

Supplementary Material

Squaric Acid Core Substituted Unsymmetrical Squaraine Dyes for Dye-sensitized Solar Cells: Effect of Electron Acceptors on their Photovoltaic Performance

*Safalmani Pradhan**, *Yuki Kurokawa*, *Suraya Shaban*, and *Shyam S. Pandey**

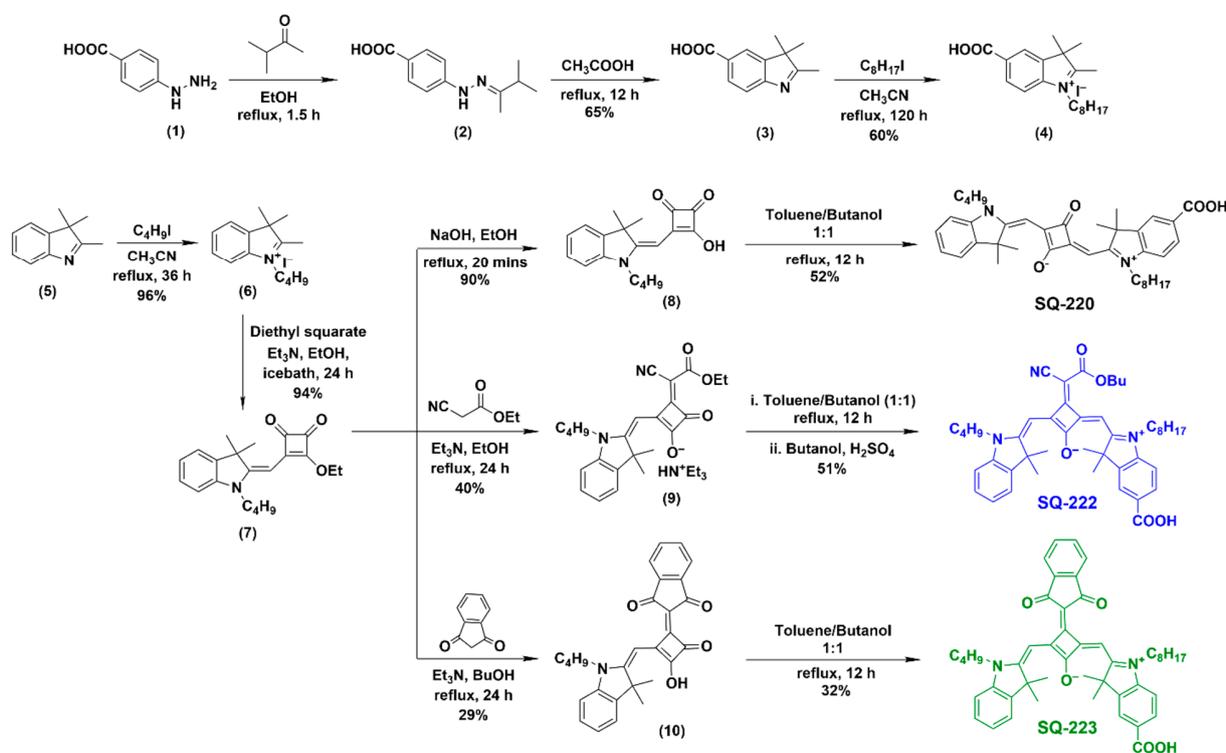
Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 2,4-Hibikino, Wakamatsu, Kitakyushu, 808-0196, Japan

*Correspondence: pradhan.safalmani542@mail.kyutech.jp (S.P.); shyam@life.kyutech.ac.jp (S.S.P)

Experimental Section

S1. Synthesis of unsymmetrical squaraine dyes, SQ-220, SQ-222 and SQ-223

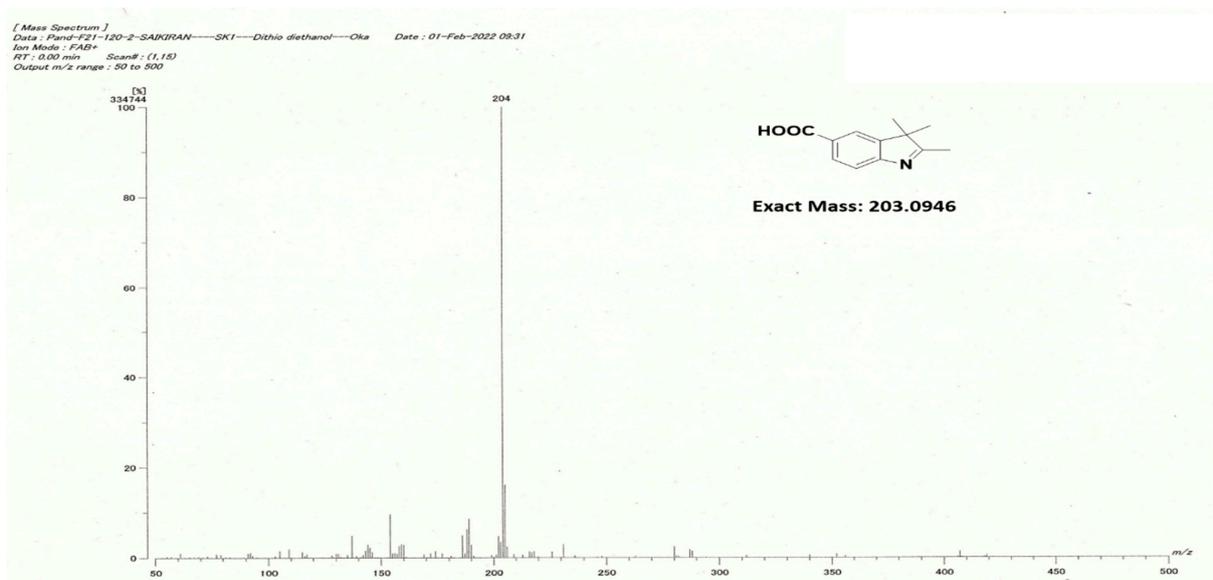
The starting compounds, 4-hydrazino benzoic acid (**1**) and 2,3,3-trimethyl-3H-indole (**5**) were purchased from Sigma-Aldrich and used without further purification. The intermediates, 4-[(1,2-Dimethylpropylidene)hydrazine]-benzoic acid (**2**), 2,3,3-trimethyl-3H-indole-5-carboxylic acid (**3**), and 5-carboxy-2,3,3-trimethyl-1-octyl-3H-indolium iodide (**4**) were synthesized according to the procedure reported by Yum et al. [1].



Scheme S1. Scheme of synthesis for the far-red-sensitive unsymmetrical squaraine sensitizers.

S1.1. 2,3,3-trimethyl-3H-indole-5-carboxylic acid (**3**)

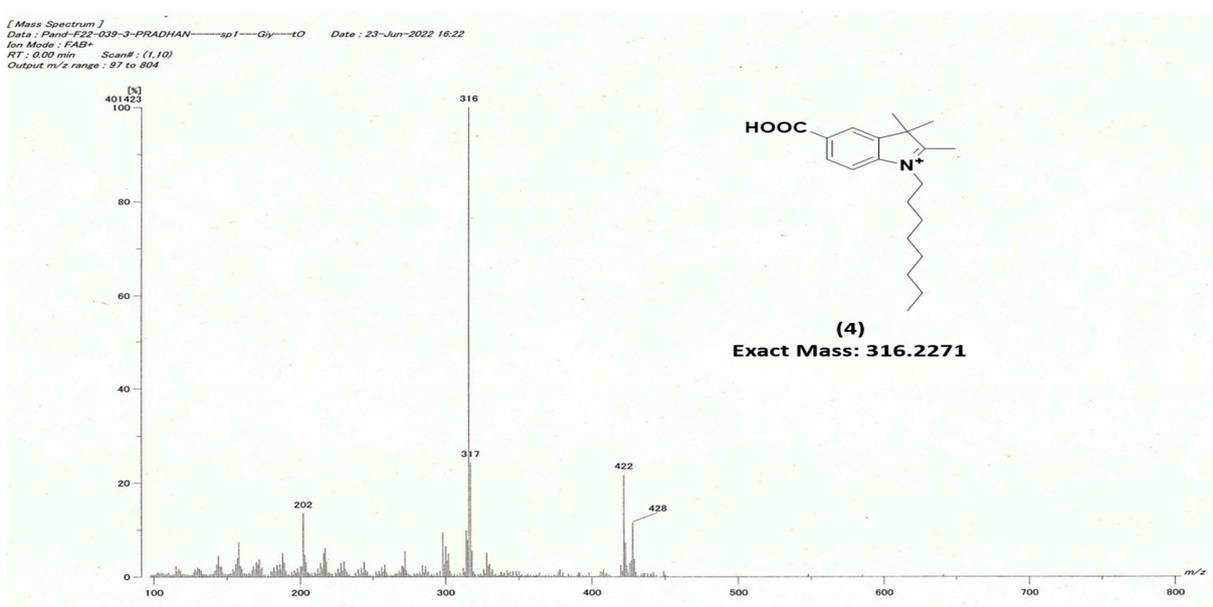
FAB-MS: C₁₂H₁₃NO₂ (calculated $m/z = 203.0946$ and measured $m/z = 204.1028$ [M+H]⁺).



FAB-MS of intermediate (3)

S1.2. 5-carboxy-2,3,3-trimethyl-1-octyl-3H-indolium iodide (4)

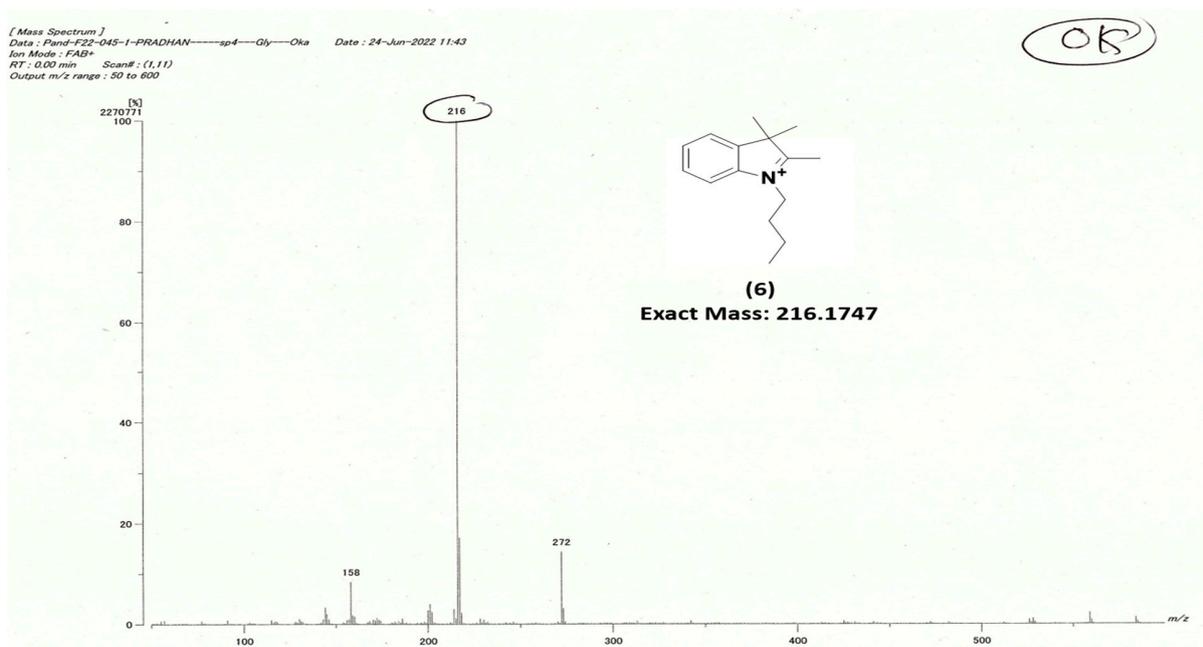
FAB-MS: $C_{20}H_{30}NO_2^+$ (calculated $m/z = 316.22$ and measured $m/z = 316.00 [M]^+$).



FAB-MS of the intermediate (4)

S1.3. Synthesis of 1-butyl-2,3,3-trimethyl-3H-indol-1-ium iodide (6)

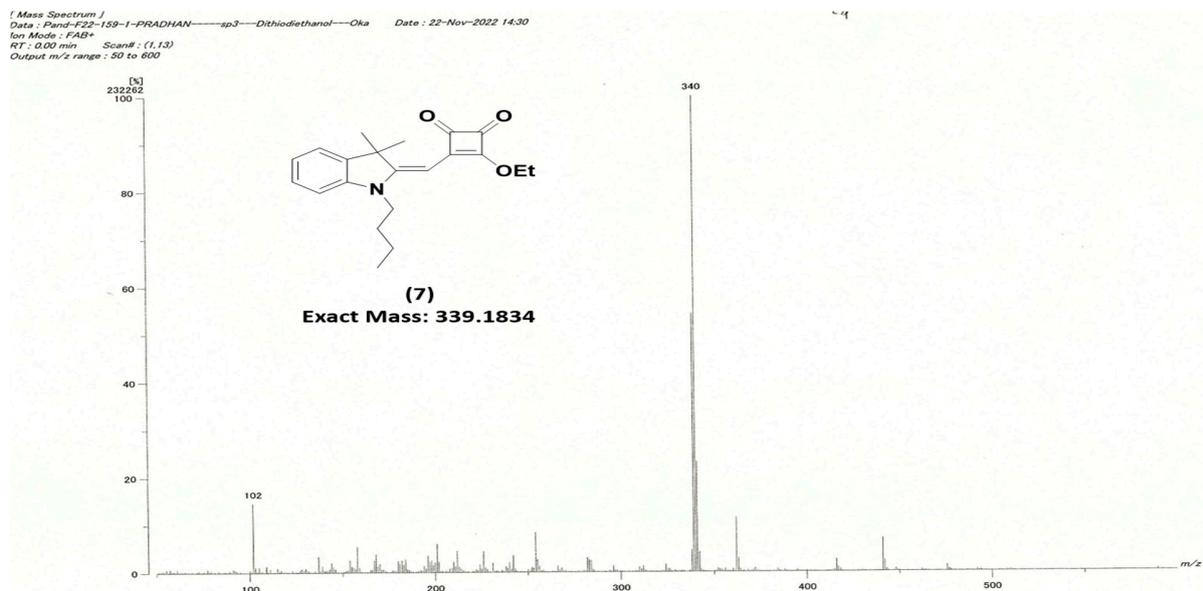
7.96 g (50 mmol) of 2,3,3-trimethyl-3H-indole (5) and 27.6 g (150 mmol) of 1-iodobutane were dissolved in 50 mL of acetonitrile taken in a round-bottomed flask fitted with a condenser. The reaction mixture was refluxed for 36 hours. Reaction monitoring was done by TLC using Hexane : Ethyl acetate (1:1) as the eluting solvent. After completion of the reaction as confirmed by TLC, the solvent was evaporated under vacuum. The product was precipitated with hexane and the solid obtained was filtered under vacuum and dried under vacuum. The vacuum dried product was collected as a brownish solid 96% yield (16.45 g). FAB-MS: $C_{15}H_{22}N^+$; (calculated $m/z = 216.17$ and measured $m/z = 216.00 [M]^+$ confirms the identity of the synthesized product.



FAB-MS of the intermediate (6)

S1.4. Synthesis of (E)-3-((1-butyl-3,3-dimethylindolin-2-ylidene)methyl)-4-ethoxycyclobut-3-ene-1,2-dione (semi-squaraine ester) (7)

5 g (14.6 mmol) of (6), 2.55 g (15 mmol) diethyl squarate and 20 mL ethanol were added into a two-necked round bottomed flask. Then, 5.67 g (56 mmol) of Triethylamine was added dropwise to the reaction mixture. The reaction was stirred in an ice-bath under argon for 24 hours. The product precipitated in the reaction vessel and it was filtered under vacuum. The bright yellow solid was obtained in 94% yield (4.67 g). FAB-MS: $C_{21}H_{25}NO_3$ (calculated $m/z = 339.1834$ and measured $m/z = 339.1855$ $[M]^+$ confirms the identity of the synthesized product.



FAB-MS of the intermediate (7)

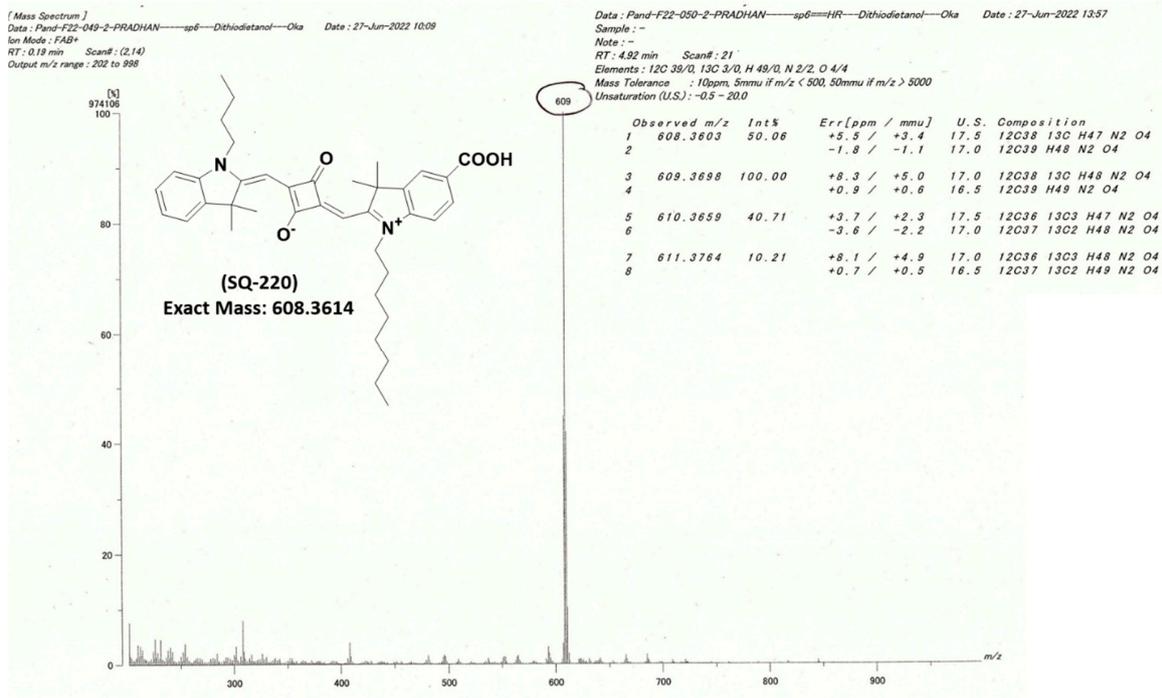
S1.5. Synthesis of (E)-3-((1-butyl-3,3-dimethylindolin-2-ylidene)methyl)-4-hydroxycyclobut-3-ene-1,2-dione (hydrolyzed semi-squaraine dye) (8)

339.18 mg (1 mmol) of semisquaraine ester (7) was then hydrolyzed using 2 mL of 10% sodium hydroxide (NaOH) solution in 15 mL ethanol. After this, 70% of the solvent was evaporated and

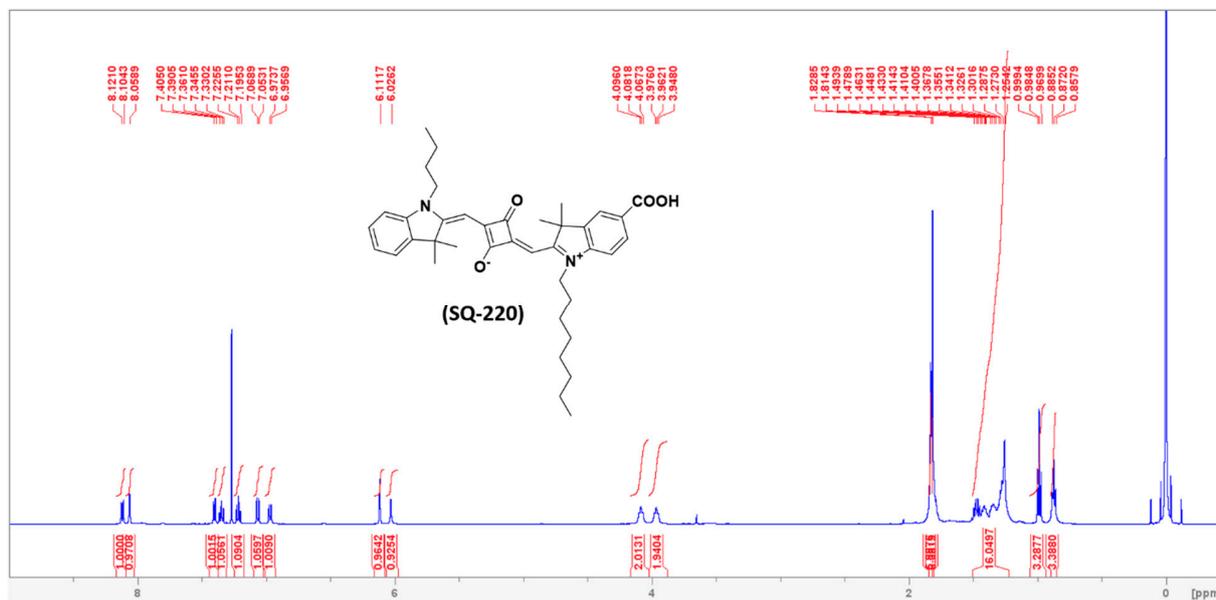
the reaction mixture was neutralized by adding further 1.5 mL of 20% HCl. After extracting the product in chloroform, it was washed thoroughly with saturated sodium bicarbonate (NaHCO₃), brine and water. The chloroform was then evaporated using rotary evaporator to give orange solid in 90% yield (280 mg).

S1.6. Synthesis of SQ-220

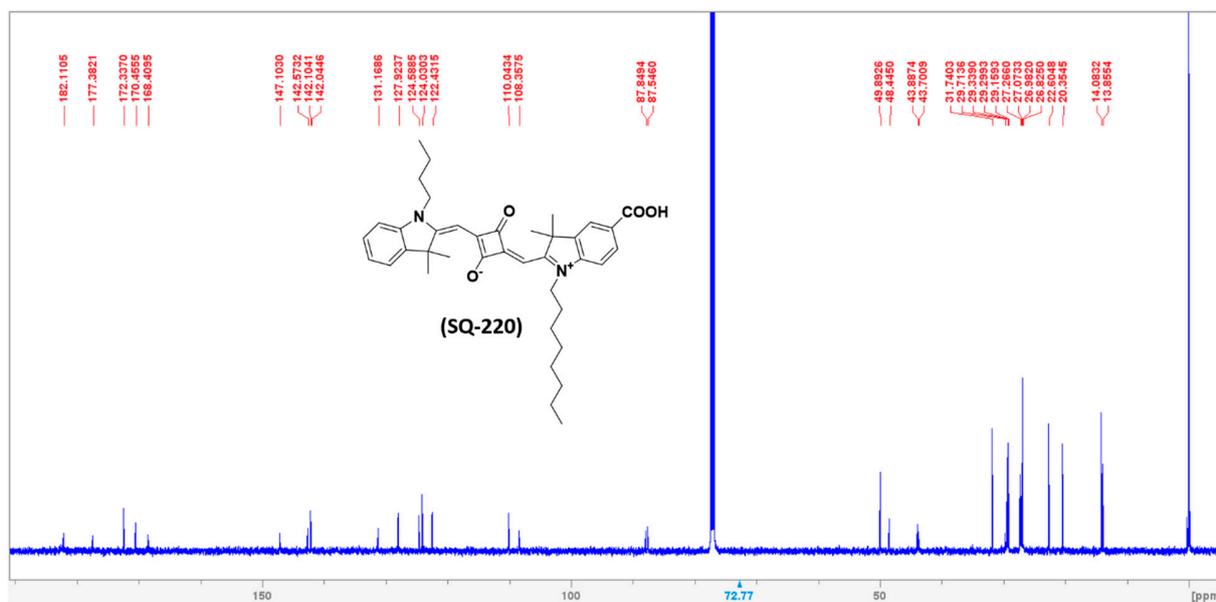
200 mg (0.64 mmol) of hydrolyzed semisquaraine dye (**8**) and 280 mg (0.64 mmol) of intermediate (**4**) were dissolved in 30 mL of toluene: butanol (1:1) taken in a round bottomed flask fitted with a condenser. The reaction mixture was then refluxed for 12 hours under argon atmosphere. After the completion of the reaction as confirmed by TLC, solvent was removed under vacuum and then the crude dye was subjected to column chromatography using methanol: chloroform as the eluting solvent. The concentration of the isolated pure fraction under vacuum gave violet solid as the titled dye in 52% yield (202 mg). HRFAB-MS: C₃₉H₄₈N₂O₄; (calculated m/z = 608.3614 and measured m/z = 608.3603 [M]⁺; ¹H NMR (500 MHz, CDCl₃): δ /ppm = 8.12 (d, 1H, CH_{arom}); 8.05 (s, 1H, CH_{arom}); 7.40 (d, 1H, CH_{arom}); 7.35 (m, 1H, CH_{arom}); 7.21 (m, 1H, CH_{arom}); 7.06 (d, 1H, CH_{arom}); 6.97 (d, 1H, CH_{arom}); 6.11 (s, 1H, CH_{methine}); 6.03 (s, 1H, CH_{methine}); 4.08 (t, 2H, N-CH_{methylene}); 3.96 (t, 2H, N-CH_{methylene}); 1.83 (s, 6H, CH_{methyl}); 1.81 (s, 6H, CH_{methyl}); 1.51-1.25 (m, 16H, CH_{methylene}); 0.98 (t, 6H, CH_{methyl}); 0.88 (t, 6H, CH_{methyl}); and ¹³C NMR (500 MHz, CDCl₃): δ /ppm = 182.11, 177.38, 172.33, 170.45, 168.40, 147.10, 142.57, 142.10, 142.04, 131.16, 127.92, 124.58, 124.03, 122.43, 110.04, 108.35, 87.84, 87.54, 49.89, 48.44, 43.88, 43.70, 31.74, 29.71, 29.33, 29.29, 29.15, 27.26, 27.07, 26.98, 26.82, 22.60, 20.35, 14.08, 13.85 confirms the identity of the synthesized product.



FAB-MS and HR FAB-MS of SQ-220



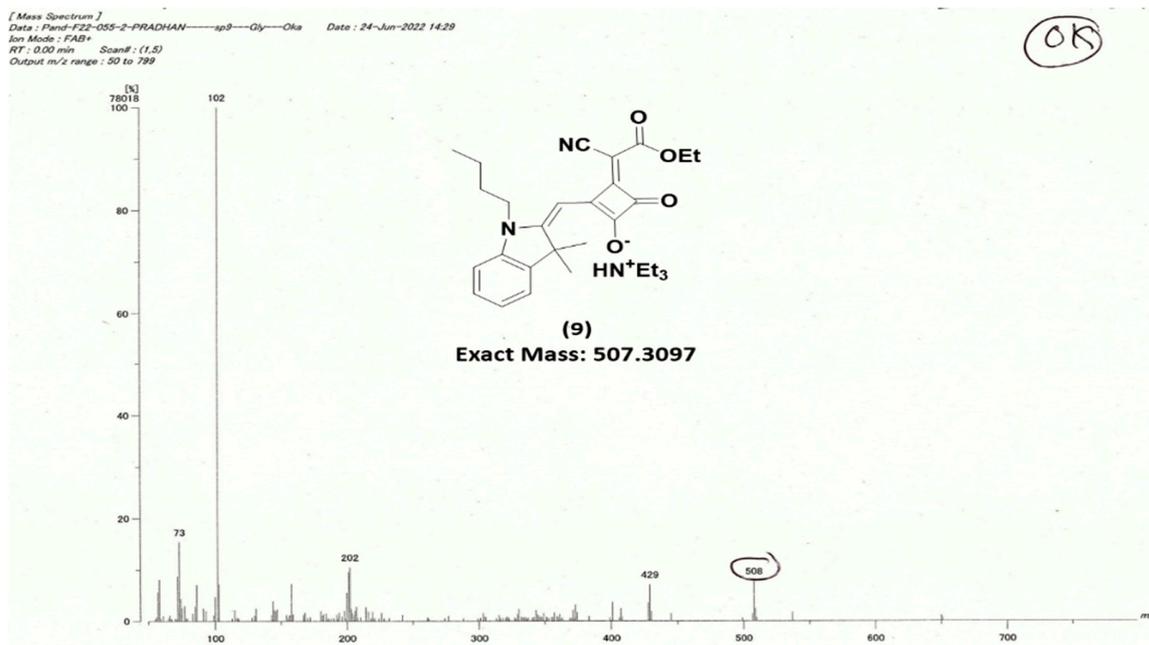
¹H-NMR of SQ-220



^{13}C -NMR of SQ-220

S1.7. Synthesis of (Z)-2-(((E)-1-butyl-3,3-dimethylindolin-2-ylidene)methyl)-3-(1-cyano-2-ethoxy-2-oxoethylidene)-4-oxocyclobut-1-en-1-olate triethylammonium (**9**)

1 mL (7 mmol) of Triethylamine was added dropwise to a mixture of 850 mg (2.5 mmol) of (**7**) and 280 mg (2.5 mmol) of ethyl cyanoacetate in 30 mL of ethanol taken in a round-bottomed flask, fitted with a condenser. The reaction mixture was then refluxed for 24 hours under an argon atmosphere. The reaction was monitored by TLC using methanol: chloroform (1:9) as the eluting solvent. After the completion of the reaction, as indicated by TLC, the solvent was evaporated under a vacuum. The crude product was purified by column chromatography using methanol: chloroform as the eluting solvent giving the titled compound (**9**) in 40% yield (504 mg). FAB-MS: $\text{C}_{30}\text{H}_{41}\text{N}_3\text{O}_4$; (calculated $m/z = 507.67$ and measured $m/z = 508.00$ $[\text{M}]^+$) confirms the identity of the synthesized product.

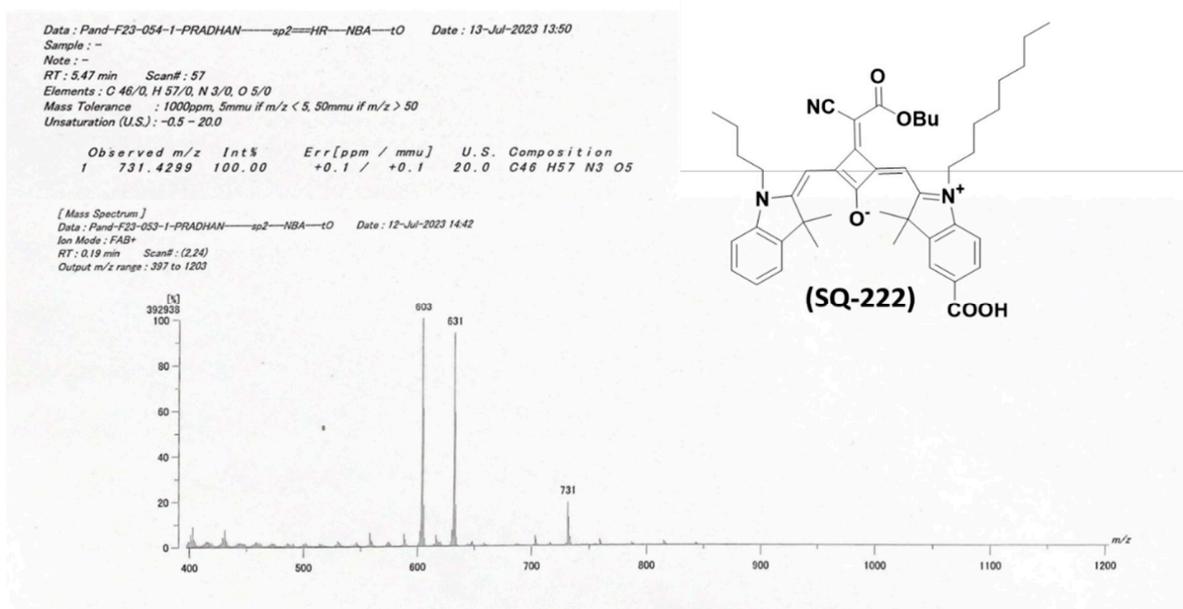


FAB-MS of the intermediate (9)

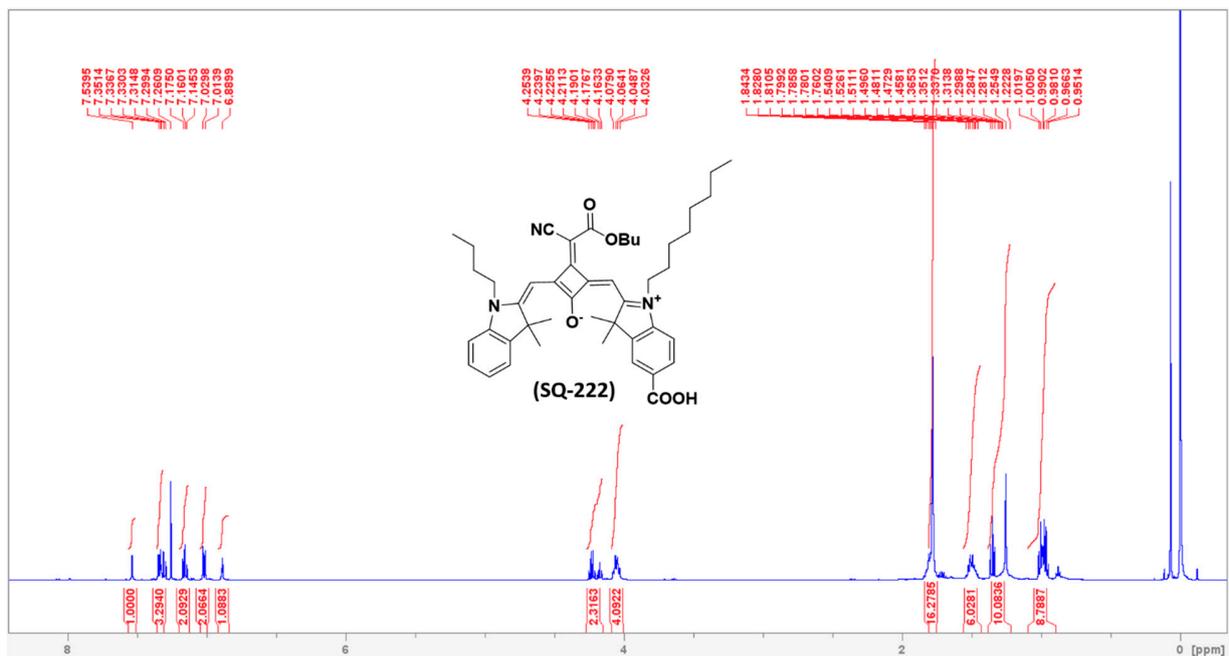
S1.8. Synthesis of SQ-222

400 mg (0.79 mmol) of intermediate (9) and 350 mg (0.79 mmol) of intermediate (4) were dissolved in 40 mL of toluene: butanol (1:1) taken in a round-bottomed flask fitted with a condenser. The reaction mixture was then refluxed for 12 hours under an argon atmosphere. After the completion of the reaction, as confirmed by TLC, the solvent was evaporated under a vacuum. Then the crude dye was subjected to column chromatography using methanol: chloroform as the eluting solvent. The isolated pure fraction was then concentrated under a vacuum to obtain a purple solid. The solid was then subjected to ester exchange reaction by dissolving in 10 of butanol followed by addition of few drops of conc. H₂SO₄. After the completion of the reaction as confirmed by TLC, solvent was evaporated under vacuum to obtain a purple solid as the final dye in 51% yield (283 mg). HR-FAB-MS: C₄₆H₅₇N₃O₅; (calculated $m/z = 731.4298$ and measured $m/z = 731.4299$ [M]⁺; ¹H NMR (500 MHz, CDCl₃): δ /ppm = 7.53 (s, 1H, CH_{arom}); 7.33 (m, 3H,

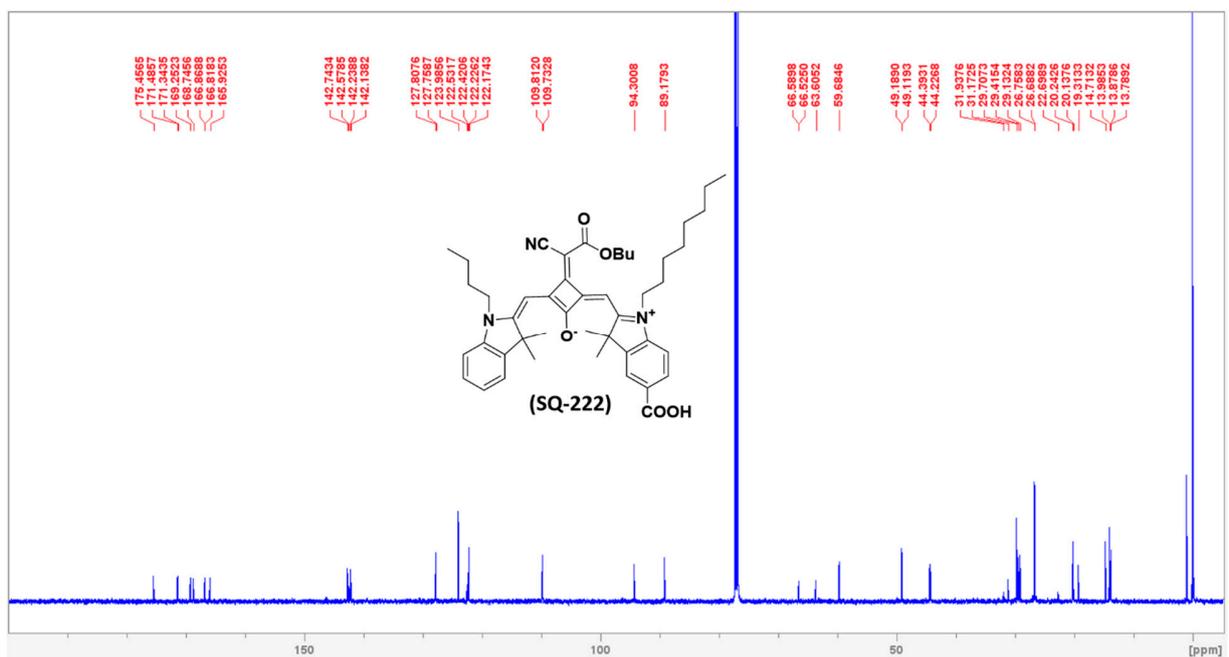
CH_{arom}); 7.16 (m, 2H, CH_{arom}); 7.02 (s, 1H, $CH_{methine}$); 7.01 (s, 1H, $CH_{methine}$); 6.88 (d, 1H, CH_{arom}); 4.23 (m, 2H, O- $CH_{methylene}$); 4.06 (m, 4H, N- $CH_{methylene}$); 1.85 – 1.75 (m, 16H, CH_{methyl} + $CH_{methylene}$); 1.55 – 1.45 (m, 6H, $CH_{methylene}$); 1.38 – 1.25 (m, 10H, $CH_{methylene}$); 1.01 – 0.95 (m, 9H, CH_{methyl}); and ^{13}C NMR (500 MHz, $CDCl_3$): δ/ppm = 175.45, 171.48, 171.34, 169.25, 168.74, 166.86, 166.81, 165.92, 142.74, 142.57, 142.23, 142.13, 127.80, 127.75, 123.98, 122.53, 122.42, 122.22, 122.17, 109.81, 109.73, 94.30, 89.17, 66.58, 66.52, 63.60, 59.68, 49.18, 49.11, 44.39, 44.22, 31.93, 31.17, 29.70, 29.41, 29.13, 26.75, 26.68, 22.69, 20.24, 20.13, 19.31, 14.71, 13.98, 13.87, and 13.78 confirms the identity of the synthesized product.



FAB-MS and HR FAB-MS of SQ-222



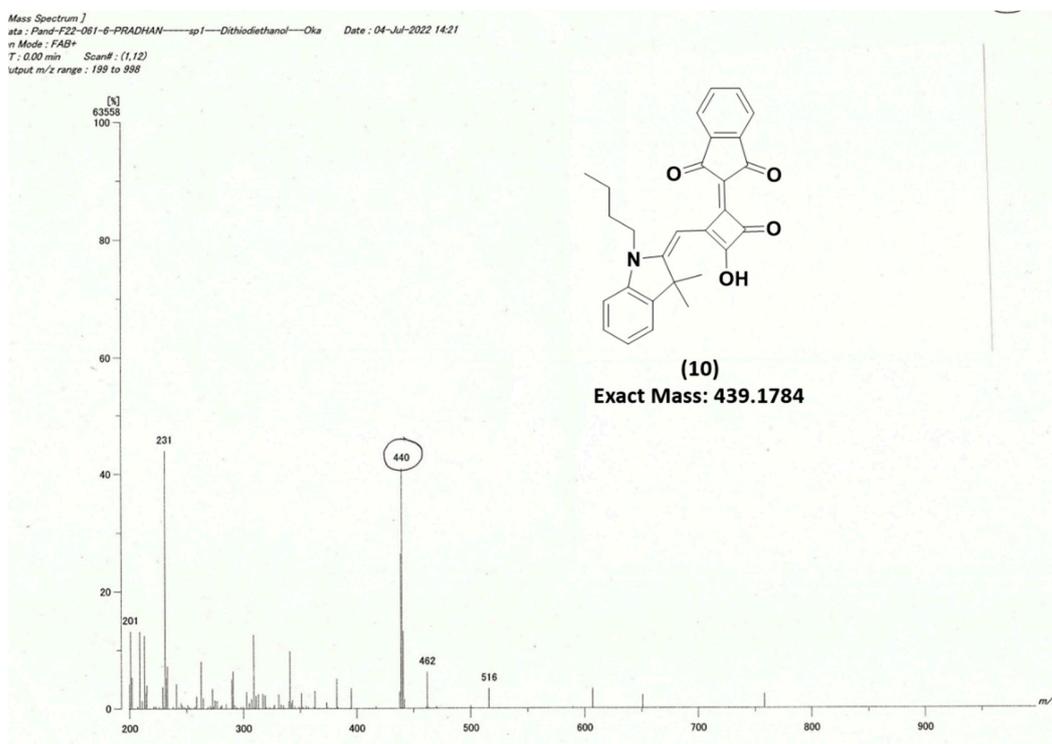
¹H-NMR of SQ-222



¹³C-NMR of SQ-222

S1.9. Synthesis of (E)-2-((1-butyl-3,3-dimethylindolin-2-ylidene)methyl)-3-(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)-4-oxocyclobut-1-en-1-olate (10)

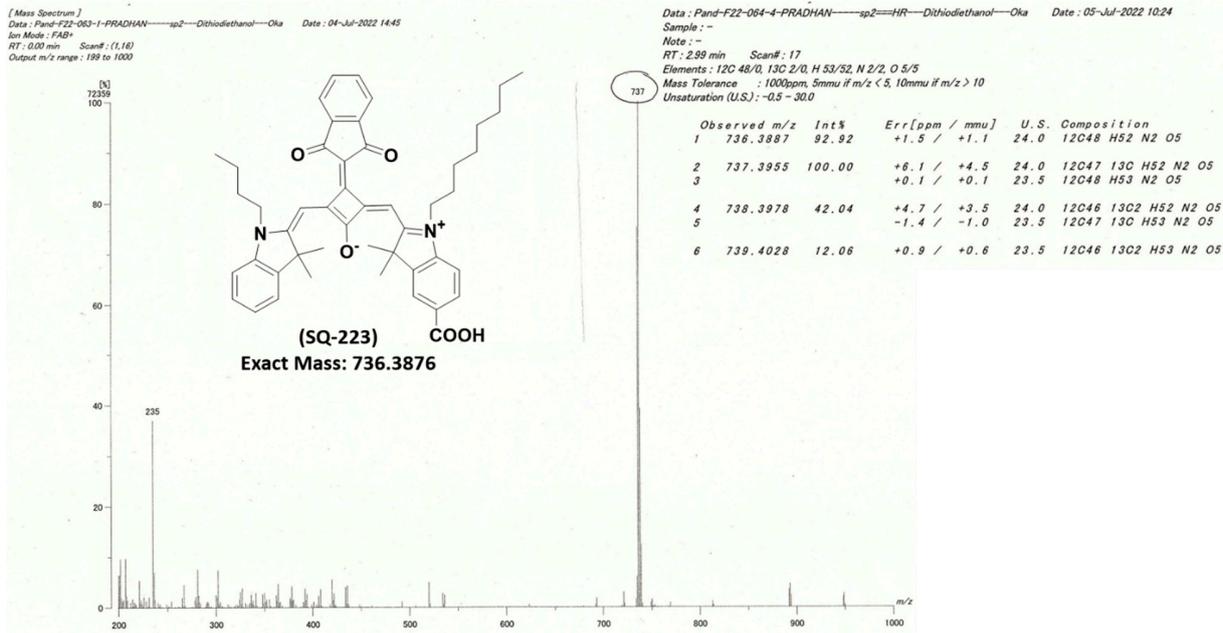
1 mL (7 mmol) of Triethylamine was added dropwise to a mixture of 1.4 g (4 mmol) of (7) and 877 mg (6 mmol) of 1,3-indandione in 50 mL of butanol taken in a round-bottomed flask, fitted with a condenser. The reaction mixture was then refluxed for 24 hours under an argon atmosphere. The reaction was monitored by TLC using methanol: chloroform (1:9) as the eluting solvent. After the completion of the reaction, as indicated by TLC, the solvent was evaporated under a vacuum. The crude product was purified by column chromatography using methanol: chloroform as the eluting solvent giving the titled compound (10) in 29% yield (325 mg). FAB-MS: $C_{28}H_{25}NO_4$; (calculated $m/z = 439.51$ and measured $m/z = 440.00 [M^+]$) confirms the identity of the synthesized product.



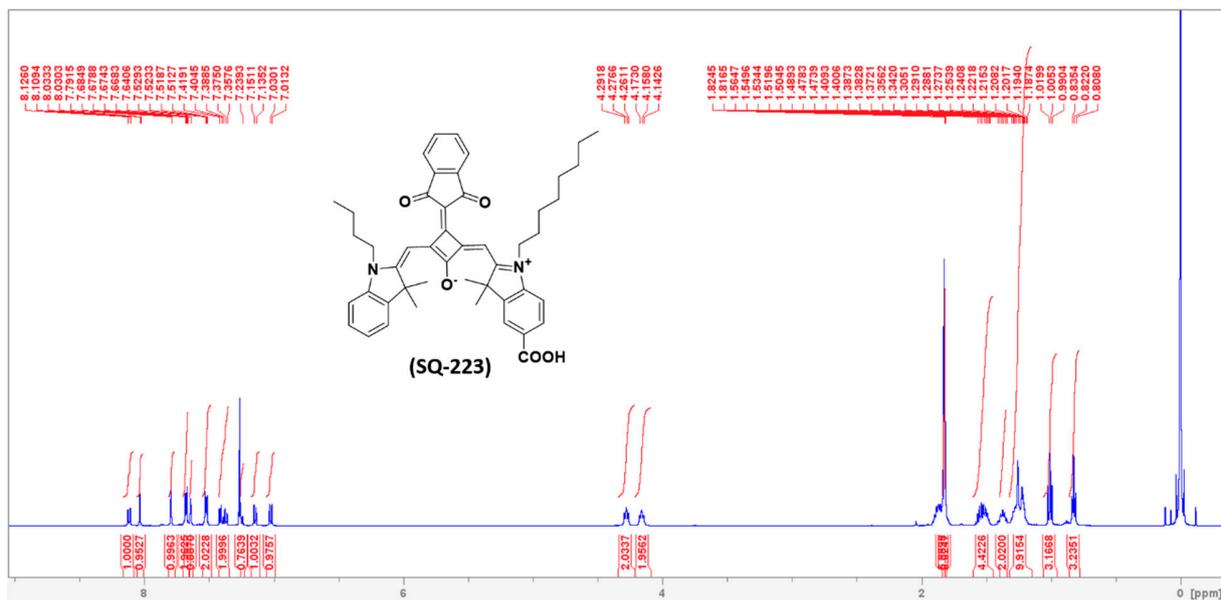
FAB-MS of the intermediate (10)

S1.10. Synthesis of SQ-223

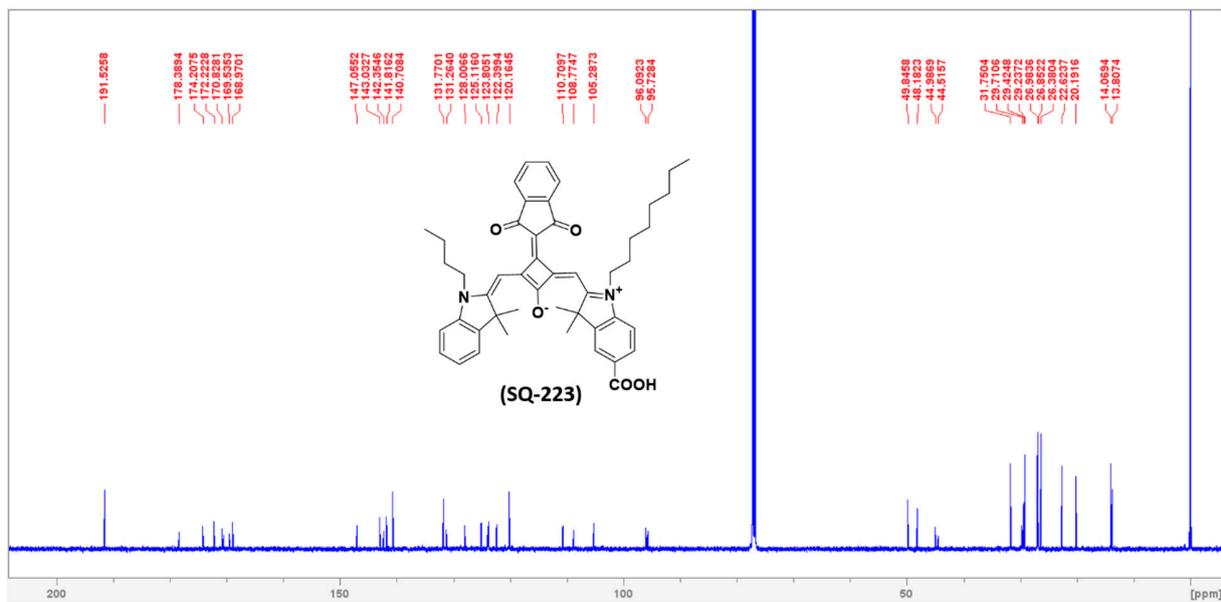
325 mg (0.6 mmol) of intermediate (**10**) and 266 mg (0.6 mmol) of intermediate (**4**) were dissolved in 30 mL of toluene: butanol (1:1) taken in a round-bottomed flask, fitted with a condenser. The reaction mixture was then refluxed for 12 hours under an argon atmosphere. After the completion of the reaction, as confirmed by TLC, the solvent was evaporated under a vacuum. Then the crude dye was subjected to column chromatography using methanol: chloroform as the eluting solvent. The isolated pure fraction was then concentrated under a vacuum to obtain a brownish solid as the final dye in 32% yield (141 mg). HR-FAB-MS: $C_{48}H_{52}N_2O_5$; (calculated $m/z = 736.3876$ and measured $m/z = 736.3887 [M]^+$); 1H NMR (500 MHz, $CDCl_3$): $\delta/ppm = 8.12$ (d, 1H, CH_{arom}); 8.03 (d, 1H, CH_{arom}); 7.79 (s, 1H, CH_{arom}); 7.67 (m, 2H, CH_{arom}); 7.64 (s, 1H, $CH_{methine}$); 7.52 (m, 2H, CH_{arom}); 7.38 (m, 2H, CH_{arom}); 7.24 (s, 1H, $CH_{methine}$); 7.14 (d, 1H, CH_{arom}); 7.02 (d, 1H, CH_{arom}); 4.27 (t, 2H, N- $CH_{methylene}$); 4.15 (t, 2H, N- $CH_{methylene}$); 1.84 (s, 6H, CH_{methyl}); 1.82 (s, 6H, CH_{methyl}); 1.58-1.48 (m, 4H, $CH_{methylene}$); 1.37 (m, 2H, $CH_{methylene}$); 1.30-1.19 (m, 10H, $CH_{methylene}$); 1.01 (t, 3H, CH_{methyl}); 0.83 (t, 3H, CH_{methyl}); and ^{13}C NMR (500 MHz, $CDCl_3$): $\delta/ppm = 191.52, 178.38, 174.20, 172.22, 170.82, 169.53, 168.97, 147.05, 143.03, 142.35, 141.81, 140.70, 131.77, 131.26, 128.00, 125.11, 123.80, 122.39, 120.16, 110.70, 108.77, 105.28, 96.09, 95.72, 49.84, 48.18, 44.98, 44.51, 31.75, 29.71, 29.42, 29.23, 26.98, 26.85, 26.38, 22.62, 20.19, 14.06, 13.80$ confirms the identity of the synthesized product.



FAB-MS and HR FAB-MS of SQ-223



¹H-NMR of SQ-223



^{13}C -NMR of SQ-223

S2. Theoretically calculated absorption spectra

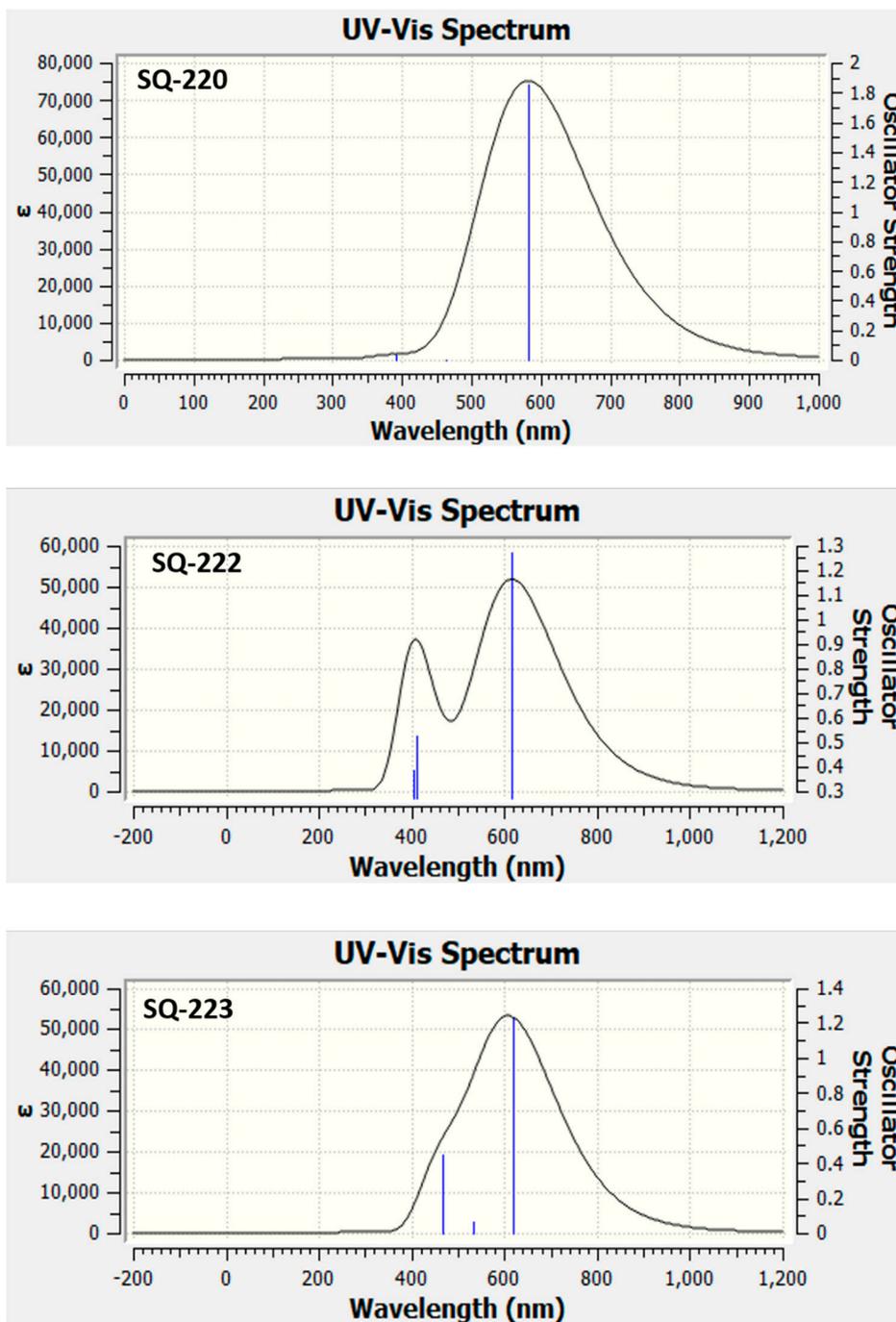


Figure S1: Theoretically calculated electronic absorption spectra of unsymmetrical squaraine dyes calculated using TD-DFT, 6-311G basis set and B3PW91 functional.

Table S1: Results of various parameters obtained after TD-DFT calculations for the unsymmetrical squaraine dyes.

Dye	State	Excitation energy (eV)	Absorption maximum (λ_{max} , nm)	Oscillator strength (f)	Main MO transitions
SQ-220	1	2.1298	582.13	1.8506	HOMO -> LUMO
	2	2.6797	462.68	0.0000	HOMO-1 -> LUMO
	3	3.1691	391.23	0.0312	HOMO -> LUMO+1
SQ-222	1	2.0103	616.75	1.2736	HOMO -> LUMO
	2	3.0118	411.66	0.5269	HOMO-1 -> LUMO
	3	3.0656	404.44	0.3881	HOMO -> LUMO+1
SQ-223	1	2.0080	617.45	1.2317	HOMO -> LUMO
	2	2.3284	532.50	0.0689	HOMO -> LUMO+1
	3	2.6558	466.85	0.4459	HOMO -> LUMO+2

**The calculations were conducted for an isolated single molecule employing a polarization continuum model (PCM) to take into account the effect of the ethanol solvent and using time-dependent density functional theory (TD-DFT), 6-311G basis set, and B3PW91 hybrid functional.*

S3. Electrochemical characterization

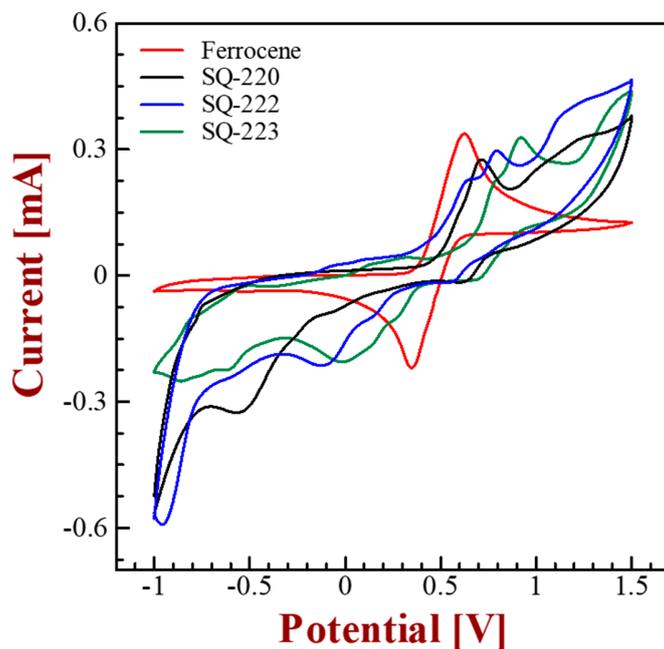


Figure S2. *Cyclic Voltammogram of the unsymmetrical squaraine dyes (2 mM) and ferrocene (2 mM) in DMF solution using tetrabutylammonium hexa-fluorophosphate (0.4 M) as electrolyte measured at a scan rate of 50 mV/s.*

S3.1. Calculation of HOMO energy levels of dyes using ferrocene as a standard reference material

HOMO energy level of Fc^+/Fc redox couple = -5.08 eV [2]

Oxidation potential of Ferrocene obtained from CV measurements = 0.62 V

First oxidation potential of SQ-223 obtained from CV measurements = 0.92 V

Shift of the first oxidation potential of SQ-223 from the oxidation potential of Ferrocene = 0.30 V

Therefore, HOMO energy level of SQ-223 = $-5.08 - 0.30 = -5.38$ eV

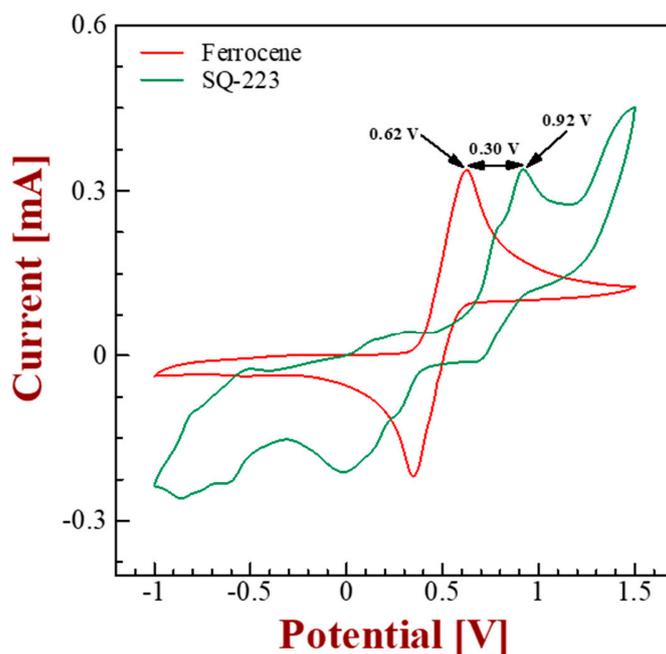


Figure S3. *Cyclic Voltammogram of ferrocene and SQ-223 explaining the calculation of potential shift of first oxidation potential of SQ-223 with respect to Ferrocene.*

S4. Dye loading studies for unsymmetrical squaraine dyes, SQ-220, SQ-222 and SQ-223

The FTO-coated substrates were screen-printed with Ti-nanoxide (T/SP) as first layer and Ti-nanoxide (D/SP) as second layer, in order to obtain a double layered mesoporous TiO₂ having a total thickness of 16 μm and an active area of 6.25 cm². For dye adsorption, the TiO₂ printed substrates were then dipped into a 0.2 mM ethanolic solution of the respective dyes, SQ-220, SQ-222 and SQ-223, consisting of 20 mM Chenodeoxycholic Acid (CDCA), for 4 hours.

For dye desorption, the dye-adsorbed substrates were then dipped into a 40 mM ethanolic solution of sodium hydroxide (NaOH) until complete desorption. The absorption spectra of the NaOH solution containing desorbed dyes were then recorded.

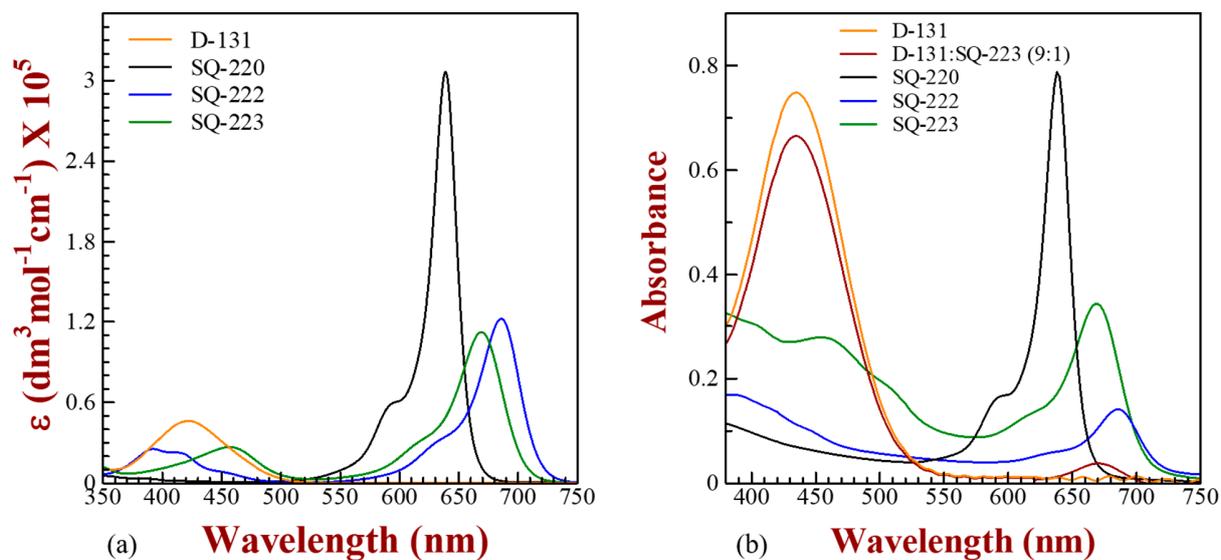


Figure S4. (a) Electronic absorption spectra of the unsymmetrical squaraine dyes desorbed into 40 mM ethanolic NaOH solution; (b) Electronic absorption spectra of 5 μM ethanolic solution of the same dyes for determination of Molar extinction coefficient (ϵ).

Table S2. Amount of dye loaded onto double layered mesoporous TiO_2 of thickness 16 μm and area 6.25 cm^2 .

Sensitizing dyes	ϵ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	A_{max}	Dye loading ($\text{nmol cm}^{-2} \mu\text{m}^{-1}$)
D-131	0.46×10^5	0.75	5.00
SQ-220	3.08×10^5	0.79	1.02
SQ-222	1.22×10^5	0.14	0.47
SQ-223	1.12×10^5	0.34	1.25
D-131: SQ-223 (9:1)	-	0.66 (D-131) 0.04 (SQ-223)	4.46 (D-131) 0.15 (SQ-223)

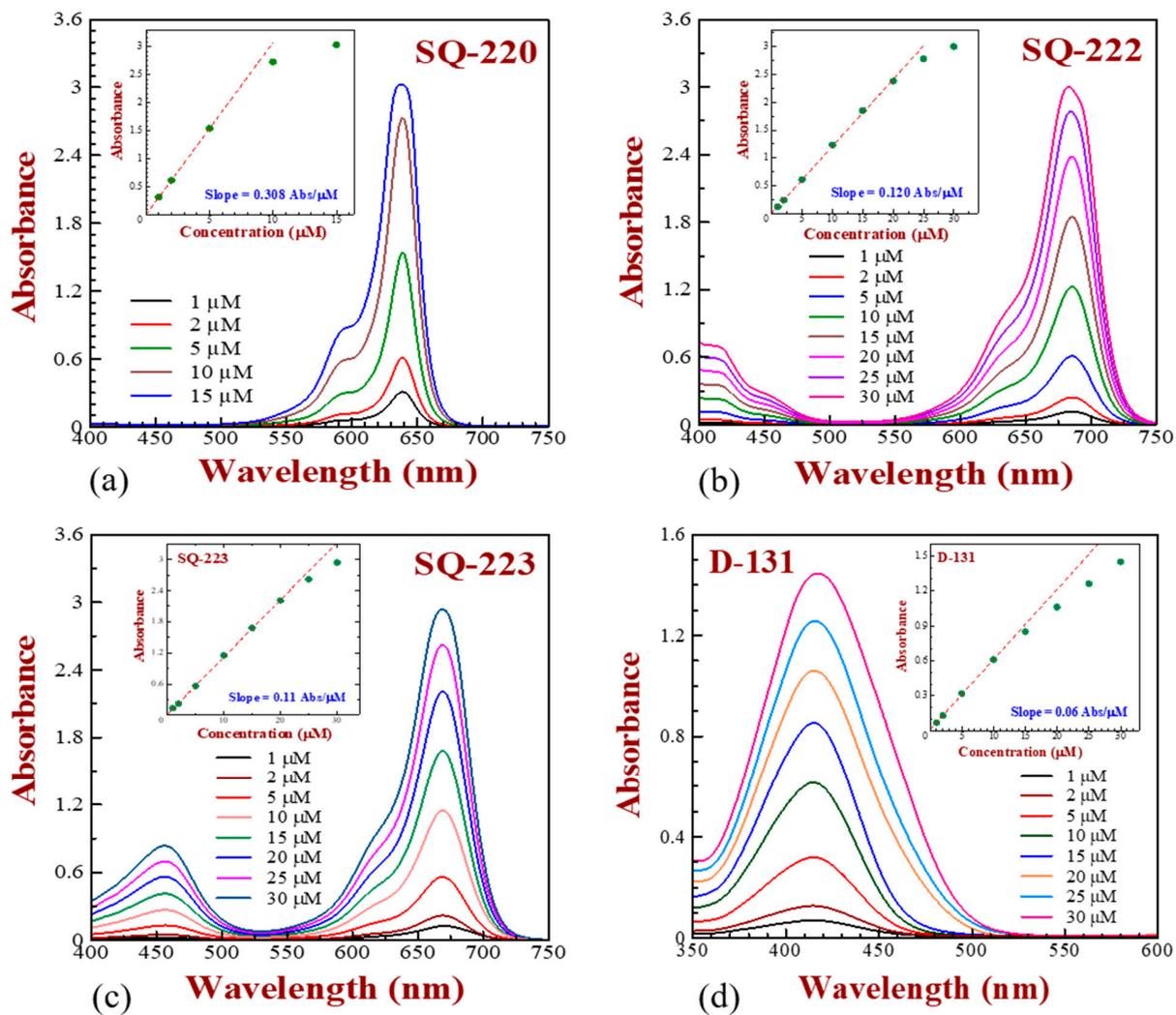


Figure S5. Electronic absorption spectra of ethanolic solution of (a) SQ-220, (b) SQ-222, (c) SQ-223, and (d) D-131 in various concentrations. The inset in all the three figures (a), (b), (c) and (d) shows the plot for absorbance versus concentration.

References

1. Yum, J.-H.; Walter, P.; Huber, S.; Rentsch, D.; Geiger, T.; Nüesch, F.; De Angelis, F.; Grätzel, M.; Nazeeruddin, M.K. Efficient Far Red Sensitization of Nanocrystalline TiO₂ Films by an Unsymmetrical Squaraine Dye. *J. Am. Chem. Soc.* **2007**, *129*, 10320–10321, doi:10.1021/ja0731470.
2. Su, B.; Girault, H.H. Absolute Standard Redox Potential of Monolayer-Protected Gold Nanoclusters. *J. Phys. Chem. B* **2005**, *109*, 11427–11431, doi:10.1021/jp051455j.