calculated = 270.1125, \( \text{M}^+ \) observed = 270.1126.

FT-IR (KBr) \( \nu/cm^{-1} \): 3770-3100 (w), 2933 (w), 1767(m), 1654(s).

UV-Visible \( \lambda_{\text{max}} \) 430 nm (37500 \text{M}^{-1}\text{cm}^{-1}) in ethanol.

**3-[(1-Ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-4-hydroxy-cyclobutene-1,2-dione (4b)** ESI-6, ESI-7

Yield 2.76 g (80 %).
1H NMR (500 MHz, DMSO-d6): δ 1.05 (t, J = 17.0 Hz, 3H, -N-CH2-CH3); 1.57 (s, 6H, -C-(CH3)2); 3.75 (q, J = 19.0 Hz, 2H, -N-CH2-CH3); 5.39 (s, 1H, -C=CH-C-); 6.83 (m, J = 18.0 Hz, 2H, Ar-H); 7.13 (d, J = 14.0 Hz, 1H, Ar-H); 7.23 (5) (d, J = 8.0 Hz, 1H, Ar-H).

13C NMR (101 MHz, DMSO-d6): δ 10.8; 18.5; 27.5; 30.7; 37.1; 45.8; 56.0; 83.8; 106.4; 119.5; 121.6; 122.0; 127.3; 140.0; 143.4; 157.1; 178.7; 195.1; 209.9.


FT-IR (KBr) ν/cm⁻¹ 3710-3090 (w), 2911 (w), 1743(m), 1637(s).

UV-Visible λmax. 430 nm (38000 M⁻¹cm⁻¹) in ethanol.

3-[(1-Hexadecyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-4-hydroxy-cyclobutene-1,2-dione (4c) ESI-6, ESI-7

Yield 5.05 g (78 %).

1H NMR (500 MHz, DMSO-d6): δ 0.84 (m, 3H, -N-(CH2)15-CH3); 1.05-1.29 (m, 25H, -N-(CH2)15-CH3); 1.54 (s, 6H, -C-(CH3)2); 1.67 (m, 2H, -N-(CH2)15-CH3); 3.4-3.6 (m, 5H, -N-(CH2)15-CH3); 5.39 (s, 1H, -C=CH-C-); 6.81(5) (d, J = 7.0 Hz, 2H, Ar-H); 7.12 (t, J = 15.0 Hz, 1H, Ar-H); 7.21(5) (d, J = 7.0 Hz, 1H, Ar-H).

13C NMR (101 MHz, DMSO-d6): δ 13.8; 19.1; 21.3; 27.6; 28.7; 28.8; 28.9 (2 signals); 29.5; 31.3; 41.5; 41.8; 45.7; 46.2; 48.6; 56.0; 84.2; 106.6; 107.3; 119.4; 121.5; 127.2; 127.5; 139.8; 144.0; 157.5; 174.8; 178.7; 195.1; 196.4.

MS (FTMS +) M⁺ calculated = 480, M⁺ observed = 480, m/e Accurate Mass (FTMS +), reference compound: NH4OAc, M⁺ calculated = 480.3472, M⁺ observed = 480.3466.

FT-IR (KBr) ν/cm⁻¹ 3690-3100 (w), 2875 (w), 1714(m), 1604(s).

UV-Visible λmax. 430 nm (36500 M⁻¹cm⁻¹) in ethanol.
1,1,2-Trimethyl-1-ethyl-1H-benzo[e]indole (5) ESI-3

A mixture of 1,1,2-trimethyl-1H-benzo[e]indole (8 g, 38 mmol) and ethyl iodide (25 g, 160 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 ethyl acetate to give a red solid. (Yield 8.1 g, 90%). A suitable crystal for X-ray analysis was prepared by slow evaporation from ethyl acetate.

\[ \delta \]

\[ \begin{array}{l}
\delta 1.57 (t, J = 15.0 \text{ Hz}, 3 \text{H}, -\text{N-CH}_2-\text{C}_3) ; 1.77 (s, 6 \text{H}, -\text{C-(CH}_3)_2) ; 4.64 (q, J = 22.0 \text{ Hz}, 2 \text{H}, -\text{N-CH}_2-\text{CH}_3) ; 7.72 (d d, J = 8.0 \text{ Hz}, J = 7.0 \text{ Hz}, 1 \text{H}, \text{Ar-H}) ; 7.79 (d d, J = 7.0 \text{ Hz}, J = 8.0 \text{ Hz}, 1 \text{H}, \text{Ar-H}) ; 8.17 (d, J = 9.0 \text{ Hz}, 1 \text{H}, \text{Ar-H}) ; 8.22 (d, J = 8.0 \text{ Hz}, 1 \text{H}, \text{Ar-H}) ; 8.30 (d, J = 9.0 \text{ Hz}, 1 \text{H}, \text{Ar-H}) ; 8.37(5) (d, J = 8.0 \text{ Hz}, 1 \text{H}, \text{Ar-H}).
\end{array} \]

\[ \delta \]

\[ \begin{array}{l}
\delta 12.9 ; 13.6 ; 21.5 ; 43.4 ; 55.5 ; 113.2 ; 123.4 ; 127.2 ; 127.3 ; 128.4 ; 129.7 ; 130.7 ; 133.0 ; 137.0 ; 138.2 ; 195.9.
\end{array} \]

\[ \text{MS (FTMS +)} \]

\[ \text{M}^+ \text{ calculated} = 238, \text{M}^+ \text{ observed} = 238. \text{m/e Accurate Mass (FTMS +), M}^+ \text{ calculated} = 238.1590, \text{M}^+ \text{ observed} = 238.1585. \]

3-Ethoxy-4-[(1-ethyl-1,3-dihydro-3,3-dimethyl-2H-benzo[e]indol-2-ylidene)methyl]-3-cyclobutene-1,2-dione (6) ESI-3

(Yield 4.9 g, 72%).

\[ \delta \]

\[ \begin{array}{l}
\delta 1.06 (t, J = 13.0 \text{ Hz}, 3 \text{H}, -\text{N-CH}_2-\text{CH}_3) ; 1.21 (t, J = 14.0 \text{ Hz}, 3 \text{H}, -\text{O-CH}_2-\text{CH}_3) ; 1.85 (s, 6 \text{H}, -\text{C-(CH}_3)_2) ; 3.88 (q, J = 21.0 \text{ Hz}, 2 \text{H}, -\text{N-CH}_2-\text{CH}_3) ; 4.38 (b s, 2 \text{H}, -\text{O-CH}_2-\text{CH}_3) ; 5.35 (s, 1 \text{H}, -\text{C=CH-C-}) ; 7.23 (m, J = 15.0 \text{ Hz}, 1 \text{H}, \text{Ar-H}) ; 7.33 (d, J = 9.0 \text{ Hz}, 1 \text{H}, \text{Ar-H}) ; 7.45 (m, J = 15.0 \text{ Hz}, 1 \text{H}, \text{Ar-H}) ; 7.83 (d, J = 25.0 \text{ Hz}, 2 \text{H}, \text{Ar-H}) ; 8.06 (d, J = 9.0 \text{ Hz}, 1 \text{H}, \text{Ar-H}).
\end{array} \]

\[ \delta \]

\[ \begin{array}{l}
\delta 11.4 ; 18.4 (2 \text{ signals}) ; 27.0 ; 37.2 ; 49.2 ; 58.3 ; 58.4 ; 83.1 ; 109.2 ; 122.3 ; 122.6 ; 126.7 ; 128.8 ; 129.2 ; 130.0 ; 131.9 ; 139.8 ; 194.7.
\end{array} \]

\[ \text{FT-IR (KBr) v/cm}^{-1} \]

2982 (w), 1746 (m), 1717 (s).
4-[(1-Ethyl-1,3-dihydro-3,3-dimethyl-2H-benz[e]indol-2-ylidene)methyl]-3-cyclobutene-1,2-dione (7a) \(^{\text{ESI-3}}\)

(Yield 3.22 g, 72%).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) 1.21 (t, \(J = 14.0\) Hz, 3H, \(-N-CH_2-CH_3\)); 1.84 (s, 6H, \(-C-(CH_3)_2\)); 3.88 (q, \(J = 22.0\) Hz, 2H, \(-N-CH_2-CH_3\)); 5.45 (s, 1H, \(-C=CH-C-\)); 7.23 (t, \(J = 15.0\) Hz, 1H, Ar-\(H\)); 7.33 (d, \(J = 8.0\) Hz, 1H, Ar-\(H\)); 7.45 (t, \(J = 15.0\) Hz, 1H, Ar-\(H\)); 7.83 (dd, \(J = 11.0\) Hz, \(J = 9.0\) Hz, 2H, Ar-\(H\)); 8.06 (d, \(J = 8.0\) Hz, 1H, Ar-\(H\)).

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)): \(\delta\) 11.2; 18.5; 26.7; 29.0; 36.2; 47.7; 56.0; 83.7; 109.7; 121.5; 121.8; 126.6; 128.7; 128.9; 129.1; 129.2; 129.5; 141.0; 158.7; 178.4; 195.1.

MS (FTMS +) [M – H]\(^-\) calculated = 332, [M – H]\(^-\) observed = 332, \(m/e\) Accurate Mass (FTMS +), reference compound: NH\(_4\)OAc, [M – H]\(^-\) calculated = 332.1292, [M – H]\(^-\) observed = 332.1289.

FT-IR (KBr) \(\nu/cm^{-1}\) 3873-3050 (w), 2910 (w), 1740 (m), 1600 (s).

UV-Visible \(\lambda_{\text{max}}\) 440 nm (39000 M\(^{-1}\)cm\(^{-1}\)) in ethanol.

3-(2-Carboxyethyl)-1,1,2-trimethyl-1H-benz[e]indolium iodide (9) \(^{\text{ESI-8}}\)

A mixture of 1,1,2-trimethyl-1H-benz[e]indole (2 g, 9.5 mmol) and 3-iodopropionic acid (3 g, 15 mmol) was heated under reflux overnight under nitrogen in anhydrous 1,2 dichlorobenzene (80 ml). After cooling, the solvent was removed \textit{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) \(\delta\) 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) \(\delta\) 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\(_4\)OAc, [M + H]\(^+\) calculated = 282.1489, [M + H]\(^+\) observed = 282.1490
5-Carboxy-2,3,3-trimethyl-1-octyl-3H-indolium iodide (11)

Compound (11) was prepared following literature procedures. ESI-3

2-((2-Ethoxy-3,4-dioxocyclobut-1-enyl)methylene)-3,3-dimethyl-1-octylindoline-5-carboxylic acid (12) ESI-9

(2 g, 65 %)

$^1$H NMR (400 MHz, MeOD) $\delta$ 0.50 – 0.74 (m, 1H), 0.74 – 2.50 (m, 59H), 1.40 – 2.50 (m, 32H), 1.66 – 250 (m, 10H), 1.72 – 250 (m, 7H), 1.86 – 250 (m, 3H), 2.10 (d, J = 57.4 Hz, 2H), 3.33 (s, 9H), 3.75 (s, 1H), 3.97 (t, J = 7.2 Hz, 4H), 4.08 – 4.27 (m, 1H), 4.82 – 5.38 (m, 23H), 5.59 (s, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.95 – 8.17 (m, 4H).

$^{13}$C NMR (101 MHz, MeOD) $\delta$ 13.0, 14.8, 19.5, 22.3, 25.9, 26.0, 26.4, 28.9 (2 signals), 31.5, 42.5, 47.0, 47.2, 47.3, 47.4, 47.6, 47.8, 48.0, 48.2, 60.1, 67.5, 70.3, 82.4, 108.2, 123.0, 124.7, 130.6, 140.7, 146.7, 168.3, 168.4, 173.5, 187.6, 188.7, 192.5.

MS (FTMS +) M$^+$ calculated = 440, M$^+$ observed = 440. m/e Accurate Mass (FTMS +), M$^+$ calculated = 440.2431, M$^+$ observed = 440.2425.

FT-IR (KBr) $\nu$/cm$^{-1}$ 3585-3260 (m), 2978 (w), 2922 (m), 2854 (w), 1738 (m), 1707 (m).

UV-Visible $\lambda_{\text{max}}$ 428 nm (131000 M$^{-1}$cm$^{-1}$) in ethanol.
ESI Figure 1 Calibration graph data calculated from UV-visible spectra for (7b), (8), (10) and (12)

ESI Table 1 Molar extinction coefficients (7b), (8), (10) and (12) calculated from the calibration graphs in ESI Figure 1 (error in parentheses)

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}$ / nm</th>
<th>$\varepsilon$ / M$^{-1}$cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7b)</td>
<td>442</td>
<td>38,000 (1,100)</td>
</tr>
<tr>
<td>(8)</td>
<td>476</td>
<td>57,700 (900)</td>
</tr>
<tr>
<td>(10)</td>
<td>442</td>
<td>116,000 (1,300)</td>
</tr>
<tr>
<td>(12)</td>
<td>426</td>
<td>133,100 (1,500)</td>
</tr>
</tbody>
</table>
ESI Table 2 Dark current data for (4a), (4b), (4c) and (7a)

<table>
<thead>
<tr>
<th>Dye</th>
<th>η/%</th>
<th>V_oc/V</th>
<th>J_sc/ma cm⁻²</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4a)</td>
<td>0.10</td>
<td>0.48</td>
<td>0.35</td>
<td>0.60</td>
</tr>
<tr>
<td>(4b)</td>
<td>0.12</td>
<td>0.50</td>
<td>0.37</td>
<td>0.64</td>
</tr>
<tr>
<td>(4c)</td>
<td>0.12</td>
<td>0.49</td>
<td>0.39</td>
<td>0.65</td>
</tr>
<tr>
<td>(7a)</td>
<td>0.13</td>
<td>0.51</td>
<td>0.40</td>
<td>0.64</td>
</tr>
</tbody>
</table>

ESI Figure 2 I-V data for (4a), (4b), (4c) and (7a) in DSC devices. (Top) dark current data and (below) under illumination.
ESI Table 3 Dark current data for (7b), (8), (10), (12) and (7b) + SQ2

<table>
<thead>
<tr>
<th>Dye</th>
<th>η/%</th>
<th>V_{oc} / V</th>
<th>J_{sc} / mA cm^{-2}</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7b)</td>
<td>0.18</td>
<td>0.60</td>
<td>0.49</td>
<td>0.61</td>
</tr>
<tr>
<td>(8)</td>
<td>0.10</td>
<td>0.44</td>
<td>0.45</td>
<td>0.51</td>
</tr>
<tr>
<td>(10)</td>
<td>0.16</td>
<td>0.49</td>
<td>0.45</td>
<td>0.71</td>
</tr>
<tr>
<td>(12)</td>
<td>0.17</td>
<td>0.52</td>
<td>0.46</td>
<td>0.72</td>
</tr>
<tr>
<td>(7b) + SQ2</td>
<td>0.18</td>
<td>0.55</td>
<td>0.47</td>
<td>0.70</td>
</tr>
</tbody>
</table>

ESI Figure 2a I-V data for (7b), (8), (10), (12) and (7b) + SQ2 in DSC devices. (Top) dark current data and (below) under illumination.
**ESI Figure 3.** Molecular structure of 4b\textit{salt} (grown fragment). All hydrogen atoms and second part of disorder are omitted for clarity.

**ESI Figure 4.** Molecular structure of 4c\textit{salt} (grown fragment). Displacement ellipsoids – 50\% probability. All hydrogen atoms are omitted for clarity.
**ESI Figure 5.** Hydrogen bond network in 4c_salt.

**ESI Table 4.** Hydrogen bonding in 4c_salt.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O1H-H1O...O3S</td>
<td>0.832(10)</td>
<td>1.899(13)</td>
<td>2.729(6)</td>
<td>175(7)</td>
</tr>
<tr>
<td>O1H-H2O...O23S'</td>
<td>0.829(10)</td>
<td>1.99(3)</td>
<td>2.768(7)</td>
<td>155(6)</td>
</tr>
<tr>
<td>O2M-H2M...O3S'</td>
<td>0.857(10)</td>
<td>2.10(3)</td>
<td>2.918(7)</td>
<td>158(7)</td>
</tr>
<tr>
<td>O1M-H1M...O23S'</td>
<td>0.850(10)</td>
<td>1.97(3)</td>
<td>2.768(6)</td>
<td>155(7)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: (i) x+1, y, z; (ii) -x+1, -y+1, -z+1
**ESI Figure 6.** Molecular structure of 8_salt (grown fragment). Only one component of disorder is shown. All hydrogen atoms are omitted for clarity.

**ESI Figure 7.** Molecular structure of 6c. Displacement ellipsoids – 50% probability.
**ESI Figure 8.** Molecular structure of 12 (II). Only one component of disorder is shown. Asymmetric part of the unit cell contains four independent molecules (Z’=4).
**ESI Table 5.** Selected bonds distances

<table>
<thead>
<tr>
<th>Bond</th>
<th>3a</th>
<th>4b_salt</th>
<th>4c_salt</th>
<th>6b</th>
<th>6c</th>
<th>12 (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-C8</td>
<td>1.361(2)</td>
<td>1.378(4)</td>
<td>1.385(7)</td>
<td>1.370(2)</td>
<td>1.372(4)</td>
<td>1.422(2)</td>
</tr>
<tr>
<td>C7-C8</td>
<td>1.534(2)</td>
<td>1.521(5)</td>
<td>1.532(8)</td>
<td>1.532(2)</td>
<td>1.532(5)</td>
<td>1.537(2)</td>
</tr>
<tr>
<td>C8-C11</td>
<td>1.375(2)</td>
<td>1.348(5)</td>
<td>1.360(8)</td>
<td>1.377(2)</td>
<td>1.365(5)</td>
<td>1.366(2)</td>
</tr>
<tr>
<td>C11-CS1</td>
<td>1.413(2)</td>
<td>1.428(5)</td>
<td>1.410(8)</td>
<td>1.414(2)</td>
<td>1.417(4)</td>
<td>1.383(2)</td>
</tr>
<tr>
<td>C1S-C2S</td>
<td>1.496(2)</td>
<td>1.452(5)</td>
<td>1.458(8)</td>
<td>1.508(2)</td>
<td>1.481(5)</td>
<td>1.503(2)</td>
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<tr>
<td>C2S-C3S</td>
<td>1.533(2)</td>
<td>1.495(5)</td>
<td>1.490(8)</td>
<td>1.530(2)</td>
<td>1.513(6)</td>
<td>1.527(2)</td>
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<tr>
<td>C3S-C4S</td>
<td>1.462(2)</td>
<td>1.478(5)</td>
<td>1.491(8)</td>
<td>1.464(2)</td>
<td>1.467(5)</td>
<td>1.477(2)</td>
</tr>
<tr>
<td>C1S-C4S</td>
<td>1.397(2)</td>
<td>1.435(5)</td>
<td>1.444(8)</td>
<td>1.394(2)</td>
<td>1.408(5)</td>
<td>1.391(2)</td>
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<tr>
<td>C2S-O1S</td>
<td>1.214(2)</td>
<td>1.229(4)</td>
<td>1.242(7)</td>
<td>1.210(2)</td>
<td>1.229(5)</td>
<td>1.214(2)</td>
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<tr>
<td>C3S-O2S</td>
<td>1.218(2)</td>
<td>1.238(4)</td>
<td>1.225(7)</td>
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<td>1.223(4)</td>
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<tr>
<td>C4S-O3S</td>
<td>1.321(2)</td>
<td>1.246(5)</td>
<td>1.256(7)</td>
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**ESI Table 6.** Selected angles.

<table>
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<tr>
<th>Angle [°]</th>
<th>3a</th>
<th>4b_salt</th>
<th>4c_salt</th>
<th>6b</th>
<th>6c</th>
<th>12 (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-C8-C7</td>
<td>108.56(13)</td>
<td>108.3(3)</td>
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<td>108.3(1)</td>
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<td>108.3(1)</td>
</tr>
<tr>
<td>N1-C8-C11</td>
<td>120.88(14)</td>
<td>121.6(3)</td>
<td>121.9(5)</td>
<td>121.2(1)</td>
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<td>121.1(1)</td>
</tr>
<tr>
<td>C7-C8-C11</td>
<td>130.51(14)</td>
<td>130.1(3)</td>
<td>130.0(5)</td>
<td>130.5(1)</td>
<td>129.9(3)</td>
<td>130.5(1)</td>
</tr>
<tr>
<td>C8-C11-C1S</td>
<td>131.90(15)</td>
<td>132.9(3)</td>
<td>131.3(5)</td>
<td>132.6(1)</td>
<td>133.0(3)</td>
<td>131.9(1)</td>
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<tr>
<td>C11-C1S-C2S</td>
<td>143.81(15)</td>
<td>143.1(3)</td>
<td>145.3(6)</td>
<td>145.2(1)</td>
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<tr>
<td>C11-C1S-C4S</td>
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<td>124.3(5)</td>
<td>125.3(1)</td>
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<tr>
<td>C2S-C1S-C4S</td>
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<td>89.1(3)</td>
<td>90.0(1)</td>
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<tr>
<td>C1S-C2S-C3S</td>
<td>88.81(12)</td>
<td>89.6(3)</td>
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<td>88.5(1)</td>
<td>90.1(3)</td>
<td>88.8(1)</td>
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<tr>
<td>C1S-C4S-C3S</td>
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<td>C2S-C3S-C4S</td>
<td>85.83(13)</td>
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<td>O1S-C2S-C1S</td>
<td>137.26(16)</td>
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<td>135.4(3)</td>
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<td>135.94(13)</td>
<td>136.5(4)</td>
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<td>137.8(4)</td>
<td>137.7(1)</td>
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ESI References


