Supporting Information

Different kinds of electro-optic cross-linkable chromophores with ultrahigh electro-optic coefficient and long-term stability

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1. Materials and instruments

The chemicals used in this paper were commercially available and do not require further purification unless otherwise stated. The solvents used in the experiment like tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and dichloromethane(DCM) were commercial ultra-dry reagents. Thin-layer chromatography on 0.25 mm-thick pre-coated silica gel plates and showed spots under UV light. Kieselgel (60-100 mesh and 200-300 mesh) silica gel chromatography was used.

The specific synthesis steps of chromophores QLD1-4 and its intermediates and the characterization data of mass spectrum, hydrogen spectrum and carbon spectrum are shown in the supporting information.

^{1}H-NMR and ^{13}C-NMR spectra were obtained by an Advance Bruker 400M (400 MHz) NMR spectrometer (tetramethylsilane was used as an internal reference). Mass spectra were obtained on a MALDITOF (matrix-assisted laser desorption/flight ionization).BIFLEXIII (Broker Inc.) spectrometer. UV-Vis spectra were performed on a Cary 5000 spectrometer.TGA was determined by TA5000-2950T. TGA was determined by TA5000-2950TGA (TA co) with a heating rate of 10 C min1, under nitrogen protection. Glass-transition temperature (Tg) was measured by differential scanning calorimetry (DSC) with a heating rate of 10 °C min^{-1} under the protection of nitrogen.

2 Experimental

2.1 Synthesis and characterization of chromophore

The synthesis strategies of chromophores QLD1-2 and QLD3-4 were different as shown in Fig 2 and 3. The main difference lies in the protection and deprotection of hydroxyl groups. The two hydroxyl groups of chromophore QLD 1-2 are protected by the same protective group, while QLD 3-4 was protected by two different groups.

The hydroxyl group on tetrahydroquinoline donor is protected by silane group to form compound 2. Compound 2 was then reacted with 4,4,6-trimethyl-7-oxabicyclo[4.1.0]heptan-2-one in sodium ethanol and 2-mercaptoethanol by knoevenagel condensation to give compound 3. The hydroxyl group of compound 3 was protected by tert-butyldimethylsilyl group was to give compound 4; Compound 4 was then reacted with diethyl phosphate by Wittig-Hornor reaction to give compound 5. Reduction of the nitrile group in compound 5 by diisobutylaluminium hydride gave compound 6. Compound 6 was hydrolyzed by acid to give compound 7.Functional group was attached to the compound 7 by Steglich esterification to yield compound 8a and 8b. Condensation of compound 8a or 8b with 2-(3-cyano-4-methyl-5-phenyl-5-(trifluoromethyl)furan-2(5H)-ylidene)malononitrile to produce said chromophore QLD1 and chromophore QLD2.

The hydroxyl group of tetrahydroquinoline donor reacted with 3, 4-dihydropyran in tetrahydrofuran to produce DHP protecting group to give compound K2. Compound K3 was obtained by knoevenagel condensation reaction between donor K2 and oxidized isophorone Bridge. The hydroxyl group of compound K3 was protected by tert-butyldiphenylsilyl group to give compound K4. Compound K5 was obtained by Wittig-Hornor reaction with diethyl phosphate.Reduction of the nitrile group in compound K5 by diisobutylaluminium hydride gave compound K6; Compound K6 was deprotected by TBAF to regenerate hydroxyl groups and give compound K7; 3,5-bis(acryloyloxy)benzoic acid and 3-(9-Anthracenyl)propionic acid were attached to the hydroxyl group of compound K7 by Steglich esterification to give compounds K8 and K8'. Compound K8 and K8' was deprotected by acid to regenerate hydroxyl groups and give compound K9 and K9';3,5-bis(acryloyloxy)benzoic acid and 6,6',6''-((ethane-1,1,1-triyltris(benzene-4,1-

diyl))tris(oxy))trihexanoic acid was attached to the hydroxyl group of compound K9 and K9' by Steglich esterification to give compounds K10 and K10'. Compounds K10 and K10' was then condensed with CF3-TCF acceptor to produce chromophore QLD3 and chromophore QLD4 .

2.2 Synthesis of intermediates and push-pull chromophores

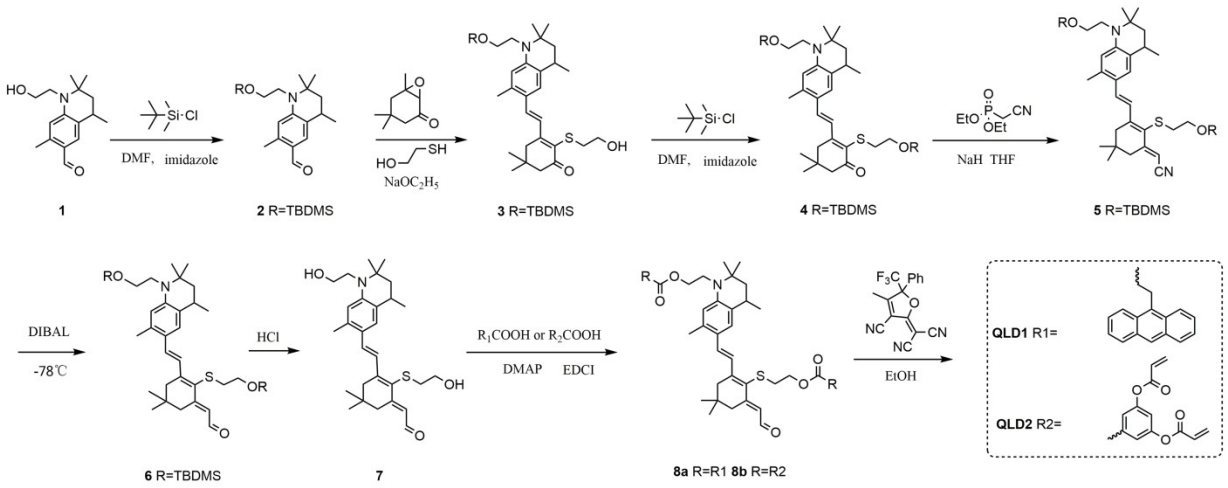


Figure S1. Synthetic routes for QLD1-2

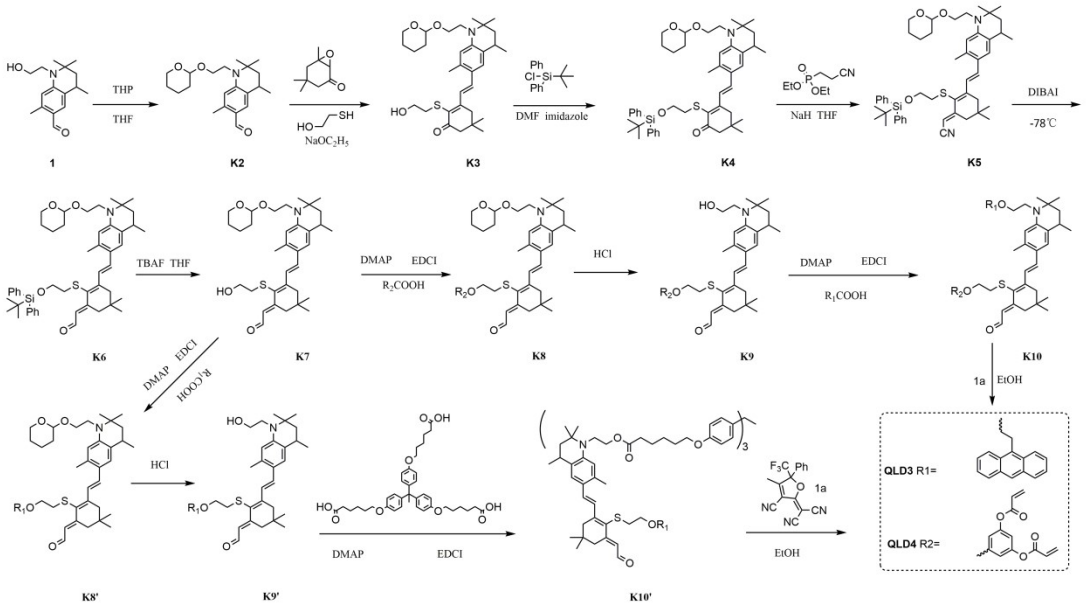


Figure S2. Synthetic routes for QLD3-4

2.2.1 Synthesis of compound 2

In a nitrogen atmosphere, imidazole (2.35 g, 34.57 mmol), tert-butyldimethylchlorosilane (5.19 g, 34.57 mmol) and compound 1 (7.53 g, 28.81 mmol) were dissolved in 25 mL of DMF. After stirring at room temperature for 3h, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography using petroleum ether and ethyl acetate (50:1 to 50:3) as eluent to give yellow oily compound 2 in 99.6% yield (10.78 g, 28.70 mmol) MS (MALDI) (M+, $C_{22}H_{37}NO_2Si$): calcd: 375.63; found : 375.69.[1] H NMR (600 MHz, $CDCl_3$) δ 9.93 (s, 1H, CHO), 7.52 (s, 1H, ArH), 6.36 (s, 1H, ArH), 3.76 - 3.65 (m, 2H, OCH_2), 3.59 - 3.46 (m, 2H, NCH_2), 2.53 (s, 3H, CH_3), 1.80 - 1.44 (m, 2H, CH_2), 1.30 (s, 6H, CH_3), 1.17 (s, 3H, CH_3), 0.88 (s, 9H, CH_3), 0.05 (s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.33, 190.08, 163.63, 149.48, 129.20, 122.94, 113.37, 77.12, 62.85, 51.82, 48.02, 35.72, 32.61, 28.09, 25.95, 24.47, 18.27, - 5.26.

2.2.2 Synthesis of compound 3

In a nitrogen atmosphere, sodium metal (1.32 g, 57.29 mmol) was dissolved in 70 mL of ethanol at 0° C and 2-mercaptoethanol (4.0 mL, 57.29 mmol) was added to the solution. After stirring at room temperature for 20 min, compound a (8.82 g, 57.29 mmol) was added. After stirring at room temperature for 1h, compound 2 (21.52g, 57.29mmol) was added. It was then stirred at 65° C overnight. The mixture was then extracted with ethyl acetate and the organic layer was concentrated in vacuo. The crude product was purified by column chromatography using petroleum ether and ethyl acetate (50:1 to 2:1) as eluent to give Compound 3 as a red oily liquid in 42.7% (14.00 g, 24.48 mmol) MS (MALDI) (M+, $C_{33}H_{53}NO_3SSi$): calcd: 571.94; found: 572.02. [1] H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 16.0 Hz, 1H, CH), 7.52 (s, 1H, ArH), 7.33 (d, *J* = 16.0 Hz, 1H, CH), 6.44 (s, 1H, ArH), 3.77 - 3.65 (m, 2H, NCH_2), 3.60 - 3.46 (m, 4H, OCH_2), 2.97 - 2.87 (m, 1H, CH), 2.85 - 2.80 (m, 2H, SCH_2), 2.66 (s, 2H, CH_2), 2.45 (s, 2H, CH_2), 2.40 (s, 3H, CH_3), 1.82 - 1.71 (m, 2H, CH_2), 1.37 (d, *J* = 6.6 Hz, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.10 (s, 6H, CH_3), 0.93 (s, 9H, CH_3), 0.10 (s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.35 , 160.79 , 146.56 , 136.87 , 136.10 , 126.57 , 126.06 , 124.49 , 123.54 , 122.29 , 113.12 , 61.11 , 60.17 , 54.62 , 51.51 , 47.02 , 46.24 , 41.32 , 38.83 , 32.31 , 29.70 , 28.34 , 26.80 , 25.94 , 24.92 , 20.12 , 18.37 , -5.26 .

2.2.3 Synthesis of compound 4

Imidazole (2.00 g, 29.38 mmol), tert-butyldimethylchlorosilane (4.41 g, 29.38 mmol) and compound 3 (14.00 g, 24.48 mmol) were dissolved in 35 mL DMF in a nitrogen atmosphere. After stirring for 3h at room temperature, the solvent was removed by rotary evaporation, and then the crude product was purified by column chromatography using petroleum ether and ethyl acetate (50:1 to 10:1) as eluent to give Compound 4 as a red oily liquid in 81.2% (13.64 g, 19.88 mmol) MS (MALDI) (M+, $C_{39}H_{67}NO_3SSi_2$): calcd: 686.20; found: 686.31. [1] H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 16.1 Hz, 1H, CH), 7.53 (s, 1H, ArH), 7.24 (d, *J* = 16.1 Hz, 1H, CH), 6.41 (s, 1H, ArH), 3.74 - 3.67 (m , 2H, NCH_2), 3.61 - 3.50 (m, 4H, OCH_2), 2.86 - 2.84 (m, 1H, CH), 2.83 - 2.77 (m, 2H, SCH_2), 2.59 (s, 2H, CH_2), 2.34 (s, 2H, CH_2), 2.31 (s, 3H, CH_3), 1.75 - 1.72 (m, 2H, CH_2), 1.27 (d, *J* = 6.6 Hz, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.15 (s, 6H, CH_3), 0.90 (s, 18H, CH_3), 0.09 (s, 12H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.40 , 163.69 , 146.22 , 136.50 , 134.65 , 129.23 , 128.00 , 124.43 , 124.28 , 122.94 , 113.37 , 62.86 , 60.99 , 55.11 , 51.83 , 47.04 , 46.46 , 41.33 , 36.30 , 32.63 , 32.29 , 29.70 , 28.11 , 26.87 , 25.88 , 24.88 , 24.50 , 20.18, 18.29 , -5.25 .

2.2.4 Synthesis of compound 5

A solution of 60% NaH (3.18 g, 79.51 mmol) and 50 mL of THF was added to a double-necked flask under a nitrogen atmosphere. Diethyl cyanomethylphosphonate (12.85 mL, 79.51 mmol) was then slowly added to the above mixture at 0° C. After gradual clarification Compound 4 (13.64g, 19.88mmol) was added. The mixture was refluxed at 68° C overnight. After extraction with ethyl acetate, it was concentrated in vacuo. The crude product was purified by column chromatography using petroleum ether and ethyl acetate (50:1 to 10:1) as eluent to give Compound 5 as a red oily liquid in 64.7% (9.13 g, 12.87 mmol) MS (MALDI) (M+, C_{41} H_{68} N_2 O_2 SSi_2): calcd: 709.24; found: 709.32.[1] H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 16.0 Hz, 1H, CH), 7.44 (s, 1H, ArH), 7.08 (d, *J* = 16.0 Hz, 1H, CH), 6.43 (s, 1H, ArH), 6.22 (s, 1H, CH),3.76 - 3.68 (m, 2H, NCH_2), 3.63 - 3.61 (m, 4H, OCH_2), 2.75 - 2.67 (m, 1H, CH), 2.62 - 2.60 (m, 2H, SCH_2), 2.50 (s, 2H, CH_2), 2.36 (s, 2H, CH_2), 2.19 (s, 3H, CH_3), 1.75 - 1.73 (m, 2H, CH_2), 1.28 (d, *J* = 6.6 Hz, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.14 (s, 6H, CH_3), 0.94 (s, 18H, CH_3), 0.09 (s, 12H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.65 , 149.24 , 145.73 , 135.99 , 132.38 , 128.36 , 125.98 , 125.04 , 124.09 , 123.10 , 119.37 , 113.13 , 62.59 , 61.34 , 54.49 , 54.13 , 47.12 , 46.53 , 43.49 , 41.66 , 37.64 , 30.21 , 29.80 , 28.10 , 26.87 , 25.97 , 24.84 , 20.14 , 18.43 , -5.18, -5.28

2.2.5 Synthesis of compound 6

Compound 5 (9.13 g, 12.87 mmol) was dissolved in 40 mL of dichloromethane in a nitrogen atmosphere, followed by the slow addition of 1.5 M diisobutylaluminium hydride (hexane) (17.2 mL, 25.75 mmol) at -78° C. After stirring for 3h at -78° C, a mixture of 20mL ethyl acetate and water was added and reacted at 0° C for 1h, extracted with dichloromethane and the organic layer was concentrated in vacuo. The crude product was purified by column chromatography using petroleum ether and ethyl acetate (50:3 to 10:1) as eluent to give compound 6 as a red oily liquid in 42.2% yield (3.87 g, 5.43 mmol) MS (MALDI) (M+, C_{41} H_{69} NO_3 SSi_2): calcd: 712.24; found: 712.16.[1] H NMR (600 MHz, CDCl) MHz, $CDCl_3$) δ 10.13 (d, *J* = 8.1 Hz, 1H, CHO), 7.90 (d, *J* = 16.1 Hz, 1H, CH), 7.46 (s, 1H, ArH), 7.10 (d, *J* = 16.1 Hz, 1H, CH), 7.00 (d, *J* = 8.1 Hz, 1H, ArH), 6.42 (s, 1H, CH), 3.76 - 3.72 (m, 2H, NCH_2), 3.71 - 3.66 (m, 2H,SCH_2), 2.92 - 2.86 (m, 1H, CH), 2.63 - 2.60 (m, 4H, OCH_2), 2.50 (s, 3H, CH_3), 2.37 (s, 2H, CH_2), 2.19 (s, 2H, CH_2), 1.55-1.51 (m, 2H, CH_2), 1.36 (d, *J* = 6.6 Hz, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.05 (s, 6H, CH_3), 0.92 (s, 18H, CH_3), 0.10 (s, 12H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.79 , 156.70 , 150.22 , 145.70 , 135.92 , 132.18 , 128.20 , 126.70 , 125.67 , 124.05 , 123.13 , 113.06 , 62.81 , 62.44 , 61.27 , 54.42 , 48.13 , 46.46 , 41.61 , 39.71 , 37.29 , 36.42 , 30.48 , 30.02 , 29.72 , 28.30 , 27.99 , 26.83 , 25.81 , 24.78 , 20.07 , 18.24 , -5.29.

2.2.6 Synthesis of compound 7

Compound 6 (3.87 g, 5.43 mmol) was dissolved in 20 mL of acetone and 22 mL of 1M HCl was added to the solution. the mixture was then stirred at room temperature for 3 h and extracted with dichloromethane. The crude product was concentrated under vacuum and purified by column chromatography using petroleum ether and ethyl acetate (25:1 to 2:3) as eluent to give a red solid compound 7 in 41.9% (1.10 g, 2.27 mmol) MS (MALDI) (M+, C_{29} H_{41} NO_3 S): calcd: 483.71; found: 483.62. [1] H NMR (600 MHz, $CDCl_3$) δ 10.14 (d, *J* = 7.4 Hz, 1H, CHO), 7.92 (d, *J* = 16.0 Hz, 1H, CH), 7.49 (s, 1H, ArH), 7.14 (d, *J* = 16.0 Hz, 1H, CH), 7.00 (d, *J* = 8.0 Hz, 1H, ArH), 6.47 (s, 1H, CH), 3.87 - 3.73 (m, 2H, NCH_2), 3.68 - 3.59 (m, 2H,SCH_2), 2.96 - 2.84 (m, 1H, CH), 2.80 - 2.73 (m, 4H, OCH_2), 2.53 (s, 3H, CH_3), 2.38 (s, 2H, CH_2), 2.04 (s, 2H, CH_2), 1.61-1.54 (m, 2H, CH_2), 1.38 (d, *J* = 6.6 Hz, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.05 (s, 6H, CH_3). ^{13}C

NMR (151 MHz, $CDCl_3$) δ 191.57 , 156.66 , 150.95 , 145.95 , 136.06 , 132.71 , 127.36 , 126.85 , 126.69 , 125.41 , 123.89 , 123.50 , 113.47 , 61.23 , 60.74 , 54.83 , 46.63 , 41.72 , 39.93 , 38.16 , 30.11 , 29.65 , 28.31 , 27.01 , 24.88 , 20.15 , 14.17 .

2.2.7 Synthesis of compound 8b

Compound c (0.55g, 2.10mmol), DMAP (0.03g, 0.21mmol), EDCI (0.40g, 2.10mmol) were dissolved in 15mL of dichloromethane at 0° C in a nitrogen atmosphere. The solution became turbid and was clarified after stirring for 45 min. After clarification, compound 7 (0.26 g, 0.53 mmol) and 20 mL of dichloromethane were added. After stirring for 2h at 0° C, the solution was brought to room temperature and allowed to reflux for a further 15h. The solution was extracted with dichloromethane. The crude product was concentrated under vacuum and purified by column chromatography using petroleum ether and ethyl acetate (25:1 to 2:1) as eluent to give a red solid compound 8b in 54.7% (0.28 g, 0.29 mmol) MS (MALDI) (M+, C_{55} H_{57} NO_{13} S): calcd: 972.12; found: 972.19. ^{1} H NMR (600 MHz,) δ 10.14 (d, *J* = 8.0 Hz, 1H, CHO), 7.91 (d, *J* = 16.0 Hz, 1H,CH), 7.77 (d, *J* = 2.2 Hz, 2H, ArH), 7.64 (d, *J* = 2.2 Hz, 2H, ArH), 7.46 (s, 1H, ArH), 7.27 (d, *J* = 2.2 Hz, 1H, ArH), 7.22 (t, *J* = 2.2 Hz, 1H, ArH), 7.10 (d, *J* = 16.0 Hz, 1H, CH), 6.99 (d, *J* = 8.0 Hz, 1H, ArH), 6.67 - 6.56 (m, 5H, CH), 6.36 - 6.25 (m, 4H, CH), 6.07-6.02 (m, 4H, CH), 4.55 - 4.34 (m, 4H, OCH_2), 3.82 - 3.44 (m, 2H,NCH_2), 2.94 (t, *J* = 7.0 Hz, 2H, SCH_2), 2.88-2.83 (m, 1H, CH), 2.75 (s, 2H, CH_2), 2.48 (s, 2H, CH_2), 2.39 (s, 3H, CH_3), 1.65 - 1.51 (m, 2H,CH_2), 1.37 (s, 3H, CH_3), 1.35 (d, *J* = 6.6 Hz, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.04 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.52 , 164.87 , 164.44 , 163.82, 156.36 , 150.97 , 150.81 , 145.52 , 136.33 , 133.54 , 132.74 , 132.09 , 127.36 , 126.89 , 125.51 , 124.14 , 123.66 , 120.44 , 120.31 , 120.16 , 113.23 , 64.53 , 63.17 , 54.86 , 46.48 , 43.24 , 41.68 , 39.93 , 33.14 , 30.13 , 29.71 , 28.32 , 26.88 , 24.81 , 20.20 .

2.2.8 Synthesis of compound 8a

Following the procedure for compound 8b, red solid compound 8a was prepared from compound 7 (0.45 g, 0.93 mmol) in 81.6% yield (0.72 g, 0.75 mmol). MS (MALDI) (M+, C_{63} H_{65} NO_5 S): calcd: 948.28; found: 948.36. ^{1} H NMR (600 MHz, $CDCl_3$) δ 10.20 (d, *J* = 8.1 Hz, 1H, CHO), 8.41 (s, 1H, ArH), 8.36 (s, 1H, ArH), 8.30 (d, *J* = 8.8 Hz, 2H, ArH), 8.24 (d, *J* = 8.8 Hz, 2H, ArH), 8.05 (d, *J* = 8.4 Hz, 2H, ArH), 8.01 (d, *J* = 8.3 Hz, 2H, ArH), 7.97 (d, *J* = 16.0 Hz, 1H, CH), 7.59 - 7.55 (m, 2H, ArH), 7.54 - 7.42 (m, 7H, ArH), 7.16 (d, *J* = 16.0 Hz, 1H, CH), 7.03 (d, *J* = 8.0 Hz, 1H, ArH), 6.48 (d, J = 14.0 Hz, 1H, CH), 4.23 - 4.13 (m, 4H, OCH_2), 4.06 - 4.01 (m, 2H, NCH_2), 3.94 - 3.90 (m, 2H, SCH_2), 3.41 - 3.18 (m, 1H, CH), 2.89 - 2.85 (m, 2H, CH_2), 2.81 - 2.76 (m, 4H, CH_2), 2.76 - 2.72 (m, 2H, CH_2), 2.56 (s, 2H, CH_2), 2.41 (s, 3H, CH_3), 2.08 (s, 2H, CH_2), 1.66 - 1.62 (m, 2H, CH_2), 1.29 (d, *J* = 5.9 Hz, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.09 (s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.51 , 172.99 , 172.66 , 156.38 , 151.10 , 145.42 , 136.20 , 132.57 , 132.20, 131.54, 129.37, 127.21 , 126.83 , 126.46 , 126.31 , 125.92, 125.53 , 124.92, 123.91, 123.47 , 113.14 , 218.30 - 19.96, 63.20 , 62.24 , 60.37 , 54.59 , 46.28 , 43.07 , 41.69 , 39.90 , 35.22 , 33.18 , 30.09 , 29.82, 31.59 - 26.85, 28.69, 31.59 - 23.35, 31.59 - 21.09, 25.85, 14.17 .

2.2.9 Synthesis of the hair chromophore QLD1

Compound 8a (0.37 g, 0.39 mmol) and compound d (0.14 g, 0.43 mmol) were dissolved in 6 mL of anhydrous ethanol under a nitrogen atmosphere. The organic phase was then refluxed at 65 ° C for 3 h. The organic

phase was concentrated under vacuum and purified by column chromatography using petroleum ether and ethyl acetate (10:1 to 2:1) as eluent to give the green solid chromophore QLD1 in 49.4% (0.24 g, 0.19 mmol). HRMS (ESI) (M+, C_{63} H_{65} NO_5 S): calcd: 948.4662; found : 948.4659. ^{1} H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H, ArH), 8.37 (s, 1H, ArH, 8.29 (d, *J* = 8.6 Hz, 2H, ArH), 8.19 (d, *J* = 8.8 Hz, 2H, ArH), 8.07 - 7.97 (m, 6H, ArH), 7.58 - 7.54 (m, 2H, CH), 7.53 - 7.42 (m, 12H, ArH, CH), 7.29 (d, *J* = 7.8 Hz, 2H, ArH), 6.50 (d, *J* = 14.6 Hz, 2H, CH), 4.22 - 4.10 (m, 4H, OCH_2), 4.05 - 4.01 (m, 2H, SCH_2), 3.92 - 3.88 (m, 2H, NCH_2), 3.41 - 3.38 (m, 2H, CH_2), 2.90 - 2.84 (m, 2H,CH_2), 2.80 (t, *J* = 6.8 Hz, 2H, CH_2), 2.78-2.75 (m, 1H, CH), 2.73 - 2.69 (m, 2H,CH_2), 2.57 (s, 2H, CH_2), 2.42 (s, 3H,CH_3), 2.07 (s, 2H,CH_2), 1.70 - 1.61 (m, 2H,CH_2), 1.31 (s, 3H,CH_3), 1.28 (s, 3H,CH_3), 1.10 (s, 3H,CH_3), 1.03 (s, 3H,CH_3), 0.95 (s, 3H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.61 , 172.97 , 172.59 , 171.13 , 162.49 , 157.62 , 154.89 , 147.14 , 146.57 , 137.76 , 135.55 , 132.05 , 131.56 , 131.22 , 129.95 , 129.67 - 129.27, 129.16 , 128.21 , 126.67 , 126.46 , 125.96 , 125.15 , 124.92 , 124.44 , 123.80 , 123.44 , 116.91 , 113.39 , 111.27 , 110.78 , 95.76 , 63.09 , 62.00 , 60.36 , 57.72 , 55.00 , 46.02 , 43.03 , 41.74 , 41.15 , 35.07 , 33.92 , 30.39 , 29.48 , 28.55 , 27.87 , 26.68 , 24.87 , 23.23 , 21.02 , 20.22 , 19.94 , 14.17 .

2.2.10 Synthesis of the hair chromophore QLD2

Compound 8b (0.28 g, 0.29 mmol) and compound d (0.11 g, 0.34 mmol) were dissolved in 6 mL of anhydrous ethanol under a nitrogen atmosphere. The organic phase was then refluxed at 65 ° C for 3 h. After concentration under vacuum, the organic phase was purified by column chromatography using petroleum ether and ethyl acetate (10:1 to 2:1) as eluent to give the green solid chromophore QLD2 in 51.6% (0.19 g, 0.15 mmol) HRMS (ESI) (M+, C_{55} H_{57} NO_{13} S): calcd: 927.3629; found: 927.3631. ^{1} H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 15.7 Hz, 2H, CH), 7.79 (d, *J* = 2.2 Hz, 2H, ArH), 7.64 (d, *J* = 2.2 Hz, 2H, ArH), 7.60 - 7.50 (m, 6H, ArH), 7.44 (d, *J* = 12.4 Hz, 1H, CH), 7.29 (dt, *J* = 6.6, 4.8 Hz, 2H, ArH), 7.25 (t, *J* = 2.2 Hz, 1H, ArH), 6.70 - 6.61 (m, 5H, CH), 6.47 (d, *J* = 14.5 Hz, 1H, CH), 6.36 (d, *J* = 10.5 Hz, 1H, CH), 6.34 (d, *J* = 4.1 Hz, 1H), 6.32 (d, *J* = 4.0 Hz, 1H, ArH), 6.30 (d, *J* = 10.5 Hz, 1H, CH), 6.13 - 6.02 (m, 4H, ArH), 4.61 - 4.33 (m, 4H, OCH_2), 3.69-3.53 (m, , 2H, NCH_2), 2.96 (t, *J* = 6.7 Hz, 2H, SCH_2), 2.94 - 2.83 (m, 1H, CH), 2.54 (s, 2H, CH_2), 2.43 (s, 3H, CH_3) , 2.22 (s, 2H, CH_2), 1.67-1.62 (m, 2H, CH_2), 1.42 (s, 3H, CH_3), 1.38 (d, *J* = 6.6 Hz, 3H,CH_3), 1.26 (s, 3H,CH_3), 1.02 (s, 3H,CH_3), 0.92 (s, 3H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.65 , 171.08 , 164.78 , 164.31 , 163.78 , 162.49 , 157.60 , 154.58 , 150.92 , 147.18 , 146.60 , 137.82 , 135.61 , 133.50 , 131.91 , 131.75 , 131.23 , 130.01 , 129.58 , 129.20 , 128.16 , 127.21 , 126.73 , 125.10 , 124.49 , 123.57 , 120.37 , 120.17 , 116.95 , 113.42 , 111.36 , 110.78 , 95.73 , 64.15 , 62.85 , 60.32 , 57.57 , 55.20 , 46.15 , 43.14 , 41.67 , 41.08 , 33.88 , 30.36 , 29.58 , 28.57 , 27.78 , 26.74 , 25.02 , 20.99 , 20.13 , 19.91 , 14.14 .

2.2.11 Synthesis of compound K2

Pyridinium 4-methylbenzenesulfonate (0.73 g, 2.90 mmol), p-methylbenzenesulfonate monohydrate (0.55 g, 2.90 mmol) and compound 1 (15.15 g, 58.00 mmol) were dissolved in 23 mL of tetrahydrofuran under nitrogen, and then 3,4-dihydro-2H-pyran (5.85 g, 69.60 mmol) was added to the mixture and stirred for 3 h at room temperature. After removal of the solvent by rotary evaporation, the crude product was purified by silica gel column chromatography using petroleum ether and ethyl acetate (8:1-3:1) as eluent to give the yellow oily compound K2 in 96.6% (19.35 g, 56.00 mmol). MS (MALDI) (M+, C_{21} H_{31} NO_3): calcd: 345.48 ; found: 345.51.^{1} H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 1H,CHO), 7.57 (d, *J* = 1.4 Hz, 1H,ArH), 6.48 (d, *J* = 14.2 Hz,

1H,ArH), 4.64 - 4.62 (m, 1H,OCH), 3.95 - 3.80 (m, 2H,OCH_2), 3.73 - 3.58 (m, 2H,NCH_2), 3.57 - 3.45 (m, 2H,OCH_2), 2.95 - 2.81 (m, 1H,CH), 2.58 (s, 3H,CH_3), 1.87 - 1.84 (m, 1H,CH_2), 1.80 - 1.72 (m, 2H, CH_2), 1.63 - 1.60 (m, 2H, CH_2), 1.58 - 1.54 (m, 2H, CH_2) , 1.52 (d, *J* = 13.0 Hz, 1H, CH_2), 1.39 - 1.32 (m, 6H, CH_3), 1.23 (s, 3H ,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.13, 149.49, 140.91, 130.23, 125.02, 122.97, 113.53, 99.36, 65.60, 62.46, 55.26, 46.05, 44.62, 30.61, 29.73, 26.64, 25.38, 19.76.

2.2.12 Synthesis of compound K3

Sodium metal (1.75g, 75.92mmol) was dissolved in 140mL of ethanol at 0° C in a nitrogen atmosphere, and 2-mercaptoethanol (5.3mL, 75.92mmol) was added to the solution. After stirring at room temperature for 20 min, compound a (17.54 g, 113.88 mmol) was added. After stirring at room temperature for 1h, compound K2 (26.23g, 75.92mmol) was added. It was then stirred at 65° C overnight. The mixture was then extracted with ethyl acetate and the organic layer was concentrated in vacuo. The crude product was purified by column chromatography using petroleum ether and ethyl acetate (10:1 to 1:1) as eluent to give compound K3 as a red oily liquid in 80.00% yield (32.90 g, 60.72 mmol) MS (MALDI) (M+, C_{32} H_{47} NO_4 S): calcd: 541.79; found: 541.76.[1] H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 15.9 Hz, 1H,CH), 7.47 (d, *J* = 1.4 Hz, 1H,ArH), 7.28 (d, *J* = 16.0 Hz, 1H,ArH), 6.45 (d, *J* = 12.8 Hz, 1H,CH), 4.59 - 4.57 (m, 1H,OCH), 3.85 - 3.76 (m, 2H,OCH_2), 3.63 - 3.54 (m, 2H,NCH_2), 3.52 - 3.48 (m, 4H,OCH_2), 2.79 - 2.74 (m, 2H $_{22222}$ 13.0 Hz, 6H,CH_3), 1.15 (d, *J* = 1.6 Hz, 3H,CH_3), 1.03 (s, 6H,CH_3), 0.96 (s, 3H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.16, 160.65, 146.51, 136.89, 136.06, 126.58, 124.51, 123.55, 122.34, 113.29, 99.24, 62.32, 60.35, 54.73, 51.63, 47.98, 41.25, 38.48, 32.28, 30.58, 28.38, 28.04, 25.38, 20.20, 19.49.

2.2.13 Synthesis of compound K4

Imidazole (8.26 g, 121.45 mmol), tert-butyldiphenylchlorosilane (31.6 mL, 121.45 mmol) and compound K3 (32.90 g, 60.72 mmol) were dissolved in 60 mL DMF in a nitrogen atmosphere. After stirring for 3h at room temperature, the solvent was removed by rotary evaporation, and then the crude product was purified by silica gel column chromatography using petroleum ether and ethyl acetate (50:1-4:1) as eluent to give compound K4 as a red oily liquid in 75.3% (35.67 g, 45.72 mmol)... MS (MALDI) (M+, C_{48} H_{65} NO_4 SSi): calcd: 780.20; found: 780.23.[1] H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 16.0 Hz, 1H,CH), 7.64 - 7.63 (m, 4H,ArH), 7.49 (t, *J* = 1.4 Hz, 1H,CH). 1.4 Hz, 1H,ArH), 7.42 - 7.37 (m, 2H,ArH), 7.35 - 7.33 (m, 4H,ArH), 7.26 (d, *J* = 16.1 Hz, 1H,ArH), 6.53 (d, *J* = 12.4 Hz, 1H,CH), 4.68 - 4.66 (m, 1H,OCH), 3.98 - 3.84 (m, 2H,OCH_2), 3.81 - 3.75 (m, 2H,OCH_2), 3.68 (d, *J* = 2.6 Hz, 2H,OCH_2), 3.60 - 3.43 (m, 2H,NCH_2), 2.99 - 2.97 (m, 2H,SCH_2), 2.91 - 2.86 (m, 1H,CH), 2.58 (s, 2H,CH_2), 2.42 (s, 3H,CH_3), 2.37 (s, 2H, CH_2), 1.93 - 1.76 (m, 4H,CH_2), 1.65 - 1.54 (m, 4H,CH_2), 1.39 - 1.30 (m, 6H,CH_3), 1.22 (d, *J* = 1.6 Hz, 3H,CH_3), 1.05 (d, *J* = 12.2 Hz, 15H,CH 12.2 Hz, 15H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.69, 157.95, 135.52, 134.66, 133.67, 129.56, 127.88, 127.64, 124.26, 113.29, 99.36, 65.92, 63.85, 62.46, 54.63, 51.97, 41.28, 36.09, 32.26, 30.67, 29.86, 28.38, 26.85, 25.45, 20.26, 19.65, 19.17.

2.2.14 Synthesis of compound K5

A solution of 60% NaH (5.40 g, 134.97 mmol) and 110 mL of THF was added to a double-necked flask under a nitrogen atmosphere. Diethyl cyanomethylphosphonate (21.8 mL, 134.97 mmol) was then slowly added to the above mixture at 0° C. After gradual clarification compound K4 (17.55 g, 24.49 mmol) was added. The

mixture was refluxed at 68° C overnight. After extraction with ethyl acetate, it was concentrated in vacuo. The crude product was purified by column chromatography using petroleum ether and ethyl acetate (50:1 to 10:1) as eluent to give compound K5 as a red oily liquid in 64.7% (12.72 g, 15.84 mmol). MS (MALDI) (M+, C_{50} H_{66} N_2 O_3 SSi): calcd: 803.23; found: 803.20.[1] H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 16.1 Hz, 1H,CH), 7.67 - 7.66 (m, 4H,ArH), 7.46 (d, *J* = 7.7 Hz, 1H,ArH) 7.46 (d, J = 7.7 Hz, 1H,ArH), 7.45 - 7.42 (m, 2H,ArH), 7.40 - 7.37 (m, 4H,ArH), 7.12 (d, *J* = 16.0 Hz, 1H,ArH), 6.56 (d, *J* = 12.2 Hz, 1H,CH), 6.25 (s, 1H,CH), 4.71 - 4.69 (m, 1H,OCH), 4.01 - 3.86 (m, 2H,OCH_2), 3.78 (t, *J* = 7.1 Hz, 2H,OCH_2), 3.73 - 3.64 (m, 2H,OCH_2), 3.62 - 3.43 (m, 2H,NCH_2), 2.91 (d, *J* = 6.5 Hz, 1H,CH), 2.77 (t, *J* = 7.0 Hz, 2H,SCH_2), 2.53 (s, 2H,CH_2), 2.46 (s, 2H,CH_2), 2.43 (s, 3H ,CH_3), 1.99 - 1.70 (m, 4H,CH_2), 1.66 - 1.55 (m, 4H,CH_2), 1.35 (d, *J* = 6.6 Hz, 6H ,CH_3), 1.24 (d, *J* = 1.8 Hz, 3H ,CH_3), 1.09 (s, 9H ,CH_3), 1.02 (d, *J* = 1.8 Hz , 6H ,CH_3). 13C NMR (151 MHz, $CDCl_3$) δ 158.61, 149.32, 135.53, 133.44, 129.79, 127.77, 125.75, 124.93, 99.35, 94.45, 63.36, 62.45, 54.65, 43.46, 41.59, 37.38, 30.71, 30.17, 28.13, 26.89, 25.50, 20.30, 19.64, 19.20.

2.2.15 Synthesis of compound K6

Compound K5 (12.72 g, 15.84 mmol) was dissolved in 35 mL of dichloromethane in a nitrogen atmosphere, followed by the slow addition of 1 M diisobutylaluminium hydride (hexane) (17.2 mL, 25.75 mmol) at -78° C. After stirring for 3h at -78° C, 70mL of a mixture of dichloromethane and water was added and the reaction was carried out at 0° C for 1h, extracted with dichloromethane and the organic layer was concentrated in vacuo. The crude product was purified by column chromatography using petroleum ether and ethyl acetate (50:3-10:1) as eluent to give compound K6 as a red oily liquid in 76.04% yield (9.49 g, 11.77 mmol). MS (MALDI) (M+, C_{50} H_{67} NO_4 SSi): calcd: 806.23; found: 806.25.[1] H NMR (600 MHz, $CDCl_3$) δ 10.14 (d, *J* = 8.0 Hz, 1H,CHO), 7.92 (d, *J* = 16.0 Hz, 1H,CH), 7.63 (t, *J* = 1.5 Hz, 4H ArH), 7.47 (d, *J* = 1.3 Hz, 1H,ArH), 7.43 - 7.39 (m, 2H,ArH), 7.36 - 7.32 (m, 4H,ArH), 7.12 (d, *J* = 16.0 Hz, 1H,ArH), 7.00 (d, *J* = 8.0 Hz, 1H,CH), 6.55 (d, *J* = 12.3 Hz, 1H,CH), 4.69 (d, *J* = 3.8 Hz, 1H,OCH), 3.99 - 3.85 (m, 2H,OCH_2), 3.82 - 3.76 (m, 2H,OCH_2), 3.73 - 3.63 (m, 2H,OCH_2), 3.60 - 3.44 (m, 2H,NCH_2), 2.92 - 2.85 (m, 1H,CH), 2.81 - 2.78 (m, 2H,SCH_2), 2.70 - 2.64 (m, 2H,CH_2), 2.47 (s, 2H,CH_2), 2.42 (s, 3H,CH_3), 1.98 - 1.75 (m, 4H,CH_2), 1.65 - 1.54 (m, 4H,CH_2), 1.38 (d, *J* = 3.1 Hz, 6H,CH_3), 1.23 (d, *J* = 1.8 Hz, 3H,CH_3), 1.08 - 1.00 (m, 15H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.52, 150.35, 135.51, 133.55, 129.66, 127.70, 126.75, 125.64, 99.35, 63.63, 62.45, 54.65, 41.60, 39.89, 37.05, 30.70, 30.06, 28.32, 26.87, 25.48, 20.30, 19.66, 19.19.

2.2.16 Synthesis of compound K7

Compound K6 (22.80 g, 28.28 mmol) was dissolved in 60 mL of tetrahydrofuran under nitrogen and then tetrabutylammonium fluoride (28.3 mL, 28.28 mmol) was added to the solution. The mixture was then stirred at room temperature for 2h and extracted with dichloromethane. The crude product was concentrated under vacuum and purified by column chromatography using petroleum ether and ethyl acetate (8:1 to 1:4) as eluent to give the red solid compound K7 in 90.7% (14.56 g, 25.64 mmol). MS (MALDI) (M+, C_{34} H_{49} NO_4 S): calcd: 567.83; found: 567.84.[1] H NMR (600 MHz, $CDCl_3$) δ 10.13 (d, *J* = 8.1 Hz, 1H,CHO), 7.94 (d, *J* = 16.0 Hz, 1H,ArH), 7.51 (d, *J* = 1.5 Hz, 1H, CH), 7.16 (d, *J* = 16.0 Hz, 1H,ArH), 7.01 (d, *J* = 8.1 Hz, 1H,CH), 6.50 (d, *J* = 12.0 Hz, 1H,CH), 4.65 (d, *J* = 4.6 Hz, 1H,OCH), 3.95 - 3.80 (m, 2H, OCH_2), 3.69 - 3.60 (m, 4H, OCH_2), 3.56 - 3.39 (m, 2H, NCH_2), 2.92 (d, *J* = 6.8 Hz, 1H,CH), 2.79 (d, *J* = 1.4 Hz, 2H, SCH_2), 2.76 - 2.75 (m, 2H, CH_2), 2.54 (s, 2H, CH_2), 2.39 (s, 3H, CH_3), 1.90 - 1.63 (m, 4H, CH_2), 1.55 (s, 4H, CH_2), 1.38 (d, *J* = 6.6 Hz,

3H, CH_3), 1.35 (d, *J* = 2.6 Hz, 3H, CH_3), 1.20 (d, *J* = 1.8 Hz, 3H, CH_3), 1.06 (s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.61, 151.12, 132.87, 126.56, 125.13, 99.31, 65.92, 62.42, 61.32, 54.59, 41.71, 39.96, 38.08, 30.64, 30.12, 28.34, 26.92, 25.43 , 20.21, 19.57.

2.2.17 Synthesis of compound K8

Compound c (3.32g, 12.68mmol), DMAP (0.26g, 2.11mmol), EDCI (4.05g, 21.14mmol) were dissolved in 40mL of dichloromethane at 0° C in a nitrogen atmosphere. The solution became turbid and was clarified after stirring for 45 min. After clarification, compound K7 (6.00 g, 10.57 mmol) and 60 mL of dichloromethane were added. After stirring for 2h at 0° C, the solution was brought to room temperature and allowed to reflux for a further 15h. The solution was extracted with dichloromethane. The crude product was concentrated under vacuum and purified by column chromatography using petroleum ether and ethyl acetate (25:1 to 2:1) as eluent to give the red oily compound K8 in 39.9% (3.44 g, 4.22 mmol). MS (MALDI) (M+, C_{47} H_{57} NO_9 S): calcd:812.03; found: 812.07.^{1} H NMR (600 MHz, $CDCl_3$) δ 10.16 (d, *J* = 8.0 Hz, 1H,CHO), 7.92 (d, *J* = 16.0 Hz, 1H,ArH), 7.66 (d, *J* = 2.2 Hz, 2H, ArH), 7.47 (d, *J* = 1.4 Hz, 1H,ArH), 7.29 - 7.23 (m, 1H,ArH), 7.12 (d, *J* = 16.0 Hz, 1H,CH), 7.01 (s, 1H,CH), 6.64 (d, *J* = 1.1 Hz, 2H,CH_2), 6.49 (d, *J* = 12.0 Hz, 1H,CH 12.0 Hz, 1H,CH), 6.31 (d, *J* = 6.8 Hz, 2H,CH), 6.07 (d, *J* = 1.1 Hz, 2H,CH_2), 4.66 - 4.64 (m, 1H,OCH), 4.46 - 4.39 (m, 2H,OCH_2), 3.96 - 3.81 (m, 2H,OCH_2), 3.70 - 3.59 (m, 2H,OCH_2), 3.57 - 3.39 (m, 2H,NCH_2), 2.96 (t, *J* = 7.0 Hz, 2H,SCH_2), 2.92 - 2.85 (m, 1H,CH), 2.76 (s, 2H,CH_2), 2.50 (s, 2H,CH_2), 2.38 (s, 3H,CH_3), 1.91 - 1.75 (m, 4H,CH_2), 1.61 - 1.52 (m, 4H,CH_2) , 1.38 - 1.33 (m, 6H,CH_3), 1.21 (d, *J* = 1.6 Hz, 3H,CH_3), 1.06 (d, *J* = 3.1 Hz, 6H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.49, 164.44, 163.77, 151.08, 150.82, 133.38, 132.90, 132.06, 127.38, 127.08, 126.75, 125.11, 120.31, 120.16, 99.35, 65.93, 64.57, 62.46, 54.59, 41.66, 39.93, 33.15, 30.66, 30.12, 28.32, 26.88, 25.44, 20.21, 19.60.

2.2.18 Synthesis of compound K9

Compound K8 (2.89 g, 3.56 mmol) was dissolved in 35 mL of acetone and 7.2 mL of 1M HCl was added to the solution. the mixture was then stirred at room temperature for 2 h and extracted with dichloromethane. The crude product was concentrated under vacuum and purified by column chromatography using petroleum ether and ethyl acetate (8:1 to 1:1) as eluent to give the red solid compound K9 in 52.9% (1.35 g, 1.85 mmol). MS (MALDI) (M+, C_{42} H_{49} NO_8 S): calcd:727.91; found: 727.88.^{1} H NMR (600 MHz, $CDCl_3$) δ 10.15 (d, *J* = 8.1 Hz, 1H,CHO), 7.92 (d, *J* = 16.0 Hz, 1H,ArH), 7.66 (d, *J* = 2.2 Hz, 2H, ArH), 7.45 (d, *J* = 1.1 Hz, 1H,ArH), 7.25 (t, *J* = 2.2 Hz, 1H,ArH), 7.11 (d, *J* = 16.0 Hz, 1H,CH), 7.01 (d, *J* = 8.0 Hz, 1H,CH), 6.64 (d, *J* = 1.1 Hz, 1H,CH_2), 6.46 (s, 1H,CH), 6.31 (d, *J* = 6.8 Hz, 1H,CH), 6.07 (d, *J* = 1.1 Hz, 1H,CH_2), 4.42 - 4.40 (m, 2H,OCH_2), 3.81 - 3.76 (m, 2H,OCH_2), 3.61 - 3.58 (m, 1H,NCH_2), 3.39 - 3.35 (m, 1H,OCH_2), 2.96 (t, *J* = 7.0 Hz, 2H,SCH_2), 2.88 (d, *J* = 6.5 Hz, 1H,CH), 2.76 (s, 2H,CH_2), 2.50 (s, 2H,CH_2), 2.37 (s, 3H, CH_3), 1.80 - 1.77 (m, 1H,CH_2), 1.54 (t, *J* = 12.9 Hz, 1H,CH_2), 1.37 - 1.32 (m, 6H,CH_3), 1.21 (s, 3H,CH_3), 1.06 (d, *J* = 3.3 Hz, 6H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.60, 163.81, 150.81, 133.45, 127.35, 120.30, 113.48, 64.53, 60.69, 54.82, 46.69, 41.65, 39.93, 33.16, 30.13, 29.68, 28.39, 26.98, 24.93, 20.26, 20.04.

2.2.19 Synthesis of compound K10

Compound b (0.36 g, 1.45 mmol), DMAP (0.029 g, 0.24 mmol) and EDCI (0.46 g, 2.42 mmol) were dissolved in 10 mL of dichloromethane at 0° C in a nitrogen atmosphere. The solution became turbid and was clarified

after stirring for 45min. After clarification, compound K9 (0.88g, 1.21mmol) and 15mL of dichloromethane were added. After stirring for 2h at 0° C, the solution was brought to room temperature and allowed to reflux for a further 15h. The solution was extracted with dichloromethane. The crude product was concentrated under vacuum and purified by column chromatography using petroleum ether and ethyl acetate (8:1 to 2:1) as eluent to give the red oily compound K10 in 58.5% (0.68 g, 0.71 mmol). MS (MALDI) (M+, C_{59} H_{61} NO_9 S): calcd:960.20; found: 960.24.^{1} H NMR (600 MHz, $CDCl_3$) δ 10.17 (d, *J* = 8.0 Hz, 1H,CHO), 8.41 (s, 1H,ArH), 8.33 - 8.26 (m, 2H, ArH), 8.04 (d, *J* = 1.2 Hz, 2H,ArH), 7.94 (d, *J* = 16.0 Hz, 1H,ArH), 7.67 (d, *J* = 2.2 Hz, 2H,ArH), 7.57 - 7.55 (m, 2H,ArH), 7.51 - 7.48 (m , 3H,ArH), 7.25 (t, *J* = 2.2 Hz, 1H,ArH), 7.13 (d, *J* = 16.1 Hz, 1H,CH), 7.02 (d, *J* = 8.1 Hz, 1H,CH), 6.64 - 6.61 (m, 2H,CH_2), 6.51 (s, 1H,CH), 6.31 (d, *J = 6.9 Hz, 2H,CH* = 6.9 Hz, 2H,CH), 6.06 (d, *J* = 1.1 Hz, 2H,CH_2), 4.42 - 4.40 (m, 2H,OCH_2), 4.33 - 4.20 (m, 2H,OCH_2), 4.05 - 4.00 (m, 2H,NCH_2), 3.56 (t, *J* = 6.1 Hz, 1H,SCH_2), 3.35 - 3.30 (m, 1H,SCH_2), 2.96 (t, *J* = 7.1 Hz, 2H,CH_2), 2.89 (d, *J* = 13.1 Hz, 1H,CH), 2.87 - 2.83 (m, 2H, CH_2), 2.77 (s, 2H,CH_2), 2.51 (s, 2H,CH_2), 2.41 (s, 3H,CH_3), 1.78 (d, *J* = 8.3 Hz, 1H,CH_2), 1.57 (t, *J* = 12.9 Hz, 1H,CH_2), 1.39 - 1.32 (m, 6H,CH_3), 1.20 (s, 3H,CH_3), 1.07 (d, *J* = 3.0 Hz, 6H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.53, 173.05, 164.45, 163.78, 150.82, 133.39, 131.62, 129.52, 127.38, 126.51, 126.01, 124.99, 123.89, 120.32, 64.55, 54.75, 35.27, 33.15, 30.14, 29.66, 26.89, 23.30, 20.26.

2.2.20 Synthesis of the chromophore QLD3

Compound K10 (0.38 g, 0.40 mmol) and compound d (0.14 g, 0.44 mmol) were dissolved in 6 mL of anhydrous ethanol under a nitrogen atmosphere. The organic phase was concentrated under vacuum and purified by column chromatography using dichloromethane and ethyl acetate (80:1~40:1) as eluent to give the green solid chromophore QLD3 in 59.6% (0.30 g, 0.24 mmol). HRMS (ESI) (M+, C_{75} H_{67} F_3 N_4 O_9 S): calcd: 1257.4659; found: 1257.4655.^{1} H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H,ArH), 8.29 (d, *J* = 8.9 Hz, 2H,ArH), 8.05 (d, *J* = 8.4 Hz, 2H,ArH), 7.65 (d, *J* = 2.2 Hz, 2H,ArH), 7.58 - 7.44 (m, 12H,ArH), 7.32 - 7.24 (m, 3H,CH), 6.63 (d, *J* = 17.3 Hz, 2H,CH), 6.54 (s, 1H,CH), 6.47 (d, *J* = 14.6 Hz, 1H,CH), 6.33 - 6.29 (m, 2H,CH), 6.08 (d, *J* = 10.5 Hz, 2H,CH), 4.39 (d, *J* = 6.6 Hz, 2H,OCH_2), 4.32 - 4.20 (m, 2H,OCH_2), 4.07 - 3.99 (m, 2H,NCH_2), 3.60 - 3.33 (m, 2H,SCH_2), 2.96 (t, *J* = 6.9 Hz, 2H,CH_2), 2.91 (s, 1H,CH), 2.88 (s, 2H,CH_2), 2.58 - 2.50 (m, 2H,CH_2), 2.43 (s, 3H,CH_3), 2.37 - 2.24 (m, 2H,CH_2), 1.81 - 1.78 (m, 1H,CH_2), 1.66 (s, 3H,CH_3), 1.57 (t, *J* = 13.0 Hz, 1H,CH_2), 1.38 (d, *J* = 6.6 Hz, 3H,CH_3), 1.36 (s, 3H,CH_3), 1.21 (s, 3H,CH_3), 1.02 (d, *J* = 2.0 Hz, 3H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.75, 173.04, 164.10 , 150.88, 146.66, 137.82, 135.68, 133.58, 132.11, 131.85, 131.62, 131.31, 130.10, 129.66, 129.47, 128.25, 127.29, 126.82, 126.55, 126.02, 125.14, 125.00, 123.86, 123.54, 120.37, 120.27, 117.04, 113.45, 111.39, 110.88, 64.25, 62.10, 55.18, 46.22, 43.11, 41.76, 41.16, 35.25, 33.96, 30.45, 29.60, 28.60, 27.87, 26.82, 25.08, 23.28, 20.28, 20.00, 14.22, 1.05.

2.2.21 Synthesis of compound K8'

Compound b (1.59g, 6.34mmol), DMAP (0.13g, 1.06mmol), EDCI (2.03g, 10.57mmol) were dissolved in 20mL of dichloromethane at 0° C in a nitrogen atmosphere. The solution became turbid and was clarified after stirring for 45 min. After clarification, compound K7 (3.00 g, 5.28 mmol) and 20 mL of dichloromethane were added. After stirring for 2h at 0° C, the solution was brought to room temperature and allowed to reflux for a further 15h. The solution was extracted with dichloromethane. The crude product was concentrated under vacuum and purified by column chromatography using petroleum ether and ethyl acetate (20:1 to 3:1) as eluent to give the red oily compound K8' in 93.0% (3.93 g, 4.91 mmol). MS (MALDI) (M+, C_{51} H_{61} NO_5 S):

calcd:800.11; found: 800.16.[1] H NMR (600 MHz, $CDCl_3$) δ 10.20 (d, *J* = 8.1 Hz, 1H,CHO), 8.36 (s, 1H,ArH), 8.26 - 8.22 (m, 2H, ArH), 8.03 - 7.94 (m, 3H,ArH), 7.54 - 7.45 (m, 5H,ArH), 7.17 (d, *J* = 16.0 Hz, 1H,CH), 7.04 (d, *J* = 8.1 Hz, 1H,CH), 6.48 (d, *J* = 11.7 Hz, 1H,CH), 4.66 - 4.65 (m, 1H,OCH), 4.21 (d, *J* = 2.8 Hz, 2H,OCH_2), 3.97 - 3.80 (m, 4H,OCH_2), 3.68 - 3.60 (m, 2H,NCH_2), 3.58 - 3.37 (m, 2H,SCH_2), 2.84 - 2.76 (m, 6H,CH_2), 2.74 (s, 1H,CH), 2.56 (s, 2H,CH_2), 2.40 (s, 3H,CH_3), 1.91 - 1.85 (m, 2H,CH $_2$), 1.82 - 1.63 (m, 4H,CH_2), 1.59 (d, *J* = 1.5 Hz, 2H,CH_2), 1.32 (d, *J* = 3.1 Hz, 3H,CH_3), 1.30 - 1.28 (m, 3H,CH_3), 1.11 (d, *J* = 2.7 Hz, 3H,CH_3), 1.10 - 1.06 (m, 6H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.58, 172.73, 132.83, 132.33, 131.58, 129.48, 129.29, 126.74, 126.37, 125.95, 124.95, 123.96, 99.38, 63.29, 41.73, 39.97, 35.18, 33.26, 30.68, 30.14, 28.40, 25.46, 23.20, 20.24.

2.2.22 Synthesis of compound K9'

Compound K8' (3.93 g, 4.91 mmol) was dissolved in 40 mL of acetone and 9.6 mL of 1M HCl was added to the solution. the mixture was then stirred at room temperature for 3 h and extracted with dichloromethane. The crude product was concentrated under vacuum and purified by column chromatography using petroleum ether and ethyl acetate (9:1 to 1:1) as eluent to give the red solid compound K9' in 49.3% (1.73 g, 2.42 mmol). MS (MALDI) (M+, C_{46} H_{53} NO_4 S): calcd: 715.99; found: 716.03. [1] H NMR (600 MHz, $CDCl_3$) δ 10.19 (d, *J* = 8.0 Hz, 1H, CHO), 8.36 (s, 1H,ArH), 8.26 - 8.22 (m, 2H, ArH), 8.04 - 7.93 (m, 3H,ArH), 7.56 - 7.45 (m, 5H,ArH), 7.16 (d, *J* = 16.0 Hz, 1H,CH), 7.04 (d, *J* = 8.1 Hz, 1H,CH), 6.45 (s, 1H,CH), 4.22 - 4.20 (m, 2H,OCH_2), 3.95 - 3.90 (m, 2H,OCH_2), 3.81 - 3.72 (m, 2H,NCH_2), 3.58 - 3.52 (m, 1H,SCH_2), 3.35 - 3.29 (m, 1H,SCH_2), 2.82 (t, *J* = 6.9 Hz, 2H,CH_2), 2.79 - 2.72 (m, 5H,CH_2 ,CH), 2.55 (s, 2H,CH_2), 2.39 (s, 3H,CH_3), 1.69 - 1.65 (m, 1H,CH_2), 1.44 (d, *J* = 12.9 Hz, 1H,CH_2), 1.31 - 1.26 (m, 6H,CH_3), 1.13 - 1.05 (m, 9H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.65, 172.74, 132.31, 131.58, 129.30, 126.81, 126.38, 125.95, 124.96, 123.95, 113.47, 63.27, 60.73, 54.71, 46.54, 41.73, 39.95 , 35.17, 33.26, 30.14, 29.66, 28.41, 26.92, 24.76, 23.20, 20.23, 14.24.

2.2.23 Synthesis of compound K10'

Compound e (0.35 g, 0.54 mmol), DMAP (0.039 g, 0.32 mmol) and EDCI (0.61 g, 3.20 mmol) were dissolved in 25 mL of dichloromethane at 0° C in a nitrogen atmosphere. After clarification, compound K9' (1.73g, 2.42mmol) and 20mL of dichloromethane were added. After stirring for 2h at 0° C, the solution was brought to room temperature and allowed to reflux for a further 15h. The solution was extracted with dichloromethane. The crude product was concentrated under vacuum and purified by column chromatography using dichloromethane and ethyl acetate (40:1 to 8:1) as eluent to give the red oily compound K10' in 78.3% (1.16 g, 0.42 mmol). MS (MALDI) (M+, C_{176} H_{201} N_3 O_{18} S_3): calcd: 2742.73; found: 2742.69.[1] H NMR (600 MHz, $CDCl_3$) δ 10.18 (d, *J* = 8.1 Hz, 3H,CHO), 8.36 (s, 3H,ArH), 8.25 - 8.20 (m, 6H,ArH), 8.01 - 7.99 (m, 6H,ArH), 7.95 (d, *J* = 16.1 Hz, 3H,ArH), 7.54 - 7.50 (m, 6H,ArH), 7.48 - 7.43 (m, 9H,ArH), 7.15 (d, *J* = 16.0 Hz, 3H,ArH), 7.03 - 6.98 (m, 9H,ArH), 6.81 - 6.77 (m, 6H,CH), 6.48 (s, 3H,CH), 4.21 - 4.12 (m, 12H, OCH_2), 3.97 - 3.90 (m, 12H,OCH_2 ,NCH_2), 3.61 - 3.57 (m, 3H,SCH_2), 3.51 (t, *J* = 7.0 Hz, 3H,CH), 3.35 (d, *J* = 5.7 Hz, 3H,SCH_2), 2.80 (d, *J* = 6.9 Hz, 12H,CH 6.9 Hz, 12H,CH_2), 2.75 - 2.72 (m, 9H,CH_3), 1.82 (d, *J* = 7.4 Hz, 6H,CH_2), 1.79 - 1.60 (m, 24H,CH_2), 1.56 - 1.51 (m, 6H,CH_2), 1.43 (t, *J* = 12.9 Hz, 3H,CH_3), 1.31 - 1.26 (m, 18H,CH_3), 1.23 (t, *J* = 7.0 Hz, 6H,CH_2), 1.08 (d, *J* = 7.5 Hz, 27H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.59, 173.60, 172.73, 157.00, 156.49, 141.77, 136.25, 132.63, 132.31, 131.56, 129.28, 127.24, 126.86, 126.36, 125.94, 125.57, 124.94, 123.94, 123.49, 113.57, 113.18, 67.51, 65.88, 63.25, 62.05, 60.43, 54.62,

46.32, 43.28, 41.72, 39.95, 35.16, 34.15, 33.22, 30.14, 29.64, 29.06 , 28.34, 26.79, 25.78, 24.72, 23.19, 20.25, 15.29, 14.22, 1.04.

2.2.24 Synthesis of the hair chromophore QLD4

Compound K10' (0.64 g, 0.23 mmol) and compound d (0.24 g, 0.77 mmol) were dissolved in 6 mL of anhydrous ethanol under a nitrogen atmosphere. The organic phase was concentrated under vacuum and then purified by column chromatography using dichloromethane and ethyl acetate (40:1-4:1) as eluent to give the green solid chromophore QLD4 in 45.4% (0.38 g, 0.10 mmol). HRMS (ESI) (M+, C_{224} H_{219} F_9 N_{12} O_{18} S_3): calcd: 3632.5687; found: 3632.5691.[1] H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 3H,ArH), 8.19 (d, *J* = 8.7 Hz, 6H,ArH), 8.04 - 7.99 (m, 9H,ArH), 7.54 - 7.48 (m, 15H,ArH), 7.48 - 7.43 (m, 21H,ArH), 7.32 - 7.28 (m, 3H,CH), 7.01 - 6.97 (m, 6H,ArH), 6.81 - 6.77 (m, 6H,CH), 6.49 (d, *J* = 15.6 Hz, 6H,CH), 4.24 - 4.11 (m, 12H,OCH_2), 3.95 (t, *J* = 6.3 Hz, 6H,OCH_2), 3.91 - 3.87 (m, 6H,NCH_2), 3.63 - 3.60 (m, 3H,SCH_2), 3.40 - 3.37 (m, 3H,SCH_2), 2.79 (t, *J* = 6.8 Hz, 6H,CH_2), 2.73 - 2.68 (m, 6H,CH_2), 2.57 - 2.54 (m, 6H,CH_2), 2.43 - 2.28 (m, 24H,CH_2), 2.11 (s, 3H,CH), 1.82 (t, *J* = 7.5 Hz, 6H,CH_2), 1.74 (d, *J* = 7.7 Hz, 6H,CH_2), 1.65 (d, *J* = 4.5 Hz, 12H,CH_3), 1.43 (d, *J* = 2.7 Hz, 3H,CH_3), 1.35 - 1.25 (m, 27H,CH_3), 1.11 (d, *J* = 2.0 Hz, 9H,CH_3), 1.02 (s, 9H,CH_3) , 0.94 (d, *J* = 2.1 Hz, 9H,CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.67, 173.57, 172.65, 157.01, 146.64, 141.77, 137.79, 132.10, 131.57, 131.29, 129.99, 129.63, 129.36, 128.27, 126.72, 126.47, 125.97, 125.22, 124.96, 123.79, 123.48, 113.56, 67.50, 63.14, 61.83, 55.04, 50.59, 46.07, 43.27, 41.79, 41.20, 35.13, 34.12, 30.44, 29.59, 29.07, 28.54, 27.88, 26.72, 25.78, 24.82, 23.17, 20.27, 20.01, 1.04.

3. NMR pictures

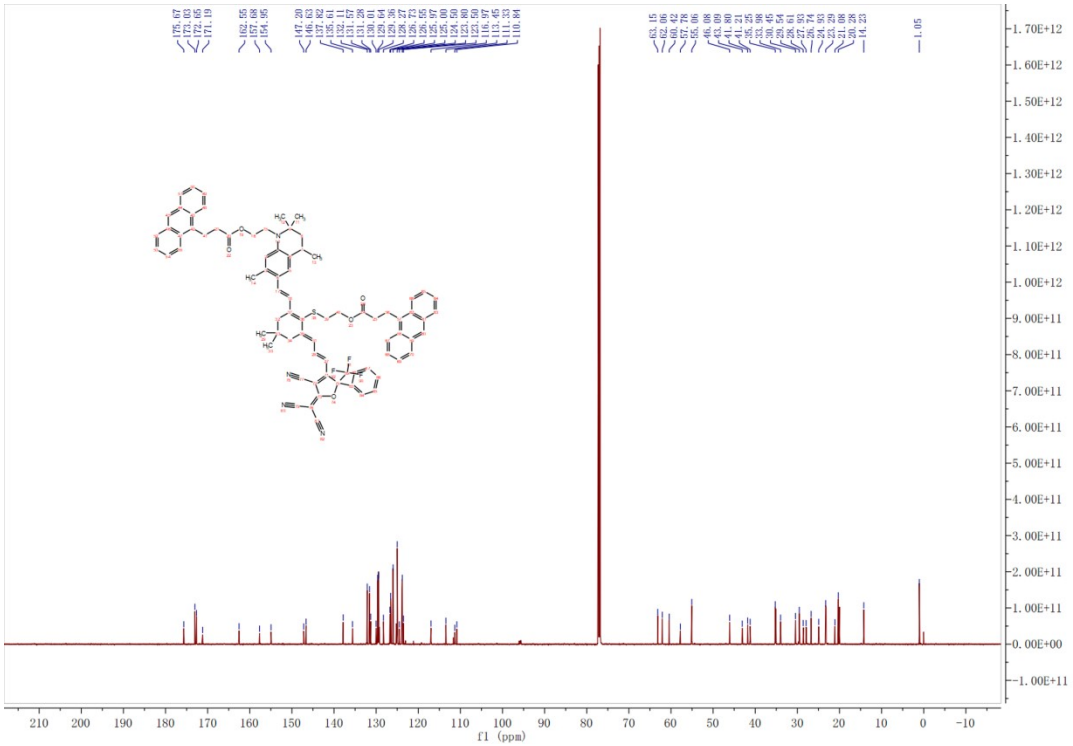


Figure S3. ^{1}H-NMR spectrum of QLD1.

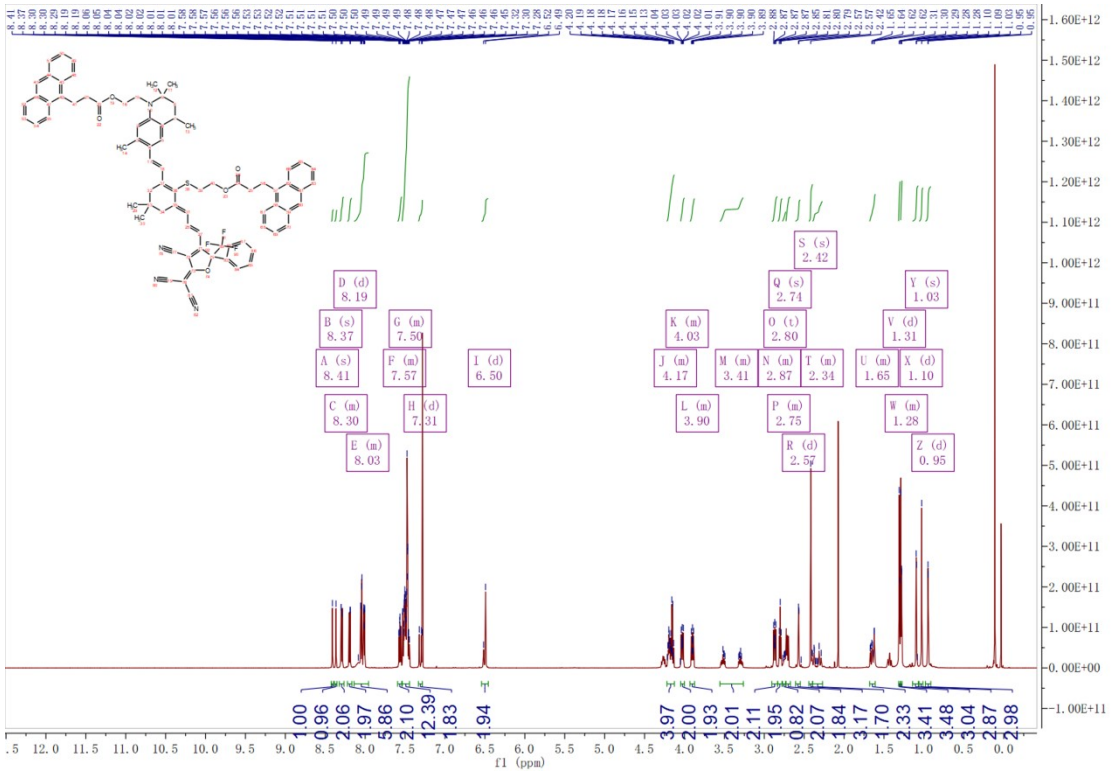


Figure S4. ^{13}C-NMR spectrum of QLD1.

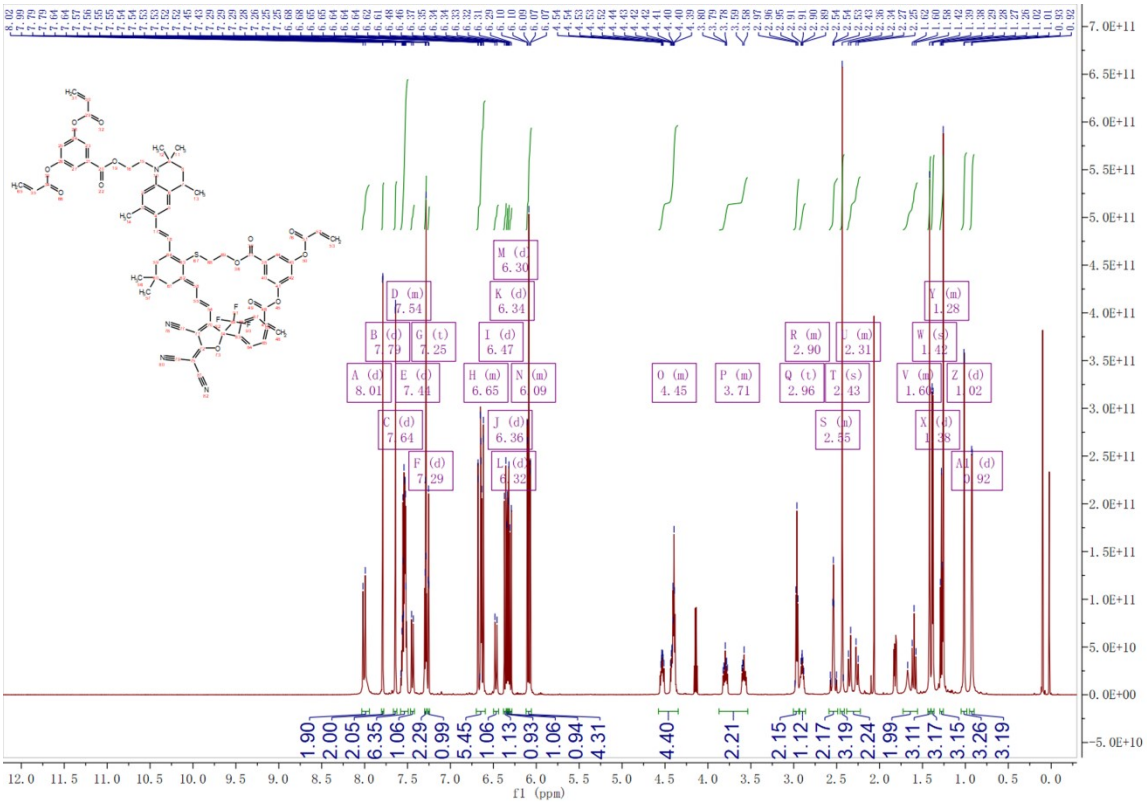


Figure S5. ^{1}H-NMR spectrum of QLD2.

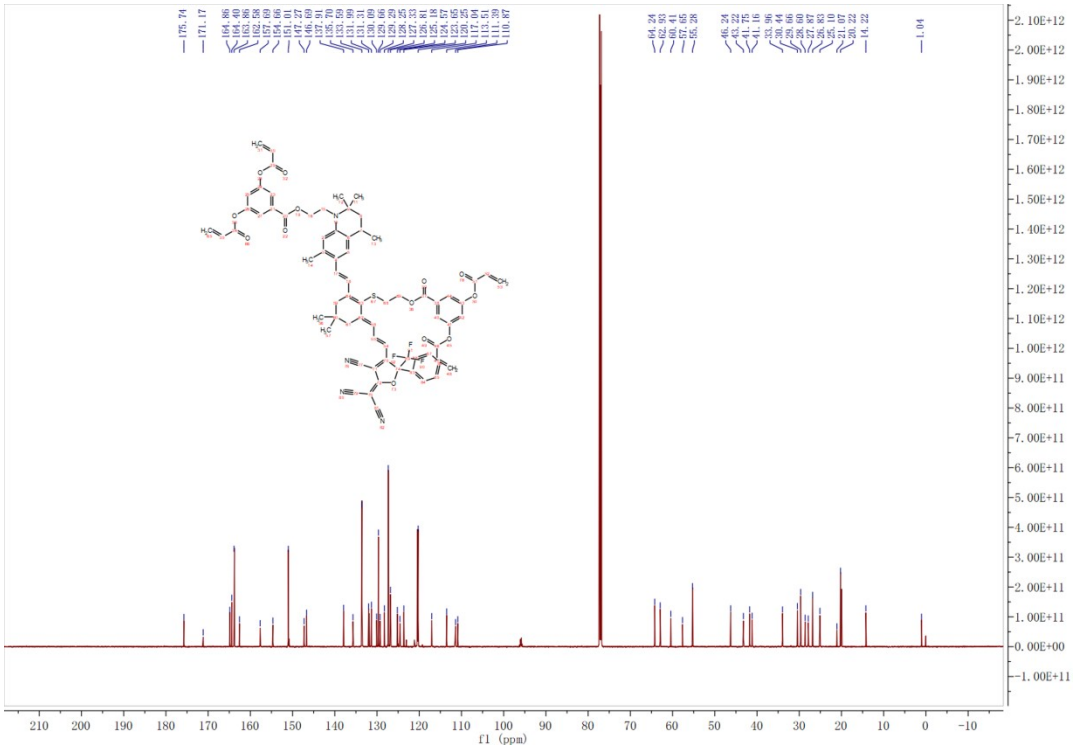


Figure S6. ^{13}C-NMR spectrum of QLD2.

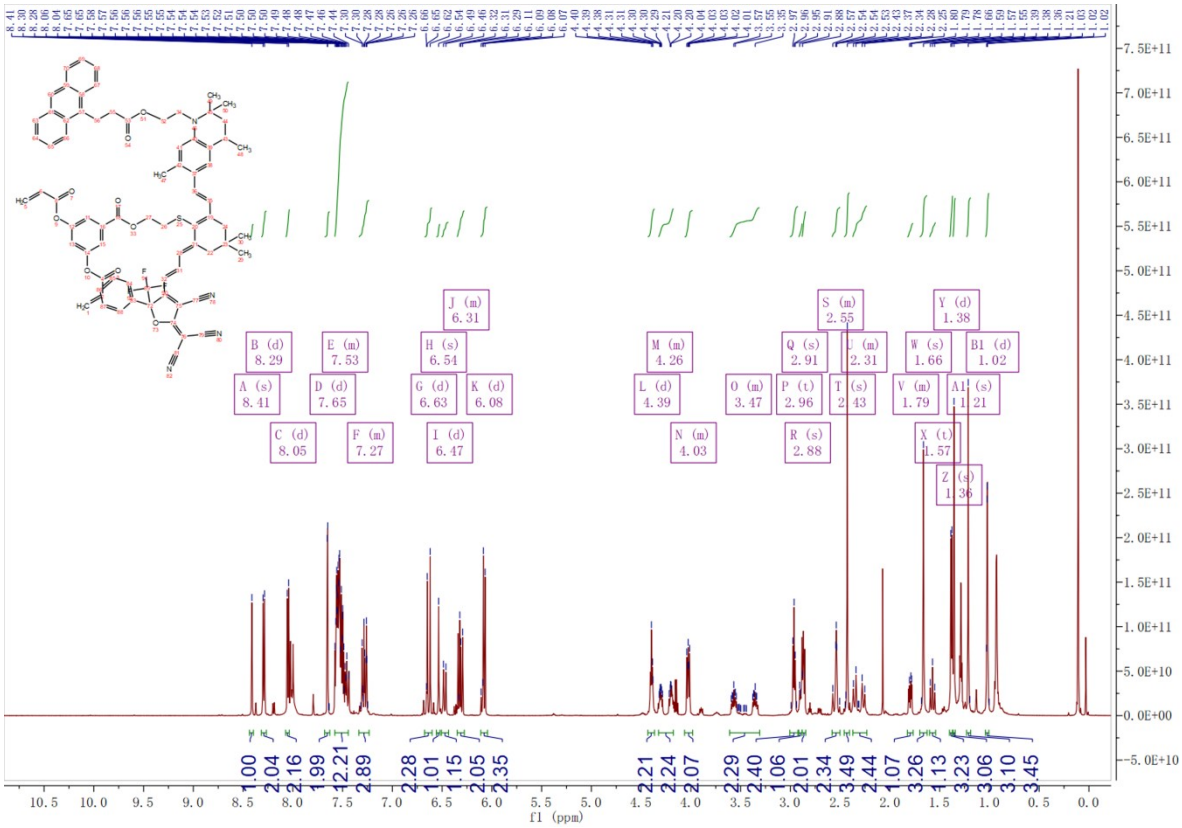


Figure S7. ^{1}H-NMR spectrum of QLD3

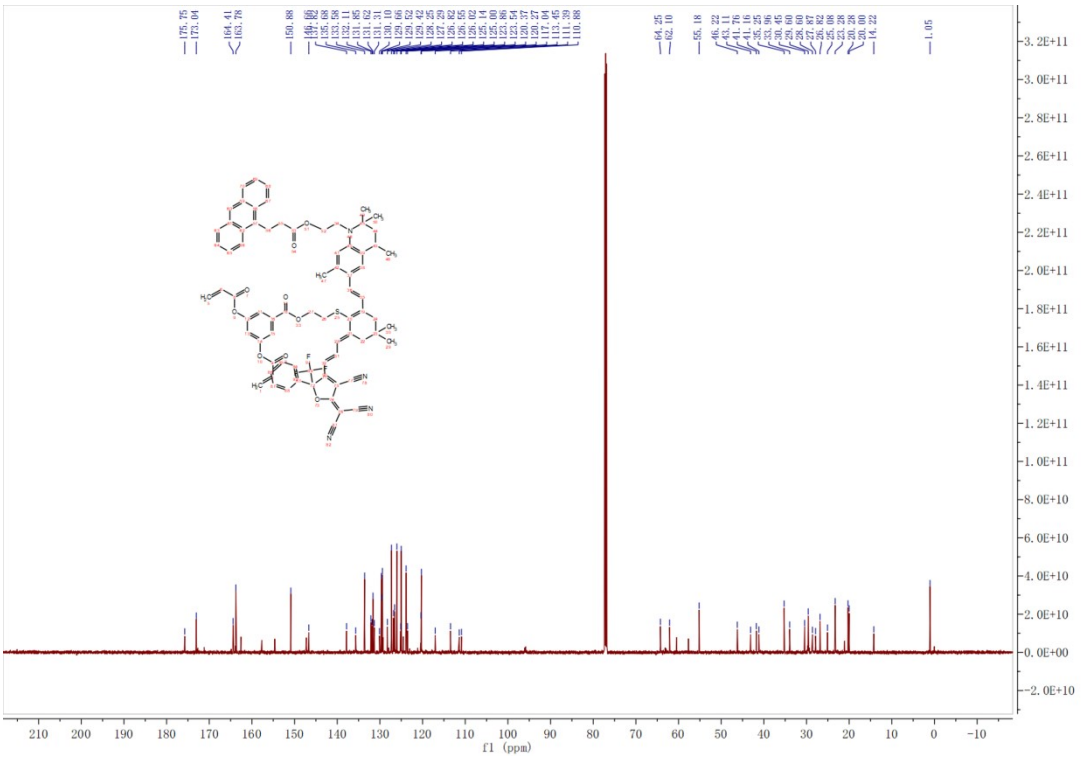


Figure S8. ^{13}C-NMR spectrum of QLD3.

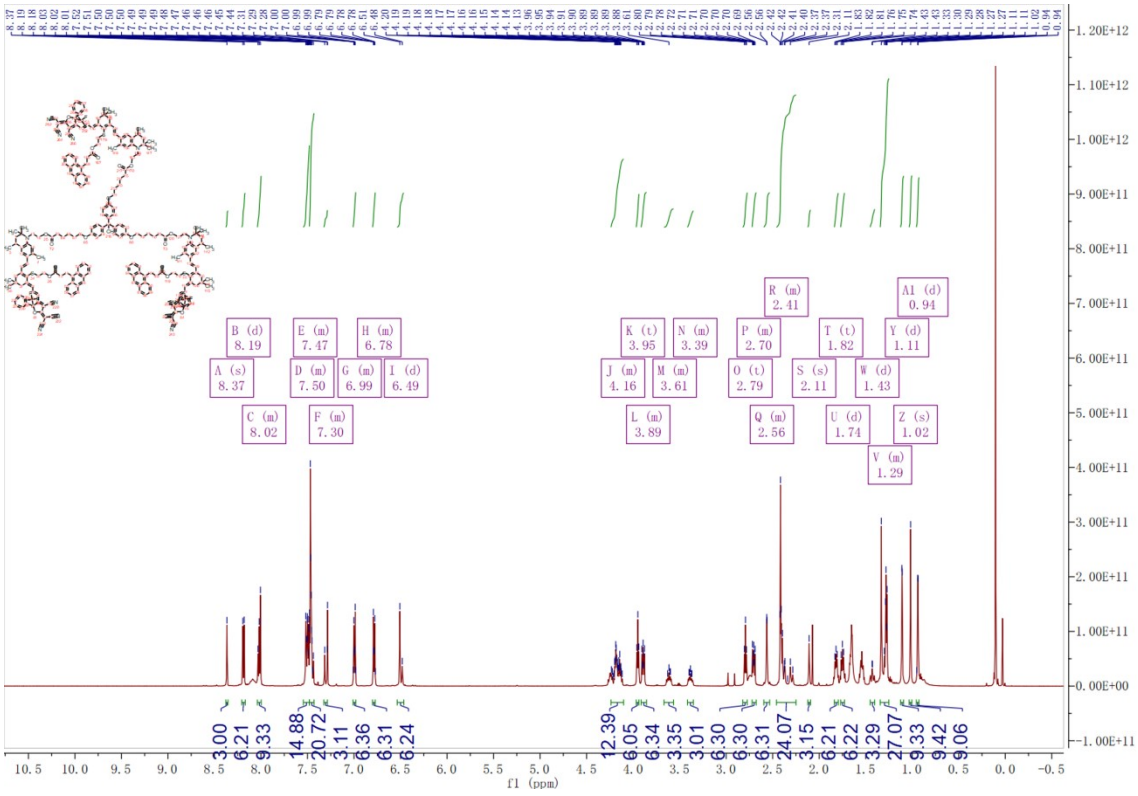


Figure S9. ^{1}H-NMR spectrum of QLD4.

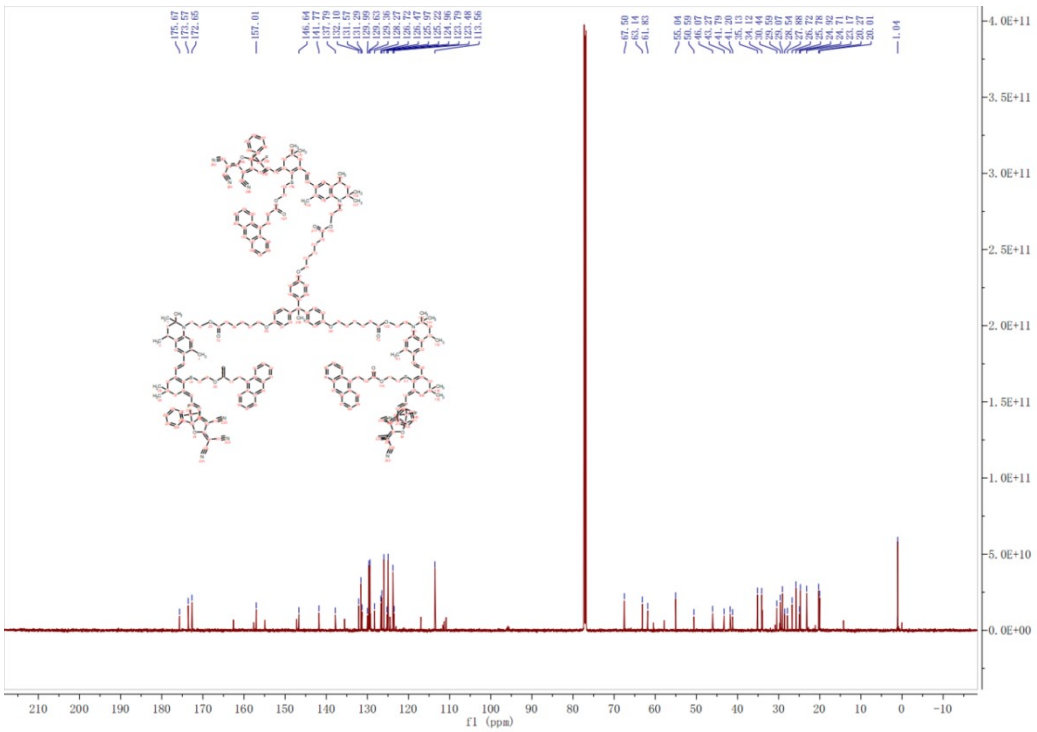


Figure S10. ^{13}C-NMR spectrum of QLD4.

4. UV-Vis Absorption Spectroscopy

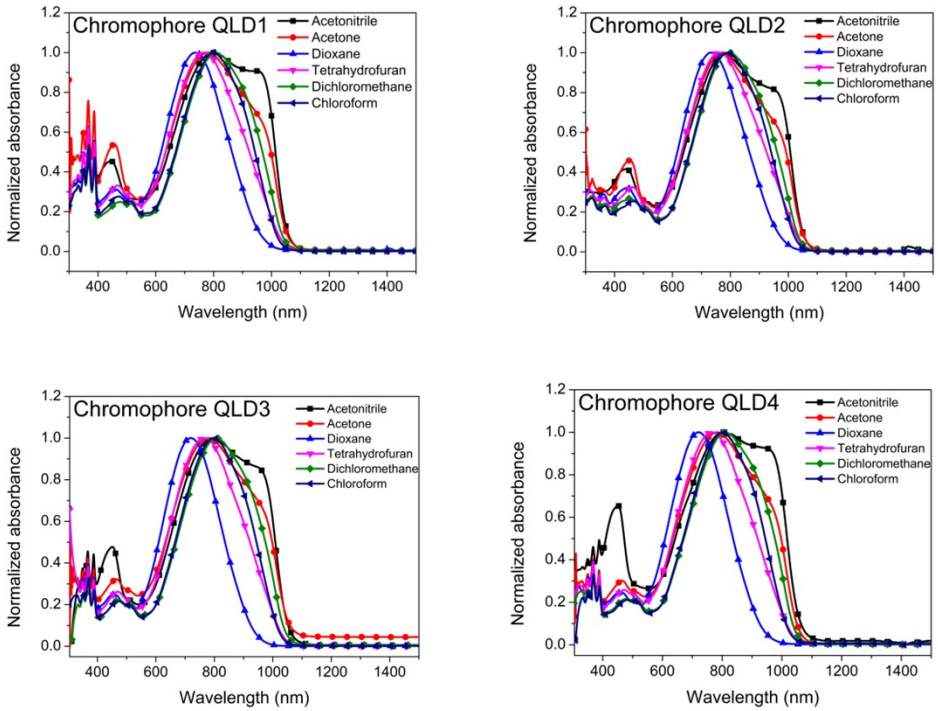


Figure S11. Normalized UV-Vis absorption spectra of chromophore QLD1-4 in seven aprotic solvents with varying dielectric constants (ε).

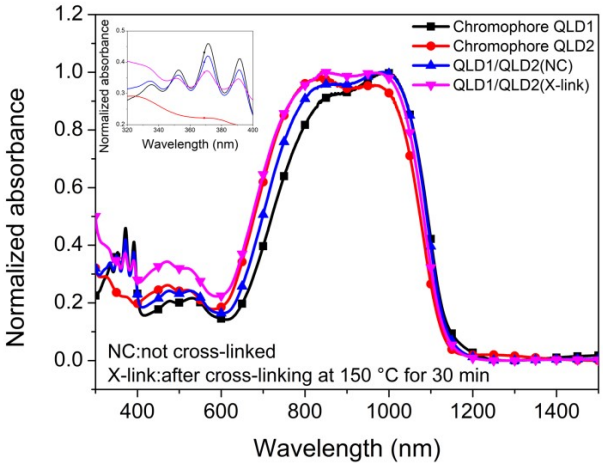


Figure S12a. UV−vis−NIR absorption spectra of thin films of 2:1 QLD1/QLD2 upon thermal curing at 150 °C for 30 min.

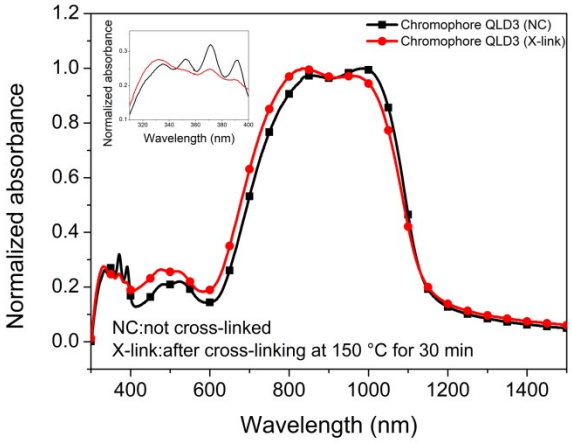


Figure S12b. UV−vis−NIR absorption spectra of thin films of QLD3 upon thermal curing at 150 °C for 30 min.

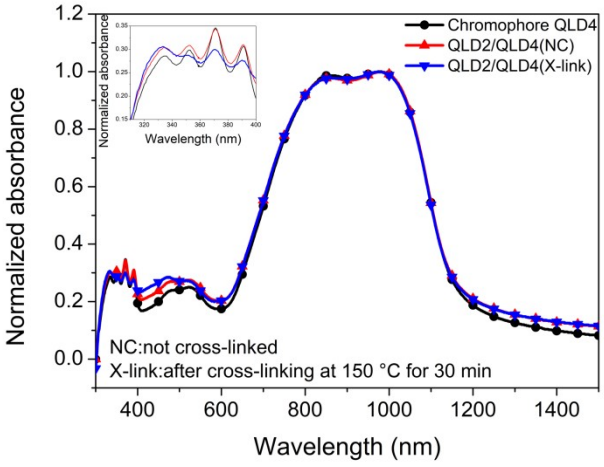


Figure S12c. UV−vis−NIR absorption spectra of thin films of 3:4 QLD2/QLD4 upon thermal curing at 150 °C for 30 min.

5. Differential Scanning Calorimetry testing

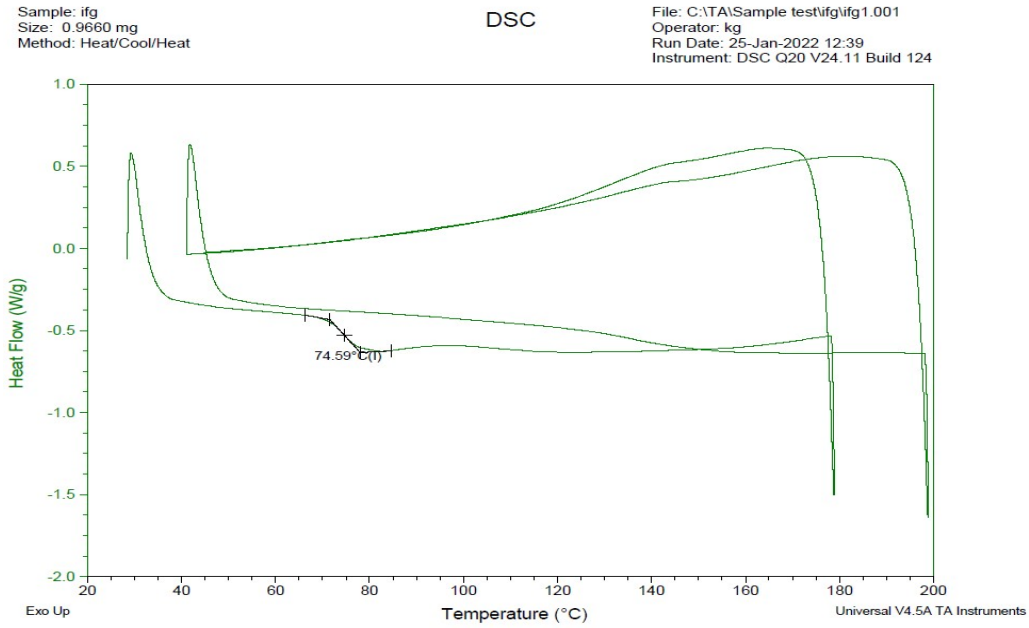


Figure S13. DSC curves for crosslinking chromophores QLD3 before crosslinking

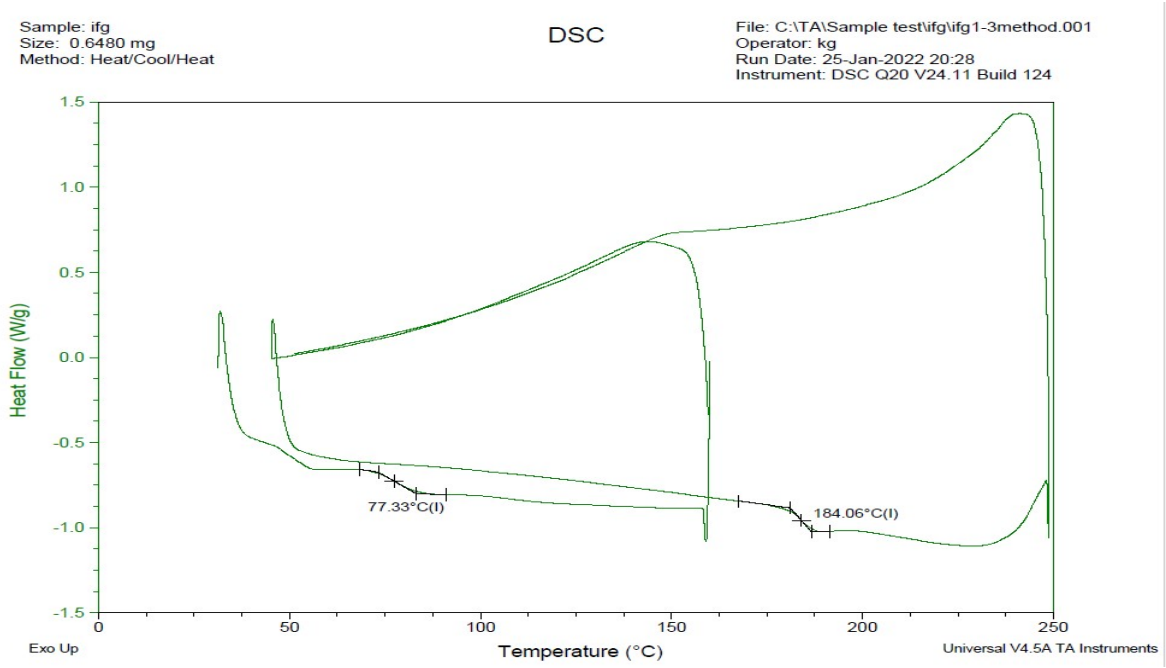


Figure S14. DSC curves for crosslinking chromophores QLD3 after crosslinking

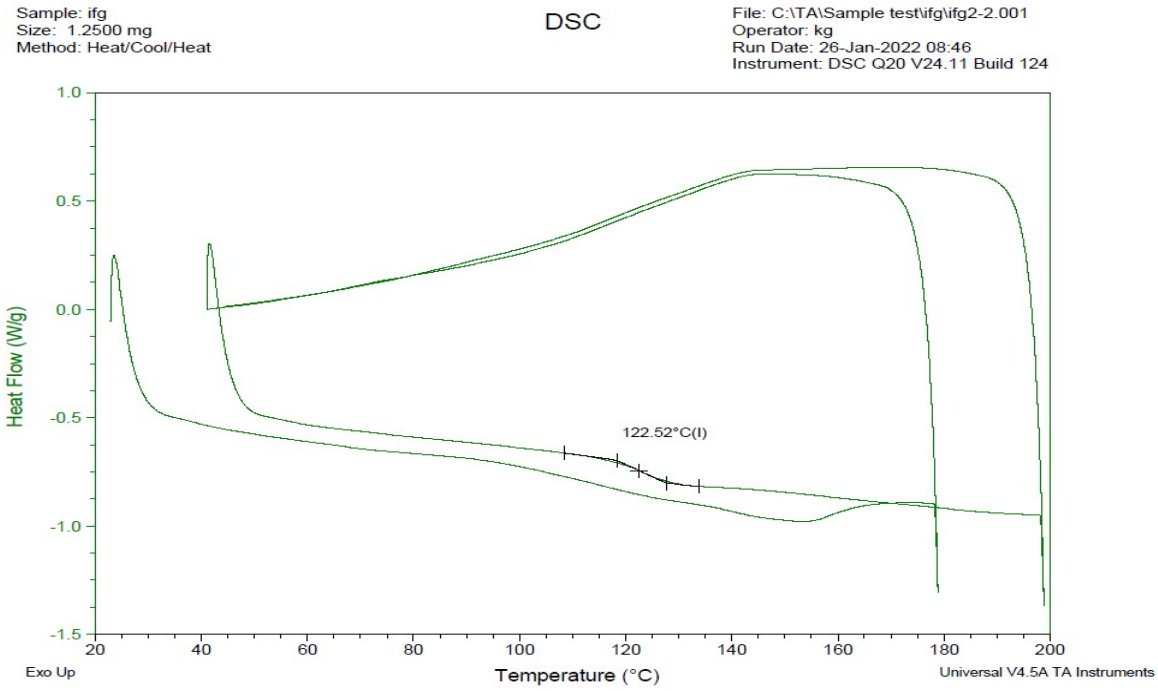


Figure S15. DSC curves for chromophore QLD4

6. Chemical structure and performance of HLD1-2 and JRD1

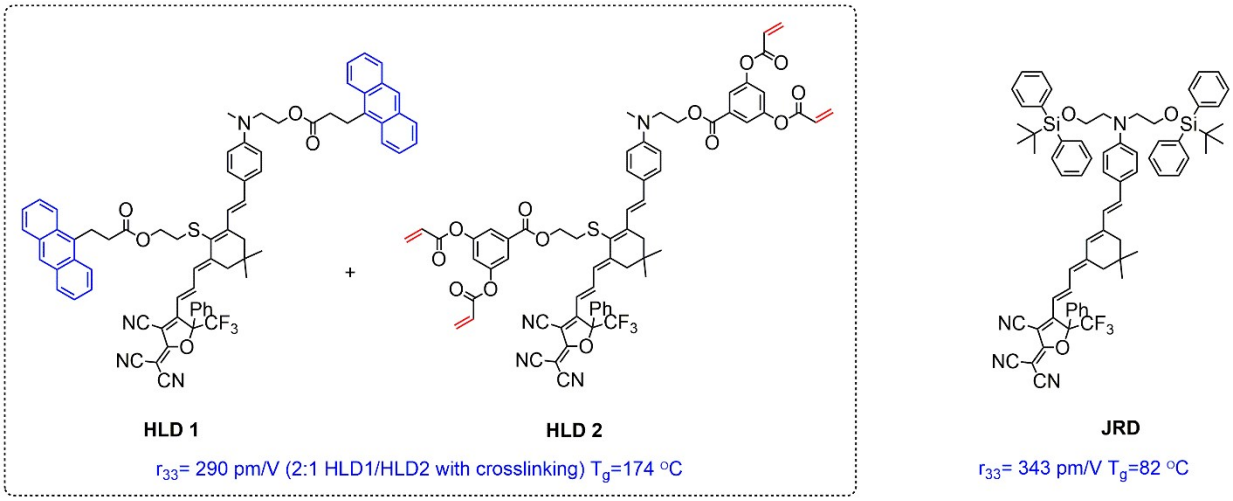


Figure S16. Chemical structure and performance of HLD1-2 and JRD1[1, 2]

7. DFT Calculations

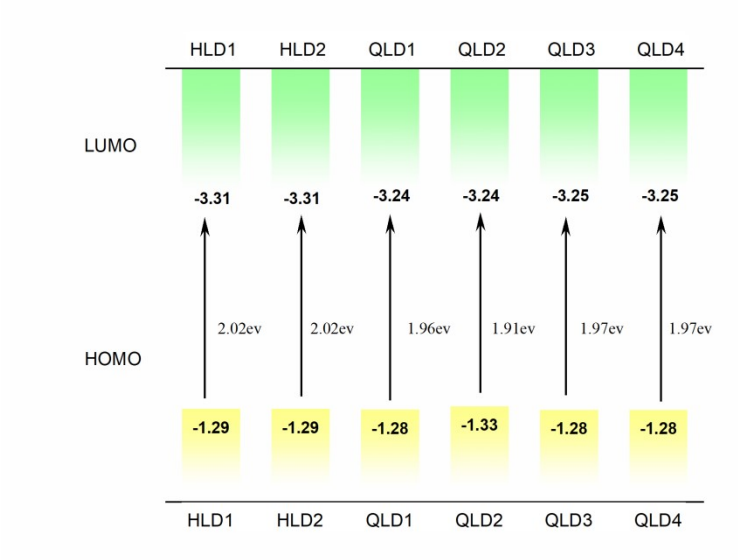


Figure S17. HOMO and LUMO energy gaps, in eV.

Table S1 β value of chromophores in solvent

Solvent	HLD1	HLD2	QLD1	QLD2	QLD3	QLD4
tetrahydrofuran	2576	2745	3128	3586	3105	3108
chloroform	2234	2384	2715	3105	2706	2694
toluene	1603	1713	1951	2221	1961	1929

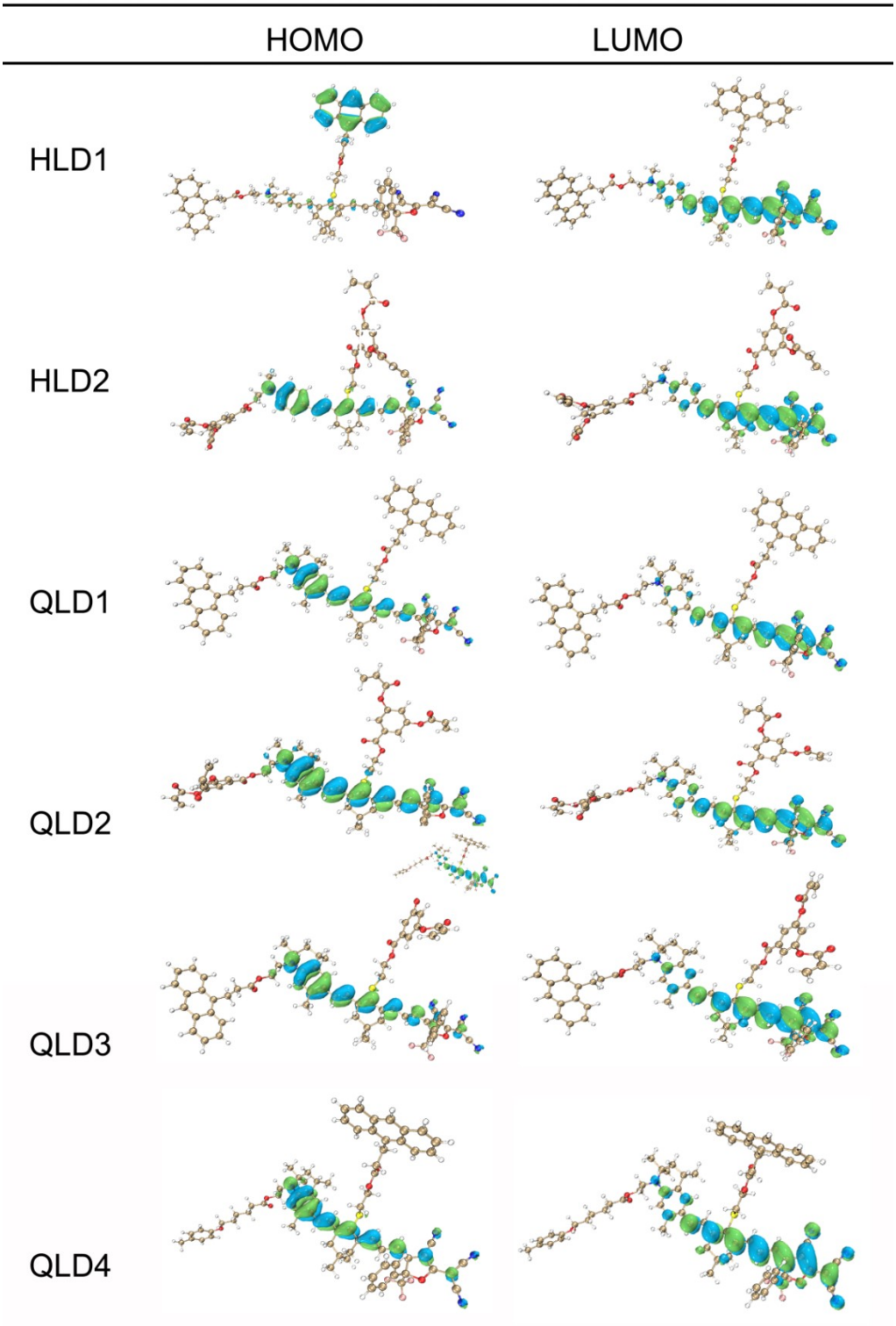
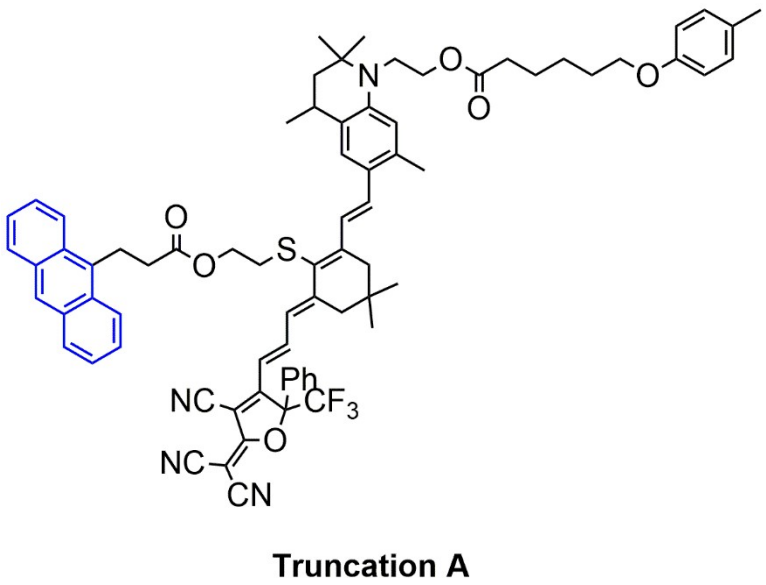


Figure S18. Frontier molecular orbitals HOMO and LUMO of chromophores HLD1 -2 and QLD1-4.



. **Figure S19.** Chemical structures for Truncation A of chromophore QLD4 used in DFT calculations.

8. Chemical structure and performance of Polymer crosslinking material

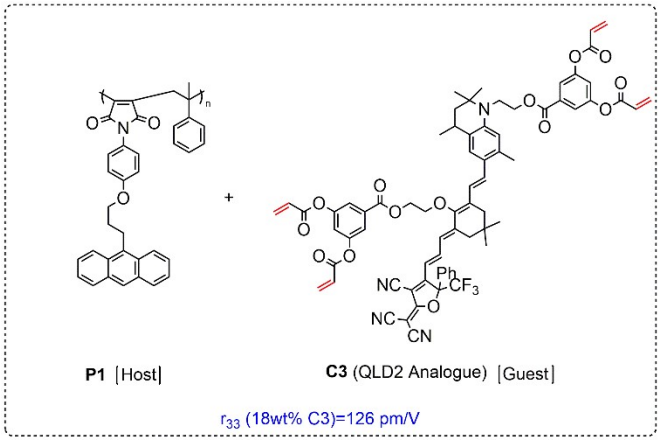


Figure S20. Chemical structures for P1,C3and their performance[3]

9. Properties of the state-of-the-art organic EO materials

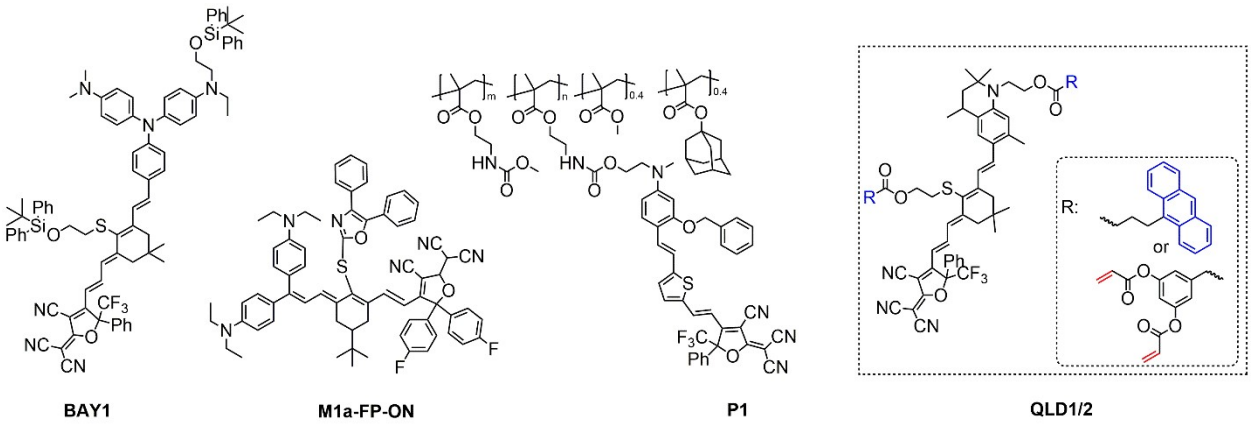


Figure S21. Chemical structures of the state-of-the-art organic EO materials.

Table S2 Properties of the state-of-the-art organic EO materials[4-6]

Cmpd	T_d (°C)	T_g (°C)	β_{tot}[a] (10^{-30}esu)	max. r_{33}/(pm/V)
BAY1	205	84	2941	460 or 1100 （with TiO_2）
M1a-FP-ON	233	--	376	127
P1	--	172	--	223
QLD1/2	273-317	185	1140	327

[a] was the first-order hyperpolarizability in vacuum calculated from DFT calculations.

Supplementary Table S2 summarizes the properties of the reported state-of-the-art organic EO materials, including monolithic chromophore (BAY1), guest-host systems (M1a-FP-ON) and polymer (P1). Although the each single performance of QLD series materials are not the highest among them, it is comparable to state-of-the-art values of the previously reported organic EO materials. Meanwhile, it possesses the highest thermal decomposition temperature (T_d) and glass transition temperature (T_g) among the 5 materials shown in Suppl. Table S2, indicating excellent high-temperature thermal stability. Hence, the presented QLD series materials stands out in terms of the high-temperature stability and EO efficiency in a well-balanced manner.

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