Supporting information for

Efficient and stable panchromatic squaraine dyes for dye-sensitized solar cells

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Contents of Supplementary Data

Table S1. Optical, redox and DSSC performance parameters of dyes

Dye	λ_{abs}[a]/nm (ε/$M^{-1}cm^{-1}$)	E_{redox}[b]/V	$E_{0\text{-}0}$[c]/V	E_{LUMO}[d]/V	J_{sc} ($mAcm^{-2}$)	V_{oc} (V)	FF	η[e] (%)
JK-216	365 (27,800), 669 (93,400)	1.00	1.72	-0.72	13.92	0.61	0.74	6.29
JK-217	367 (28,900), 672 (77,900)	0.92	1.68	-0.76	13.73	0.58	0.70	5.54

[a]Absorption spectra were measured in THF. [b]E_{ox} is oxidation potential. Red-ox potential of dyes on TiO_2 were measured in CH_3CN with 0.1M $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 50 mVs^{-1} (*vs*. Fc/Fc^+). [c]$E_{0\text{-}0}$ is voltage of intersection point between absorption and emission spectra. $E_{0\text{-}0}$ was determined from intersection of absorption and emission spectra in THF. [d]E_{LUMO} was calculated by $E_{ox} - E_{0\text{-}0}$. [e]Performances of DSSCs were measured with 0.175 cm^2 working area. Electolyte : 0.6 M DMPImI, 0.05 I_2, 0.1 M LiI and 0.1M TBP in acetonitrile

Table S2. Character Table of Calculated Vertical Excitation 1 and 2 for **JK-216**

n	λ (nm)	f[a]	Composition		Contribution (%)
			Occupied oritals	Empty orbitals	
1	654	1.48	HOMO-1	LUMO	23.4
			HOMO	LUMO	66.6
2	553	0.70	HOMO-2	LUMO	11.4
			HOMO-1	LUMO	64.8
			HOMO	LUMO+2	12.4

[a]Oscillator strength

Table S3. Detailed photovoltaic parameters with **JK-216**, **JK-217** under different incident light intensities.

Dye	P_{in} ($mW\ cm^{-2}$)	J_{sc} ($mA\ cm^{-2}$)	V_{oc} (mV)	FF (%)	η (%)
JK-216	12	1.79	568	79.4	6.73
	36	5.08	593	78.4	6.59
	54	7.55	603	77.4	6.53
	100	13.92	610	74.0	6.29
JK-217	12	1.80	537	74.8	6.61
	36	5.29	560	72.8	6.29
	54	7.86	566	71.7	6.10
	100	13.73	583	70.2	5.54

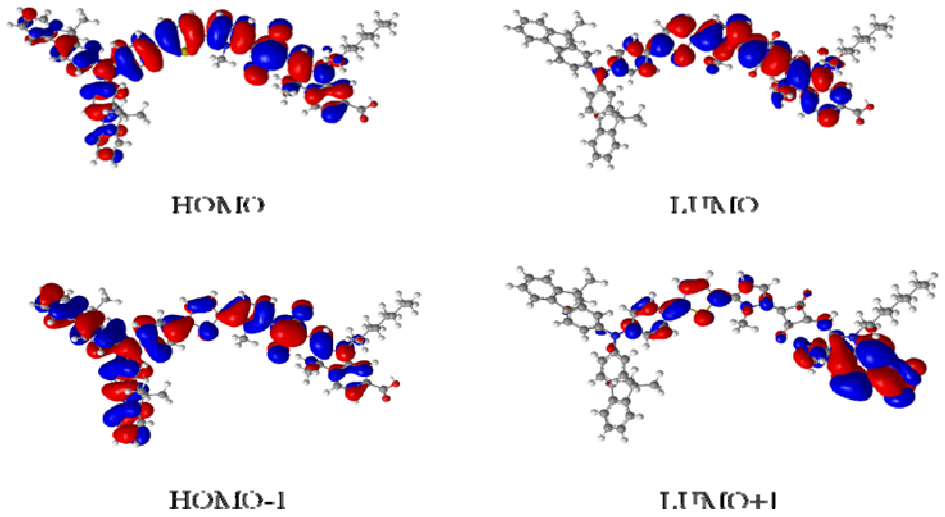

Figure S1. Isodensity surface plots of the HOMO-1, HOMO, LUMO and LUMO+1 of **JK-216.**

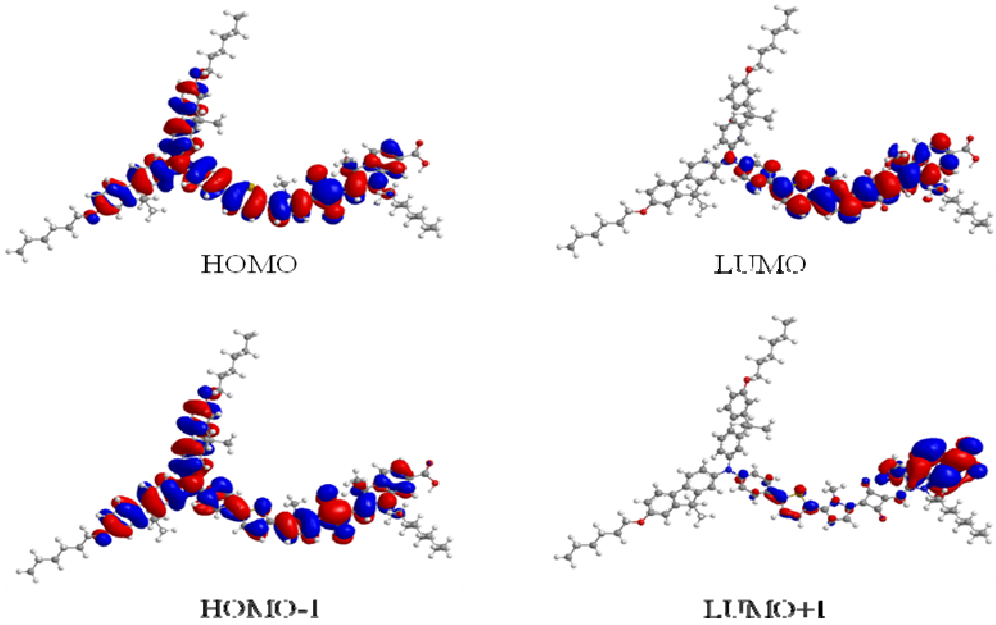

Figure S2. Isodensity surface plots of the HOMO-1, HOMO, LUMO and LUMO+1 of **JK-217.**

Experimental section

General methods. All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma-Aldrich, TCI and Acros Organics. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 600 spectrometer. Elemental analyses were performed with a Carlo Elba Instruments CHNS-OEA 1108 analyzer. Mass spectra were recorded on a JEOL JMS-SX102A instrument. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 2S UV-visible spectrometer and a Perkin LS fluorescence spectrometer, respectively. Cyclic voltammogram was carried out with a BAS 100B (Bioanalytical System, Inc.). A three electrode system was used and consisted of a gold disk, working electrode, and a platinum wire electrode. Redox potential of dyes on TiO_2 was measured in CH_3CN with a scan rate at 100 mVs^{-1}(*vs.* Fc/Fc^{+}).

Fabrication of DSSC. FTO glass plates (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 30 min, rinsed with water and ethanol. The FTO glass plates were immersed in 40 mM $TiCl_4$ (aq.) at 70 °C for 30 min and washed with water and ethanol. A transparent nanocrystalline layer on the FTO glass plate was prepared by doctor blade printing TiO_2 paste (Solaronix, Ti-Nanoxide T/SP) and then dried for 2 h at 25 °C. The TiO_2 electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min .The thickness of the transparent layer was measured by using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, CA), a paste for the scattering layer containing 400 nm sized anatase particles (CCIC, PST-400C) was deposited by doctor blade printing and then dried for 2 h at 25 °C. The TiO_2 electrodes were gradually heated under an air flow at

325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The TiO_2 electrodes were treated again by $TiCl_4$ at 70 °C for 30 min and sintered at 500 °C for 30 min. The TiO_2 electrodes were immersed into the **JK-216** and **JK-217** (0.1 mM in EtOH, containing 3a,7a-dihydroxy-5b-cholic acid (Cheno)) and kept at room temperature for overnight. The FTO plate for counter electrodes cleaned with ultrasonic bath in H_2O, acetone and 0.1 M HCl *aq*., subsequently. Counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg of Pt in 1 mL of ethanol) on a FTO plate and heating at 400 °C for 15 min. The dye adsorbed TiO_2 electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell by heating at 80 °C with a hot-melt ionomer film (Surlyn) as a spacer between the electrodes. A drop of electrolyte solution was placed on the drilled hole in the counter electrode of the assembled cell and was driven into the cell *via* vacuum backfilling. Two electrolytes were used for device evaluation. Electrolyte A : 0.6 M 1,2-dimethyl-3-propylimidazolium iodie, 0.05 M iodine, 0.1 M LiI, 0.1 M *tert*-butylpyridine in acetonitrile. Electrolyte B : DMII / 1-ethyl-3-methylimidazolium iodide / 1-ethyl-3-methylimidazolium tetracyanoborate / I_2 /N-butylbenzimidazole / GNCS (molar ratio : 12/12/16/1.67/3.33/0.67). Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness).

***N*-(9,9-Dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-*N*-(4-(5-(1-methyl-1*H*-pyrrol-2-yl)thiophen-2-yl)phenyl)-9*H*-fluoren-2-amine 1.** Under nitrogen atmosphere, a mixture of *N*-(4-(5-bromothiophen-2-yl)phenyl)-*N*-(9,9-dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-9*H*-fluoren-2-amine (0.4 g, 0.62 mmol), 1-methyl-2-(trimethylstannyl)-1H-pyrrole (0.17 g, 0.74 mmol), $Pd(PPh_3)_4$ (0.072 g, 0.062 mmol) in dry toluene (40 ml) was refluxed 2 days. After cooling to room temperature, the solution was evaporated. The residue was dissolved dichloromethane and washed with distilled water (2 times). The organic layer was separated and dried over

anhydrous magnesium sulfate. The solvent was removed in *vacuo*. The pure product **1** was obtained by silica gel chromatography (eluent, dichloromethane : hexane = 1 : 4). Mp : 113 ^{o}C. MS: *m/z* 637 [M^{+}]. ^{1}H NMR($CDCl_3$) : δ 7.65 (d, 2H, ^{3}J = 7.8 Hz), 7.61 (d, 2H, ^{3}J = 8.4 Hz), 7.51 (d, 2H, ^{3}J = 8.4 Hz), , 7.36 (d, 2H, ^{3}J = 7.2 Hz), 7.32 (t, 2H), 7.28 ~ 7.23 (m, 4H), 7.20 (d, 1H, ^{3}J = 3.6 Hz), 7.18 (d, 2H, ^{3}J = 9.0 Hz), 7.11(dd, 2H, ^{3}J = 7.2 Hz), 6.97 (d, 1H, ^{3}J = 4.2 Hz), 6.71 (m, 1H), 6.36 (m, 1H), 6.17 (m,1H), 3.77 (s, 3H), 1.40 (s, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$) : δ 155.3, 153.7, 147.4, 147.2, 139.1, 134.5, 133.8, 128.8, 128.5, 127.5, 127.2, 126.7, 126.5, 125.8, 124.4, 124.1, 123.4, 122.7, 122.6, 120.8, 119.6, 118.8, 110.5, 108.1, 47.0, 35.6, 27.2. Anal. Calc. for $C_{45}H_{38}N_2S$: C, 84.60; H, 6.00. Found : C, 84.35; H, 6.11.

7-(Hexyloxy)-*N*-(7-(hexyloxy)-9,9-dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-*N*-(4-(5-(1-methyl-1*H*-pyrrol-2-yl)thiophen-2-yl)phenyl)-9*H*-fluoren-2-amine 2. 2 was synthesized by a procedure to **1** except that *N*-(4-(5-bromothiophen-2-yl)phenyl)-7-(hexyloxy)-*N*-(7-(hexyloxy)-9,9-dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-9*H*-fluoren-2-amine (0.4 g, 0.48 mmol) was used in place of *N*-(4-(5-bromothiophen-2-yl)phenyl)-*N*-(9,9-dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-9*H*-fluoren-2-amine. Mp : 96 ^{o}C. MS: *m/z* 838 [M^{+}]. ^{1}H NMR($CDCl_3$) : δ 7.54 (d, 2H, ^{3}J = 8.4 Hz), 7.50 (d, 2H, ^{3}J = 8.4 Hz), 7.48 (d, 2H, ^{3}J = 9.0 Hz), 7.20 (s, 2H), 7.19 (d, 1H, ^{3}J = 4.2 Hz), 7.16 (d, 2H, ^{3}J = 9.0 Hz), 7.07 (dd, 2H, ^{3}J = 7.8 Hz), 6.97 (d, 1H, ^{3}J = 4.2 Hz), 6.93 (s, 2H), 6.86 (dd, 2H, ^{3}J = 7.8 Hz), 6.70 (m, 1H), 6.36 (m, 1H), 6.17 (m, 1H), 4.01 (t, 4H), 3.77 (s, 3H), 1.84 (m, 4H), 1.49 (m, 4H), 1.39 (s, 12H), 1.36 (m, 8H), 0.91 (t, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$) : δ 158.9, 155.6, 154.8, 147.7, 146.2, 134.6, 131.9, 128.0, 126.4, 125.8, 124.3, 123.6, 123.1, 122.5, 122.1, 120.3, 119.8, 119.0, 117.7, 113.1, 110.0, 109.5, 108.1, 68.5, 47.0, 35.5, 31.8, 29.6, 27.3, 26.0, 22.8, 14.2. Anal. Calc. for $C_{57}H_{62}N_2O_2S$: C, 81.85; H, 7.45. Found : C, 81.99; H, 7.31.

3-(5-(5-(4-(Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)phenyl)thiophen-2-yl)-1-methyl-1*H*-

pyrrol-2-yl)-4-hydroxycyclobut-3-ene-1,2-dione 3.[1] Squarilyum chloride (0.047 g, 0.31 mmol) was added directly as a solid to a solution of **1** (0.2 g, 0.31 mmol) in dry Et_2O (20 ml). Color readily turns deep yellow and a red precipitate is formed. Mixture was stirred at r.t. for 1 h. The suspension was concentrated to about 20 ml volume and the red precipitate was filtered and washed with hexane directly on the filter. The emichloride was immediately converted in the corresponding emisquaraine. The red precipitate was thus dissolved in 20 ml of acetone and 0.2 ml of NEt_3 were added. After 6 h stirring at r.t. solvent was removed. The residue was dissolved dichloromethane and wash with distilled water (2 times). The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed in *vacuo*. The pure product **3** was obtained by silica gel chromatography (eluent, dichloromethane : methanol = 10 : 1). Mp : 153 ^{o}C. MS: *m/z* 734 [M^+]. ^{1}H NMR(DMSO-d_6) : δ 7.76 (d, 2H, ^3J = 8.4 Hz), 7.74 (d, 2H, ^3J = 8.4 Hz), 7.61 (d, 2H, ^3J = 7.8 Hz), 7.50 (d, 2H, ^3J = 7.2 Hz), 7.45 (d, 1H, ^3J = 4.2 Hz), 7.33 ~ 7.26 (m, 7H), 7.11 (d, 2H, ^3J = 8.4 Hz), 7.05 (d, 2H, ^3J = 8.4 Hz), 6.90 (d, 1H, ^3J = 4.2 Hz), 6.45 (d, 1H, ^3J = 4.2 Hz), 4.16 (s, 3H), 1.37 (s, 12H). ^{13}C{^{1}H} NMR (DMSO-d_6) : δ 194.3, 192.2, 191.1, 155.4, 153.7, 147.5, 147.2, 143.1, 138.7, 135.8, 129.6, 129.2, 128.4, 127.8, 126.7, 126.1, 125.4, 124.4, 124.0, 123.7, 122.1, 121.6, 121.1, 120.4, 118.8, 111.1, 109.1, 47.2, 35.5, 27.2. Anal. Calc. for $C_{49}H_{38}N_2O_3S$: C, 80.08; H, 5.21. Found : C, 80.65; H, 5.11.

3-(5-(5-(4-(Bis(7-(hexyloxy)-9,9-dimethyl-9*H*-fluoren-2-yl)amino)phenyl)thiophen-2-yl)-1-methyl-1*H*-pyrrol-2-yl)-4-hydroxycyclobut-3-ene-1,2-dione 4. 4 was synthesized by a procedure to **3** except that **2** was used in place of **1**. Mp : 139 ^{o}C. MS: *m/z* 934 [M^+]. ^{1}H NMR(DMSO-d_6) : δ 7.63 (d, 2H, ^3J = 8.4 Hz), 7.61 (d, 2H, ^3J = 8.4 Hz), 7.58 (d, 2H, ^3J = 7.8 Hz), 7.42 (d, 1H, ^3J = 4.2 Hz), 7.24 (m, 2H), 7.09 (s, 2H), 7.05 (d, 2H, ^3J = 8.4 Hz), 7.00 (d, 2H, ^3J = 8.4 Hz), 6.90 (d, 1H, ^3J = 4.2 Hz), 6.87 (d, 2H, ^3J = 8.4 Hz), 6.44 (d, 1H, ^3J = 4.2 Hz), 4.16 (s, 3H), 3.99 (t, 4H), 1.72 (m, 4H), 1.45 (m, 4H), 1.34 (s, 12H), 1.31 (m, 8H), 0.88

(t, 6H). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6) : δ 193.1, 192,5, 191.4, 159.2, 157.4, 157.1, 149.7, 148.8, 136.1, 135.8, 130.7, 128.9, 127.1, 126.3, 124.6, 124.2, 123.6, 122.8, 120.6, 120.1, 119.4, 118.3, 113.9 111.2, 110.2, 109.2, 68.4, 47.2, 35.8, 31.9, 28.9, 27.5, 26.1, 22.4, 14.3. Anal. Calc. for $C_{61}H_{62}N_2O_5S$: C, 78.34; H, 6.68. Found : C, 78.01; H, 6.49.

(*E*)-2-(5-(5-(4-(Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)phenyl)thiophen-2-yl)-1-methyl-1*H*-pyrrol-2-yl)-4-((5-carboxy-3,3-dimethyl-1-octyl-3*H*-indolium-2-yl)methylene)-3-oxocyclobut-1-enolate JK-216. 3 (0.1g 0.13 mmol) and 5-carboxy-2,3,3-trimethyl-1-octyl-3H-indolium (0.06 g 0.13 mmol) were dissolved in a mixture of 30 ml benzene and 30 ml n-butanol. The mixture was refluxed with a Dean–Stark apparatus for 18 h. The solvent was partly removed until the product precipitated. The pure product **JK-216** was obtained by silica gel chromatography (eluent dichloromethane : methanol = 10 : 1). Mp : 178 ^{o}C. MS: *m/z* 1031 [M^{+}]. ^{1}H NMR(DMSO-d_6) : δ 8.14 (s, 1H), 8.04 (d, 1H, ^{3}J = 8.4 Hz), 7.72 (m, 3H), 7.67 (d, 2H, ^{3}J = 8.4 Hz), 7.62 (d, 2H, ^{3}J = 8.4 Hz), 7.59 (d, 1H, ^{3}J = 3.6 Hz), 7.56 (d, 1H, ^{3}J = 3.6 Hz), 7.52 (d, 2H, ^{3}J = 7.2 Hz), 7.49 (d, 1H, ^{3}J = 4.2 Hz), 7.35 ~ 7.27 (m, 6H), 7.12 (d, 2H, ^{3}J = 8.4 Hz), 7.05 (d, 2H, ^{3}J = 7.8 Hz), 6.85 (d, 1H, ^{3}J = 4.2 Hz), 6.11 (s, 1H), 4.36 (s, 3H), 4.27 (m, 2H), 1.76 (s, 6H), 1.51 (m, 2H), 1.39 (s, 12H), 1.34 ~ 1.20 (m, 10H), 0.84 (m, 3H). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6) : δ 197.7, 193.9, 181.5, 162.1, 159.1, 158.3, 155.9, 151.7, 148.1, 147.8, 146.6, 145.9, 144.2, 140.3, 139.6, 137.9, 135.4, 134.6, 131.8, 129.9, 129.6, 128.4, 128.1, 127.6, 125.0, 123.9, 122.1, 121.6, 121.0, 120.7, 119.0, 117.7, 113.1, 110.0, 109.5, 108.1, 54.9, 47.5, 35.7, 33.7, 31.3, 28.9, 27.1, 26.7, 26.0, 25.1, 22.0, 20.8, 13.9. Anal. Calc. for $C_{69}H_{65}N_3O_4S$: C, 80.28; H, 6.35; N, 4.07. Found : C, 79.99; H, 6.41; N, 4.11.

(*E*)-2-(5-(5-(4-(Bis(7-(hexyloxy)-9,9-dimethyl-9*H*-fluoren-2-yl)amino)phenyl)thiophen-2-yl)-1-methyl-1*H*-pyrrol-2-yl)-4-((5-carboxy-3,3-dimethyl-1-octyl-3*H*-indolium-2-yl)me-thylene)-3-oxocyclobut-1-enolate JK-217. JK-217 was synthesized by a procedure to **JK-216** except that **4** (0.1g 0.08 mmol) was used in place of **3**. Mp : 162 ^{o}C. MS: *m/z* 1231

[M^+]. ^{1}H NMR(DMSO-d_6) : δ 8.13 (s, 1H), 8.01 (d, 1H, ^3J = 7.2 Hz), 7.65 ~ 7.62 (m, 7H), 7.59 (m, 1H), 7.54 (m, 1H), 7.47 (d, 1H, ^3J = 4.2 Hz), 7.26 (s, 2H), 7.10 (s, 2H), 7.06 (d, 2H, ^3J = 7.8 Hz), 7.02 (d, 2H, ^3J = 7.8 Hz), 6.88 (d, 2H, ^3J = 9 Hz), 6.85 (d, 1H, ^3J = 4.2 Hz), 6.09 (s, 1H), 4.35 (s, 3H), 4.29 (m, 2H), 4.00 (t, 4H), 1.75 (m, 8H), 1.73 (s, 6H), 1.44 (m, 10H), 1.35 (s, 12H), 1.34 ~ 1.23 (m, 10H), 0.89 (t, 6H), 0.82 (t, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6) : δ 199.1, 195,5, 189.5, 177.3, 171.1, 162.6, 160.8, 159.7, 159.4, 154.3, 149.9, 148.1, 146.3, 145.9, 144.3, 137.1, 136.2, 135.1, 134.3, 133.6, 128.9, 128.3, 127.2, 126.8, 124.1, 123.7, 123.1, 122.5, 121.5, 121.1, 120.4, 118.1, 114.2, 113.1, 111.8, 110.5, 109.3, 68.4, 54.7, 47.5, 46.1, 35.9, 35.6, 33.2, 31.9, 31.7, 28.8, 28.1, 27.5, 27.2, 26.1, 25.8, 25.2, 24.8, 22.5, 22.1, 20.1, 13.7, 13.3. Anal. Calc. for $C_{81}H_{89}N_3O_6S$: C, 78.92; H, 7.28; N, 3.41. Found : C, 78.77; H, 7.21; N, 3.29.

Reference

1. L. Beverina, R. Ruffo, G. Patriarca, F. De Angelis, D. Roberto, S. Righetto, R. Ugoc and G. A. Pagani, *J. Mater. Chem.*, 2009, **19**, 8190–8197.