Panchromatic Symmetrical Squaraines: A step forward in molecular engineering of low cost blue-greenish sensitizers for Dye-Sensitized Solar Cells

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Figure 1ESI. Structures of well performing unsymmetrical squaraine dyes reported in literature.
<table>
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<tr>
<th>No.</th>
<th>Compound</th>
<th>$\lambda_{abs}$ [nm]</th>
<th>TiO$_2$ Thickness [µm]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [V]</th>
<th>$FF$</th>
<th>$\eta$ [%]</th>
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8. \begin{align*}
\text{HOOC-} & \text{N} \backslash \text{CO} \text{H} \\
\text{O} & \text{C} \text{H}_2
\end{align*}
\begin{align*}
\text{642} \\
9 \\
\text{[MeOH]} \\
11.6 \\
0.49 \\
0.54 \\
3.9 \\
[4]
\end{align*}

9. \begin{align*}
\text{HOOC-} & \text{N} \backslash \text{CO} \text{H} \\
\text{O} & \text{C} \text{H}_2
\end{align*}
\begin{align*}
\text{632} \\
6.5 \\
2.8 \\
0.45 \\
0.57 \\
1.7 \\
[5]
\end{align*}

10. \begin{align*}
\text{EtNH}^+ & \text{O} \text{C} \\
\text{O} & \text{EtNH}^+
\end{align*}
\begin{align*}
\text{663} \\
12+4^* \\
8.6 \\
0.59 \\
0.73 \\
3.7 \\
[6]
\end{align*}

11. \begin{align*}
\text{HOOC-} & \text{S} \text{C} \text{O} \\
\text{N} & \text{S} \text{C} \text{O}
\end{align*}
\begin{align*}
\text{463-473} \\
7.3+4^* \\
12.68 \\
0.61 \\
0.73 \\
5.7 \\
[7]
\end{align*}

12. \begin{align*}
\text{HOOC-} & \text{N} \backslash \text{CO} \\
\text{S} & \text{S} \text{N} \text{PO}
\end{align*}
\begin{align*}
\text{510} \\
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0.50 \\
0.69 \\
1.3 \\
[7]
\end{align*}
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<td>12+4*</td>
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18. 

![Molecule 18](image)

445

[DMF] 12+4* 9.95 0.60 0.61 3.59 [10]

19. 

![Molecule 19](image)

489

[DMF] 12+4* 10.60 0.67 0.7 4.91 [10]

20. 

![Molecule 20](image)

424

[1,4-Dioxane] 7 1.50 0.47 0.58 0.67 [11]

21. 

![Molecule 21](image)

417

[1,4-Dioxane] 7 1.30 0.49 0.59 0.61 [11]

22. 

![Molecule 22](image)

473

[THF] 18 9.83 0.59 0.61 3.52 [12]

23. 

![Molecule 23](image)

484

[THF] 18 12.27 0.61 0.63 4.73 [12]
24

\[
\begin{array}{c}
\text{HOOC-} \text{NC-} \text{CN-} \text{H}_2 \text{C}_6 \text{H}_4 \text{SCN-} \text{H}_2 \text{C}_6 \text{H}_4 \text{SCN-} \text{COOH}
\end{array}
\]

557 18 9.80 0.58 0.65 3.70 [12]

[THF]

25

\[
\begin{array}{c}
\text{HOOC-} \text{NC-} \text{CN-} \text{H}_2 \text{C}_6 \text{H}_4 \text{SCN-} \text{H}_2 \text{C}_6 \text{H}_4 \text{SCN-} \text{COOH}
\end{array}
\]

564 18 3.83 0.50 0.65 1.24 [12]

[THF]

26

\[
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\end{array}
\]

435

[DMSO: EtOH (1:1)]

27

\[
\begin{array}{c}
\text{HOOC-} \text{NC-} \text{CN-} \text{H}_2 \text{C}_6 \text{H}_4 \text{SCN-} \text{H}_2 \text{C}_6 \text{H}_4 \text{SCN-} \text{COOH}
\end{array}
\]

419 5 5.18 0.77 0.51 2.37 [14]

[DMF]

28

\[
\begin{array}{c}
\text{HOOC-} \text{NC-} \text{CN-} \text{H}_2 \text{C}_6 \text{H}_4 \text{SCN-} \text{H}_2 \text{C}_6 \text{H}_4 \text{SCN-} \text{COOH}
\end{array}
\]

446 5 1.67 0.83 0.62 1.02 [14]

[DMF]

29

\[
\begin{array}{c}
\text{HOOC-} \text{NC-} \text{CN-} \text{H}_2 \text{C}_6 \text{H}_4 \text{SCN-} \text{H}_2 \text{C}_6 \text{H}_4 \text{SCN-} \text{COOH}
\end{array}
\]

421 5 5.56 0.71 0.47 2.17 [14]

[DMF]
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42 \[ \text{[THF]} \]

43 \[ \text{[THF]} \]

44 \[ \text{[DCM]} \]

45 \[ \text{[THF]} \]

46 \[ \text{[THF]} \]
47

[CHCl₃] 10  8.56  0.47  0.71  2.86  [23]

48

[CHCl₃] 10  11.21  0.41  0.68  3.15  [23]

49

[CHCl₃] 10  13.16  0.53  0.66  4.64  [23]

50

[DMF] 16+5*  15.61  0.56  0.65  5.66  [24]

* Transparent layer + Scattering layer


Experimental Section

General. All the chemicals were purchased from Sigma Aldrich and TCI Europe and used without any further purification. The glassware used for the quaternarization syntheses was heated overnight in an oven at 150 °C and assembled in the oven, then cooled under Ar flux before starting the reactions. All microwave reactions were performed in single-mode Biotage Initiator 2.5. TLC were performed on silica gel 60 F254 plates using DCM and methanol (90:10) as eluents. Column chromatography were performed on Biotage Isolera Flash purification system.

ESI-MS spectra (positive ions) were recorded using a LCQ Deca XP plus spectrometer (Thermo), with electrospray interface and ion trap as mass analyzer. The flow injection effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas.

$^1$H NMR (200 MHz) and $^{13}$C NMR (50 MHz) spectra were recorded on a Brucker Avance 200 NMR in DMSO-d$_6$ using the DMSO signal as a reference.
1 Synthesis of symmetrical squaraine dyes

Scheme ESI-1. Synthesis of symmetrical SQ dyes, VG10-C2 and VG10-C8. Reagents and conditions: a) 0 °C, then 125-130 °C, 24 h, then 50 °C, 2-propanol; b) CH$_3$COOH, 3-methyl-2-butanone, 25 °C, 24 h; dissolved in a NaHCO$_3$ solution, then HCl to pH 5; c) CH$_3$CN, iodoalkane, MW, 155 °C, 40 min; d-1) toluene/butanol (1:1), MW, 160 °C, 30-40 min; d-2) toluene/butanol (1:1), reflux, 16 h.

6-hydrazinyl-2-naphthamide (1): 6-hydroxy-2-naphthoic acid (20 g, 106 mmol) was cooled to 0 °C, then hydrazine monohydrate (30 ml, 618 mmol) was added. After few minutes a turbid yellow solution is obtained and is heated at 125-130 °C for 24 hours. The turbid yellow-orange solution soon becomes a clear and transparent solution which assumed a red colour after 20 hours. The reaction mixture was cooled to 60 °C and 2-propanol (100 ml) was added to obtain a yellow solid which is then filtered. This solid should not be dried to avoid explosion risks and can be used as it is for the following step.

1,1,2-trimethyl-1H-benzo[e]indole-7-carboxylic acid (2): 6-hydrazinyl-2-naphthamide (raw material from 1) was dissolved in acetic acid (60 ml) and 3-methyl-3-butanone (70 ml, 654 mmol) was added to obtain a red solution. The mixture was mixed at room temperature for one night and then heated up to reflux to distill most of the solvent away. At the remaining solution, HCl 32% (70 ml) was added and the mixture was heated at reflux for one night. After cooling, the resulting light brown precipitate was filtered, washed several times with 2-propanol and dried under vacuum. This raw material was dissolved in an aqueous solution of NaHCO$_3$ and then acidified to pH 5 by 1M HCl solution. The expected product was obtained by precipitation and washed several times with diethyl ether (19.3 g, yield: 70% from starting material).
MS (ESI): m/z 253 (M-). ¹H-NMR (DMSO-d₆): δ(ppm) 8.68 (1H, s, Ar-H), 8.12 (3H, m, Ar-H), 7.77 (1H, d, Ar-H), 2.33 (3H, s, CH₃), 1.47 (6H, s, (CH₃)₂).

7-carboxy-3-ethyl-1,1,2-trimethyl-1H-benzo[e]indoleninium iodide (3a): Anhydrous conditions. 1,1,2-trimethyl-1H-benzo[e]indole-7-carboxylic acid (2.5 g, 9.9 mmol) was mixed with ethyl iodide (6.2 g, 39.9 mmol) and anhydrous acetonitrile (20 ml) and put in a closed vessel. The reaction mixture was heated up in a microwave reactor for 40 min. at 155 °C. The solvent was removed and the crude product was washed several times with diethyl ether, filtered and dried to obtain a brownish solid (6.21 g, 38%).

MS (ESI): m/z 282 (M+). ¹H-NMR (DMSO-d₆): δ(ppm) 8.88 (1H, s, Ar-H), 8.50 (2H, t, 8Hz Ar-H), 8.22 (2H, t, 10Hz, Ar-H), 4.65 (2H, q, 8HzN(CH₂CH₃)), 3.23 (3H, s, CH₃), 1.77 (6H, s, (CH₃)₂), 1.50 (3H, t, 8HzN(CH₂CH₃)).

7-carboxy-1,1,2-trimethyl-3-octyl-1H-benzo[e]indoleninium (3b): Anhydrous conditions. 1,1,2-trimethyl-1H-benzo[e]indole-7-carboxylic acid (2.5 g, 9.9 mmol) was mixed with octyl iodide (9.5 g, 39.5 mmol) and anhydrous acetonitrile (10 ml) and put in a closed vessel. The reaction mixture was heated up in a microwave reactor for 40 min. at 155 °C. The solvent was removed and the crude product was washed several times with diethyl ether, filtered and dried to obtain a yellow-brown solid (2.48 g, 51%).

MS (ESI): m/z 366 (M+). ¹H-NMR (DMSO-d₆): δ(ppm) 8.87 (1H, s, Ar-H), 8.50 (2H, t, 8Hz Ar-H), 8.22 (2H, t, 8Hz, Ar-H), 4.57 (2H, q, 8HzN(CH₂CH₃)), 2.96 (3H, s, CH₃), 1.77 (6H, s, (CH₃)₂), 1.25 (12H, m, N((CH₂)₆CH₃)), 0.84 (3H, m, N(CH₂CH₃)).

VG10-C2:

(classic) 7-carboxy-3-ethyl-1,1,2-trimethyl-1H-benzo[e]indoleninium iodide (2 g, 4.89 mmol) and squaric acid (279 mg, 2.44 mmol) were added to a round-bottomed flask. 5 ml toluene and 5 ml butanol were added and the mixture was heated to reflux for 16 h, during which period of time water was removed using a Dean-Stark trap. The reaction mixture was cooled to room temperature and put in the fridge to let crystallization of the squaraine dye which was then washed with diethyl ether and purified by further crystallization in acetone to give a sparkling dark green solid in 32% yield (501 mg).

(microwave) 7-carboxy-3-ethyl-1,1,2-trimethyl-1H-benzo[e]indoleninium iodide (500 mg, 1.22 mmol) and squaric acid (70 mg, 0.61 mmol) were dissolved in a 10 ml mixture of toluene and n-butanol (1:1). The mixture was heated by microwave irradiation at 160°C for 30 min until the reaction was completed as judged by TLC or UV spectra. After reaction, the solvent was removed by distillation and the crude product was crystallized by n-butanol, filtered off and washed with diethyl ether to get product as a sparkling dark green solid in 84% yield (656 mg).
MS (ESI): \( m/z \) 640 (M-). \(^1\)H-NMR (DMSO-\( d_6 \)): \( \delta (\text{ppm}) \) 8.68 (2H, s, Ar-H), 8.28 (2H, m, Ar-H), 8.07 (4H, d, 10Hz Ar-H), 7.80 (4H, d, 8Hz Ar-H), 5.92 (2H, s, Ar-H), 4.31 (4H, m, N(CH\(_2\)CH\(_3\))), 1.97 (12H, s, (CH\(_3\))\(_2\)), 1.37 (6H, t, 4Hz(CH\(_2\)CH\(_3\))). HRMS (M+): calcd 640.26, found 641.2610.

VG10-C8:

(classic) 7-carboxy-1,1,2-trimethyl-3-octyl-1H-benzo[e]indoleninium (2 g, 4.05 mmol) and squaric acid (231 mg, 2.03 mmol) were added to a round-bottomed flask. 5 ml toluene and 5 ml butanol were added and the mixture was heated to reflux for 16 h, during which period of time water was removed using a Dean-Stark trap. The reaction mixture was cooled to room temperature and put in the fridge to let crystallization of the squaraine dye which was then washed with diethyl ether and purified by further crystallizations in acetone, butanol and ethanol and acetic acid to give a light blue solid in 35.5% yield (719 mg).

(microwave) 7-carboxy-1,1,2-trimethyl-3-octyl-1H-benzo[e]indoleninium (500 mg, 1.01 mmol) and squaric acid (58 mg, 0.50 mmol) were dissolved in a 10 ml mixture of toluene and \( n \)-butanol (1:1). The mixture was heated by microwave irradiation at 160°C for 40 min until the reaction was completed as judged by TLC or UV spectra. After reaction, the solvent was removed by distillation and the crude product was crystallized by \( n \)-butanol, filtered off and washed with diethyl ether to get product as a light blue solid in 63% yield (514 mg).

MS (ESI): \( m/z \) 808 (M-). \(^1\)H-NMR (200MHz, DMSO-\( d_6 \)): \( \delta (\text{ppm}) \) 8.66 (2H, s, Ar-H), 8.25 (2H, m, Ar-H), 8.06 (4H, d, 6Hz Ar-H), 7.78 (4H, d, 6Hz Ar-H), 5.91 (2H, s, Ar-H), 4.24 (4H, m, N(CH\(_2\)CH\(_3\))), 1.95 (12H, s, (CH\(_3\))\(_2\)), 1.28 (24H, m, N((CH\(_2\))\(_6\)CH\(_3\))), 0.80 (3H, m, N(CH\(_2\)CH\(_3\))), \(^1\)C-NMR (50MHZ, DMSO-\( d_6 \)): \( \delta (\text{ppm}) \) 180.94, 178.94, 170.84, 167.43, 142.14, 133.72, 132.57, 131.74, 130.00, 126.94, 126.37, 122.43, 112.03, 86.96, 50.68, 31.31, 28.86, 28.72, 27.06, 26.55, 26.38, 22.18, 14.0. HRMS (M+): calcd 808.45, found 809.4481.

2 Synthesis of unsymmetrical squaraine dyes

\[ \text{Scheme ESI-2. Synthesis of unsymmetrical SQ dye, VG13. Reagents and conditions: e) CH}_3\text{CN, iodoalkane, MW, 155 }^\circ\text{C, 40 min; f) EtOH, pyridine, reflux, 20 min; g) toluene/butanol (1:1), MW, 160 }^\circ\text{C, 35 min.} \]
(E)-2-((2-ethoxy-3,4-dioxocyclobut-1-enyl)methylene)-1,1-dimethyl-3-octyl-2,3-dihydro-1H-benzo[e]indole-7-carboxylic acid (4): 7-carboxy-1,1,2-trimethyl-3-octyl-1H-benzo[e]indoleneininium (500 mg, 1.01 mmol), 3,4-diethoxycyclobut-3-ene-1,2-dione (344 mg, 2.02 mmol) and triethylamine (307 mg, 3.03 mmol) were added to a round-bottomed flask. Ethanol was added and the mixture was heated to reflux for 20 min. The reaction mixture was cooled to room temperature. The solvent was removed in vacuum and purified by column chromatography. The product was obtained with 46.7% yield (231 mg).

$^1$H-NMR (200MHz, DMSO-d$_6$): $\delta$(ppm) 8.57 (1H, s, Ar-H), 8.04 (2H, s, Ar-H), 7.90 (1H, d, 8Hz Ar-H), 7.22 (1H, d, 8Hz Ar-H), 5.44 (1H, s), 4.87 (2H, q, O(CH$_2$CH$_3$)), 3.88 (2H, t, N(CH$_2$CH$_3$)), 1.83 (6H, s, (CH$_3$)$_2$), 1.51 (3H, t, O(CH$_2$CH$_3$)), 1.19 (12H, m, N((CH$_2$)$_6$CH$_3$)) 0.80 (3H, t, N(CH$_2$CH$_3$)).

VG13: (E)-2-((2-ethoxy-3,4-dioxocyclobut-1-enyl)methylene)-1,1-dimethyl-3-octyl-2,3-dihydro-1H-benzo[e]indole-7-carboxylic acid (150 mg, 0.31 mmol) and 3-ethyl-1,1,2-trimethyl-1H-benzo[e]indoleneininium iodide$^1$ (112 mg, 2.02 mmol) were dissolved in a 6 ml mixture of toluene and $n$-butanol (1:1). The mixture was heated by microwave irradiation at 160°C for 35 min until the reaction was completed as judged by TLC or UV spectra. After reaction, the solvent was removed by distillation and the crude product was crystallized by n-butanol, filtered off and washed with diethyl ether to get product as a dark blue solid in 53% yield (112 mg).

MS (ESI): $m/z$ 679.2 (M-). $^1$H-NMR (200MHz, DMSO-d$_6$): $\delta$(ppm) 8.66 (1H, s, Ar-H), 8.23 (3H, m, Ar-H), 8.05 (3H, m, Ar-H), 7.74 (2H, d, 6Hz, Ar-H), 7.64 (1H, t, Ar-H), 7.50 (1H, t, Ar-H), 5.91 (2H, s, Ar-H), 4.30 (4H, m, N(CH$_2$CH$_3$)), 1.96 (12H, s, (CH$_2$)$_2$), 1.36 (12H, t, N((CH$_2$)$_6$CH$_3$)) 0.80 (6H, m, N(CH$_2$CH$_3$)). $^{13}$C-NMR (50MHZ, DMSO-d$_6$): $\delta$(ppm) 180.95, 179.41, 171.11, 169.41, 167.56, 142.28, 139.40, 133.88, 132.80, 131.78, 131.29, 130.13, 129.94, 128.15, 127.78, 125.88, 60.60, 51.09, 50.36, 34.94, 31.38, 28.95, 28.84, 26.53, 26.42, 26.28, 22.29, 18.89, 14.19, 14.09, 12.40. HRMS (M+): calcd 680.36, found 681.3631.

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3 Spectroscopic characterization

UV-Vis absorption as well as steady-state fluorescence emission spectra show, in general, a negative solvatochromism which accounts for a higher polarity of the ground state with respect to the excited state.

3.1 UV-Vis spectra. Every dye was weighed, (7-10 mg), and diluted to 10 ml in a flask using DMSO. From this solution, 0.25 ml were taken and diluted to 25 ml with the proper solvent (mother solution). Three dilutions were prepared by diluting 1.0, 2.5 and 5 ml of this solution to 25 ml. Those solutions were analyzed by UV-Vis spectroscopy (Cary 300 Bio) using quartz cuvettes (1 cm pathway length). Absorbance at the $\lambda_{\text{max}}$ for every daughter solution was plotted vs. dye concentration and a linear fitting was performed. The slope of the plot is the molar absorption coefficient ($\epsilon$). The determination was made, in duplicate, by preparing two separate concentrated dye mother solutions in DMSO. The log $\epsilon$ obtained from the two separate data set was compared: if their difference is less or equal to 0.02 respect to their average, the data were considered acceptable and the average of the two values was taken as the official value. Otherwise, a further concentrated dye mother solution in DMSO was prepared, the whole procedure was repeated and the log $\epsilon$ data were compared.

Figure ESI 2: UV-Vis solvatochromic behavior for VG10-C2 (left), VG10-C8 (right) and VG13 (bottom).
Table 2 ESI: Absorption maxima ($\lambda_{\text{max}}$), loge, FWHM and oscillator strengths for VG10-C2, VG10-C8 and VG13 in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>VG10-C2</th>
<th>VG10-C8</th>
<th>VG13</th>
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<tr>
<td></td>
<td>$\lambda_{\text{max}}$ [nm]</td>
<td>Loge</td>
<td>$\lambda_{\text{max}}$ [nm]</td>
</tr>
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<td>THF</td>
<td>676</td>
<td>5.47</td>
<td>679</td>
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<tr>
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<td>679</td>
</tr>
<tr>
<td>DMSO</td>
<td>683</td>
<td>5.44</td>
<td>686</td>
</tr>
<tr>
<td>ACN</td>
<td>670</td>
<td>5.39</td>
<td>674</td>
</tr>
<tr>
<td>EtOH</td>
<td>670</td>
<td>5.37</td>
<td>673</td>
</tr>
<tr>
<td>MeOH</td>
<td>667</td>
<td>5.43</td>
<td>671</td>
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</table>

3.2 Fluorescence measurements were recorded using a Fluorolog 2 from Jobyn Ivon. The excitation wavelength was set at 650 nm. The range for fluorescence emission recording was from 670 to 850 nm. Excitation and emission slits (3 nm) were arranged in order that all fluorescence spectra could be recorded under the same conditions.

Few mg of dye were put in a test tube and few ml of proper solvent were added. The sample was used to prepare much diluted solutions, and their absorbance at $\lambda_{\text{max}}$ was determined in order to ensure that the absorbance is maintained lower of 0.1 units of absorbance. For every solution fluorescence emission spectrum was detected and $\lambda_{\text{em}}$ was obtained.

Two standards, Rhodamine 101 dissolved in EtOH/0.01 HCl and Cresyl Violet in MeOH, were measured under the same conditions of squaraine samples.

Operative conditions (Rhodamine 101 quantum yield = 1 and Cresyl Violet = 0.54)$^2$:
- Rhodamine 101: $\lambda_{\text{ex}}$ = 535, emission range: 545-800 nm, excitation and emission slits: 3 nm.
- Cresyl Violet: $\lambda_{\text{ex}}$ = 520, emission range: 530-800 nm, excitation and emission slits: 3 nm.

The quantum yield$^3$ is determined by:

$$\phi_x = \Phi_{ST} \frac{A_x}{A_{ST}} \frac{I_{ST}}{I_x} \left( \frac{\eta^2_x}{\eta^2_{ST}} \right)$$

(eq. 1)

where $\Phi_x$ is the measured quantum yield for the unknown sample, $\Phi_{ST}$ in the quantum yield of the standard reference (Rhodamine 101 or Cresyl violet) to which the measurement are referred,

---


$A_x$ and $A_{ST}$ are the integrated areas under the fluorescence emission curve of the unknown sample and standard reference respectively, $I_{ST}$ and $I_x$ are the absorbance of the standard reference and unknown sample respectively, $\eta_x$ and $\eta_{ST}$ are the refractive indexes for the solvents in which the unknown sample and standard reference are dissolved respectively. The reported quantum yield is the average of the values obtained vs Rhodamine 101 and Cresyl Violet respectively.

**3.3 Fluorescence lifetimes** were obtained on a Fluorolog2 spectrofluorimeter, equipped with proper NanoLED source (emitting at 635nm) and using a photon counting detector (TBX04).

The same solutions used for quantum yield determination were used. The data were fitted to a single exponential function giving the lifetime.

**Table 3 ESI:** Emission maxima, Stokes shift, lifetime, quantum yield, fluorescence constant and non-radiative constant for VG1-C2, VG1-C8, VG10-C2, VG10-C8 and VG13.

<table>
<thead>
<tr>
<th>Solvent</th>
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<th>Stokes shift [nm]</th>
<th>$\Delta E_{0,0}$ [eV]</th>
<th>$\tau$ [ns]</th>
<th>$\Phi_0$</th>
<th>$\lambda_{em}$ [nm]</th>
<th>Stokes shift [nm]</th>
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**Table 3 continued:** Emission maxima, Stokes shift, lifetime, quantum yield, fluorescence constant and non-radiative constant for VG10-C2, VG10-C8, VG10-C8 and VG13.

<table>
<thead>
<tr>
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<th>Stokes shift [nm]</th>
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4 Electrochemistry

Electrochemical measurements (cyclic voltammetry and differential pulse voltammetry) were performed using a PC controlled AutoLab PSTAT10 electrochemical workstation in 0.1 M Bu$_4$NPF$_6$ in dimethylformamide (DMF) using a glassy carbon working electrode, a platinum plate auxiliary electrode, and a platinum wire quasi-reference electrode. Ferrocene was used as an internal reference and added in the last potential scans.

Figure 3a ESI: Cyclic voltammograms of VG10-C8 with (red-dotted line) and without (solid line) ferrocene at scan rate 100 mV s$^{-1}$, 2$^{nd}$ scan is shown.

Figure 3b ESI: Results of different pulse voltammetry of VG10-C2 (left) and VG10-C8 (right)
5 Computational analysis of dye structure and electron distribution

The theoretical analysis carried on in the present work is based on results of density functional theory (DFT) calculations and on its time-dependent formulation (TD-DFT). The PBE0 functional has been employed,\textsuperscript{4} together with the standard Pople 6-311G(d) basis set. The PBE0 functional has proven to be able to correctly describe a wide range of electronic states typologies in systems containing extended conjugation\textsuperscript{5}. Bulk solvent effects have been taken into account by using the polarizable continuum model (PCM). The state specific solvation model has been used in both cases\textsuperscript{6}.

All the calculations have been performed on the VG10-C2 molecule, but the qualitative description of the excited states properties is expected to hold also for VG10-C8.

Six main conformations of VG10-C2 have been considered, which can be obtained by proper rotations of 180 degrees around the two C-C bonds which link the squarainic ring to the benzoindoline moiety (see Figure 4-ESI). The possible conformations arising from the motion of the two ethyl groups have been neglected since they are believed to have a negligible effect on the electronic properties of the molecule. The relative energies of the conformers and their structures, obtained from full structure optimization in solvent, are reported in Figure 4-ESI. Isomers are labelled according to the relative positions of the two nitrogen atoms, and of the two hydrogen atoms adjacent to the squaric ring, e.g. a cis N/H configuration is labelled with the letter Z, and trans H/H configuration is labelled as E, accordingly we can have six different isomers labelled as EEE, EZE, EEZ, ZZE, ZEZ and ZZZ.

---


Vertical excitation energies of the first ten singlet states have been computed for all the six isomers using time-dependent density functional theory (TD-DFT) with the PBE0 functional and a 6-311G(d) basis set. Results are reported in Table 4-SI. It is worth noting that the ZZZ isomer shows two fairly intense transitions at 430 nm and 397 nm, thus the increase in absorption around 400 nm when the molecule is adsorbed on the titania surface can be partially accommodated by assuming an increase in the population of this isomer.

**Figure 4 ESI**: Relative energies of the six conformers considered in the computational study. The energies are obtained at PBE0/6-311G(d) level in DMSO. Solvent effects are taken into account by using the PCM model. Only the nitrogen atoms of the benzoindoline rings are shown.
**Table 4 ESI:** Excitation energies and oscillator strengths of the first ten singlet states computed at TD-DFT/PBE0 level using the 6-311G(d) basis set in DMSO. Oscillator strength are in parenthesis.

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<th>State /Isomer</th>
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</tr>
<tr>
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</table>
6 ATR-FTIR

Figure 5 ESI: ATR FTIR spectra of sensitizers in powder and adsorbed on the electrode.
Figure 7-ESI: Comparison between NMR spectra of VG10-C8 (top) and VG10-C2 (bottom) in DMSO-\(d_6\).

The peaks around 5.9 ppm in both spectra can be attributed to the proton of the double bond of the conjugated chain. In a symmetrical squaraine, when the rotation is allowed, we can recognize only one signal with integration 2. On the contrary, for unsymmetrical squaraine we can see two signals with integration 1 each. VG10-C2 behaves as a standard symmetrical squaraine dye where we cannot recognize different conformers in solution.

On the other hand, VG10-C8 presents two signals (total integration = 2) with different intensity, which can suggest the contemporary presence of more than one conformer in solution in the time of the experiment.

This can be explained as a difficult intramolecular rotation due to the steric hindrance of the octyl chains, as confirmed by the experiment at different temperatures in Figure 6 ESI.
Figure 8-ESI: Temperature dependent NMR spectra of VG10-C8 in DMSO-\textit{d}_6 at RT, 30, 50 and 70 °C (from the bottom)

By increasing the temperature of the experiment, it is evident the partial disappearance of the small peak and the change of ratio between the two peaks. The small peak is restored if we come back to room temperature after the experiment.
The photovoltaic performance was evaluated using a TiO$_2$ film consisting of 8 μm of transparent layer and 5 μm of scattering layer. The transparent electrodes composed of ~20 nm anatase on fluorine doped tin oxide (FTO) conducting glass (4 mm thickness, 10 ohms/sq, Nippon Sheet Glass, Japan) were controlled to get a desired thickness by the number of screen printing passes. A ~4-5 μm scattering layer (400 nm, CCIC, HPW-400) was printed on the top of the transparent layer to increase light path length by scattering. The TiO$_2$ electrodes were immersed into a dye solution with 3α,7α-dihydroxy-5β-cholic acid (CDCA) in THF and kept for 15 h at room temperature. The concentration of dye and CDCA are described in the main text. The applied electrolyte consists of 0.6 M 1,3-dimethylimidazolium iodide, 0.03 M I$_2$, 0.05 M LiI, 0.05 M guanidinium thiocyanate, and 0.25 M 4-tert-butylpyridine in 15/85 (v/v) mixture of valeronitrile and acetonitrile. The dye-adsorbed TiO$_2$ electrode and platinized counter electrode on FTO (TEC 15 ohms/sq, Pilkington) were assembled into a sealed sandwich type cell with a gap of a hot-melt ionomer film, Surlyn (25 μm, Du-Pont). A 450 W xenon light source (Oriel, USA) was used to characterize the solar cells. The spectral output of the lamp was matched in the region of 350–750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) so as to reduce the mismatch between the simulated and true solar spectra to less than 4%. The current–voltage characteristics of the cell under these conditions were obtained by applying external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). For IPCE measurement, a modulated light intensity data acquisition system was used to control the Incident Photon-to-Current conversion Efficiency (IPCE) measurement. The modulation frequency was about 2 Hz. Light from a 300 W Xenon lamp (ILC Technology, USA) was focused through a computer controlled Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the photovoltaic cell under test. A white light bias was used to bring the total light intensity on the device under test closer to operating conditions. The devices were masked to attain an illuminated active area of 0.2 cm$^2$. Photovoltage transients were observed by using a pump pulse generated by 4 red light emitting diodes controlled by a fast solid-state switch with a white light bias. The pulse of red light with widths of 50 ms was incident on the photoanode side of the cell, and its intensity was controlled to keep a suitably low level to generate the exponential voltage decay where the charge recombination rate constants are obtained directly from the exponential decay rate. A white bias light, also incident on the same side of the device, was supplied by white diodes. Small perturbation transient photocurrent measurements were performed in a similar manner to the open-circuit voltage decay measurement.
Figure 9 ESI. a) Changes in interfacial electron lifetime as a function of capacitance and b) capacitance as function of the open circuit voltage generated from VG10-C2 and VG10-C8 sensitized solar cells.

Figure 9ESI-a shows the electron lifetime which is the reciprocal recombination rate of the injected electron leading to a change of electron density in TiO$_2$ and then $V_{oc}$ change of DSCs.
9 Photo and thermal stability

The photostability was evaluated using a TiO$_2$ film consisting of 6 µm of transparent layer (~20 nm, anatase) screen printed on fluorine doped tin oxide (FTO) conducting glass (2 mm thickness, TEC 15 ohms/sq, Pilkington). The photoelectrodes were washed in ethanol, dried, heated at 400°C for 1h and cooled at RT. Then they were immersed into an ethanolic dye solution (0.1 mM) and kept for 4 h at room temperature in the dark under continuous stirring. The electrodes were rinsed in pure ethanol and softly dried with paper. The dye-adsorbed TiO$_2$ electrodes were sealed with microscope slides using a double sided tape, properly holed. The photostability tests
were performed under irradiation (Solarbox 3000e, 2500 W xenon lamp, CO.FO.ME.GRA) and the degradation of dye was monitored step by step by UV-Vis spectroscopy (Cary 300 Bio).

TGA measurements were collected on a TGA/DTA LF1100/851e, equipped with Store Software (Mettler Toledo, Novate Milanese, MI, Italy) instrument, using the following standard conditions: equilibration step at 60°C for 30 minutes, followed by a ramp at 10°C/min rate up to 600°C. Measurements were collected under nitrogen flow.

**Figure 11 ESI.** Thermostability study of SQ01, VG1-C2, VG1-C8, VG10-C8 and VG13 dyes.