Supporting Information

Highly thermally stable binary cross-linkable organic nonlinear optical materials based on different Diels-Alder or Huisgen cycloaddition reaction

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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 QLD1-6 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 500M (500 MHz) NMR spectrometer (tetramethyl silane was used as an internal reference). Mass spectra were obtained on a MALDITOF (matrix-assisted laser desorption/flight ionization). BIFLEX III (Broker Inc.) spectrometer. UV-Vis spectra were performed on a Cary 5000 spectrometer. TGA was determined by TA5000-2950TGA (TA co) with a heating rate of 10 C min$^{-1,}$ under nitrogen protection. Glass-transition temperature (T_g) was measured by differential scanning calorimetry (DSC) with a heating rate of 10 °C min^{-1} under the protection of nitrogen.

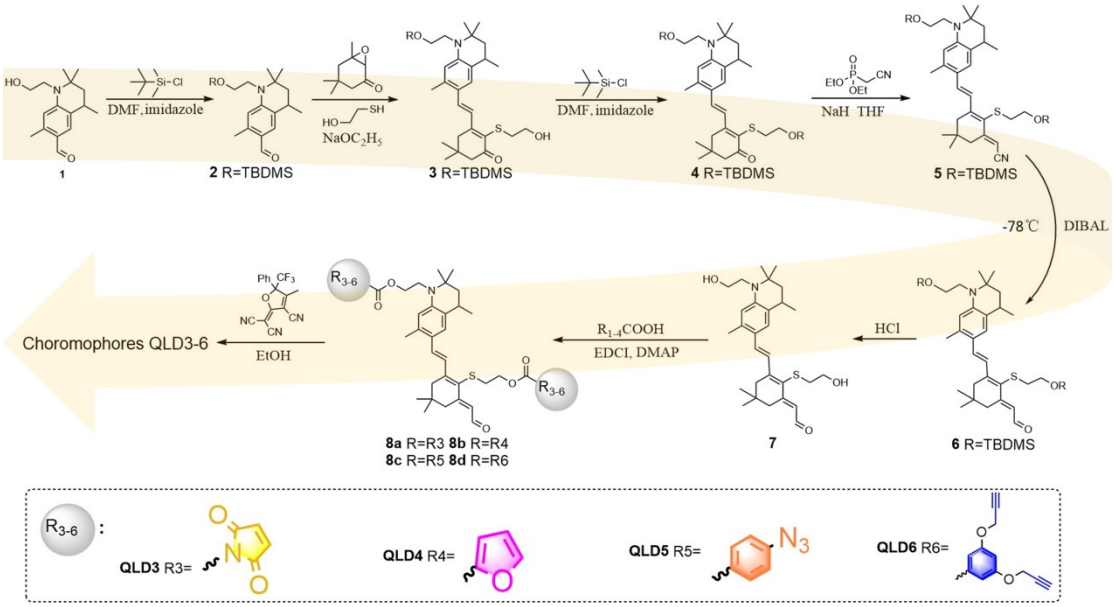


Figure S1. Synthetic routes for chromophores QLD3–6.

2 Experimental

2.1 Synthesis of 8a

Refer to previous literature.[1]

2.2 Synthesis of 8b

Refer to previous literature.[1]

2.3 Synthesis of 8c

Compounds 3-(2,5-dioxo-2,5-dihydro-1H-pyrrolidin-1-yl) propionic acid (2.22g, 19.85mmol), DMAP (0.24g,

1.98mmol) and EDCI (3.79g, 19.85mmol) were placed in a dry and clean round-bottom double-mouth vial, then added 15mL of dichloromethane to the bottle. The whole process above was under ice bath condition and Ar environment, subsequently, the solution became turbid, and stirred for 45minutes. After the solution was clear, add compound 7 (4.0 g, 8.27 mmol) and 20 mL of dichloromethane. Under ice bath condition, it was urgent to stir for 2 hours, and after the solution returned to room temperature, transfer to the oil bath at 45 °C and reflux for 15 hours. After the reaction was complete, it was extracted with dichloromethane. After vacuum concentration, the crude product was purified by column chromatography with petroleum ether and ethyl acetate (8:1~2:1) as the eluent, and the red solid compound 8c was obtained with a yield of 64.8% (4.21g, 5.36mmol). HRMS(ESI) (M+, $C_{43}H_{51}N_3O_9S$): calcd:786.3424; found: 786.3420. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.11 (d, J = 8.1 Hz, 1H，CH), 7.86 (d, J = 16.0 Hz, 1H, CH), 7.43 (s, 1H, CH), 7.10 (d, J = 16.0 Hz, 1H, CH), 6.92 (d, J = 8.1 Hz, 1H, CH), 6.69 (s, 2H, CH), 6.62 (d, J = 4.3 Hz, 2H, ArH), 6.47 (d, J = 8.8 Hz, 1H, CH), 4.26 - 4.11 (m, 2H, NCH_2), 3.86 - 3.80 (m, 2H, OCH_2), 3.70 (t, J = 7.0 Hz, 2H, OCH_2), 3.63 - 3.31 (m, 2H, NCH_2), 2.87 (tq, J = 12.2, 6.0 Hz, 1H, CH), 2.76 (t, J = 6.9 Hz, 2H, CH_2), 2.74 (d, J = 8.2 Hz, 2H, CH_2), 2.67 - 2.62 (m, 2H, CH2), 2.53 (t, J = 7.1 Hz, 2H, CH_2), 2.51 (d, J = 3.4 Hz, 2H, CH_2), 2.37 (s, 3H, CH_3), 1.75 (dd, J = 13.1, 4.8 Hz,1H, CH_2), 1.57 - 1.48 (m, 1H, CH_2), 1.34 (d, J = 6.6 Hz, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.03 (s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.49, 170.63, 170.43, 170.13, 156.40, 151.03, 145.50, 136.31, 134.19, 132.61, 127.21, 126.84, 126.23, 125.58, 124.08, 123.55, 113.19, 63.35, 62.45, 60.36, 54.74, 46.44, 43.12, 41.66, 39.88, 33.64, 33.48, 33.03, 32.72, 30.11, 29.66, 28.34, 27.01, 26.86, 24.76, 21.05, 20.17, 14.21.

2.4 Synthesis of 8d

In the Ar environment, the compounds furan-2-carboxylic acid (3.36 g, 19.85 mmol), DMAP (0.24 g, 1.98 mmol), and EDCI (3.79 g, 19.85 mmol) were placed in a dry and clean round-bottom double-mouth vial. Add 35 mL of dichloromethane to the ice bath, the solution became turbid, stirred for 45 minutes. After the solution was clear, compound 7 (4.0 g, 8.27 mmol) and 40 mL of dichloromethane were added. After the solution returned to room temperature, transfer to an oil bath and reflux at 45 °C for 15 h. After the reaction was completed, dichloromethane was used for extraction. After vacuum concentration, petroleum ether and ethyl acetate (10:1~4:1) were used as eluents for column chromatographic purification, and the red solid compound 8b was obtained, with a yield of 59.3% (3.57g, 4.90mmol). HRMS(ESI) (M+, $C_{43}H_{53}NO_7S$): calcd:728.3621; found: 728.3630. ^{1}H NMR (600 MHz, CDCl3) δ 10.12 (t, J = 5.4 Hz, 1H, ArH), 7.89 (d, J = 16.0 Hz, 1H, CH), 7.45 (s, 1H, CH), 7.28 (d, J = 1.1 Hz, 1H, ArH), 7.23 (s, 1H, CH), 7.13 - 7.08 (m, 1H, CH), 6.95 (d, J = 8.1 Hz, 1H, CH), 6.47 (s, 1H, CH), 6.27 - 6.19 (m, 2H, CH), 6.01 (d, J = 2.6 Hz, 1H, CH), 5.93 - 5.89 (m, 1H, CH), 4.28 - 4.13 (m, 2H, OCH_2), 3.60 - 3.31 (m, 2H, OCH_2), 2.98 (t, J = 7.6 Hz, 2H, NCH_2), 2.84 (dd, J = 15.0, 7.3 Hz, 3H, CH_2), 2.75 (dd, J = 13.7, 6.9 Hz, 4H, CH_2), 2.67 (dd, J = 16.2, 8.8 Hz, 2H, SCH_2), 2.58 - 2.53 (m, 2H, CH_2), 2.50 (s, 2H, CH_2), 2.36 (d, J = 6.3 Hz, 3H, CH_2), 1.73 (dd, J = 13.1, 4.8 Hz, 1H, CH_2), 1.51 (dd, J = 24.3, 11.4 Hz, 1H, CH), 1.34 (d, J = 6.6 Hz, 3H, CH_3), 1.30 (d, J = 8.2 Hz, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.03 (d, J = 1.4 Hz, 6H, CH_3).^{13}C NMR (151 MHz, $CDCl_3$) δ 191.66, 172.58, 172.28, 156.53, 154.09, 151.22, 145.63, 141.41, 141.27, 136.39, 132.69, 127.36, 126.97, 126.34 , 125.72 , 124.19, 123.67, 113.31, 110.31, 105.53, 105.37, 63.14, 62.36, 54.82, 46.56 , 43.35, 41.81 , 40.03, 33.35, 32.81, 32.58, 30.23, 29.77, 28.46, 26.99, 24.84 , 23.60 , 23.41, 20.30.

2.5 Synthesis of 8e

In an Ar atmosphere, compound 4-azidobenzoic acid (3.24 g, 19.85 mmol), DMAP (0.24 g, 1.98 mmol), and EDCI (3.79 g, 19.85 mmol) were placed in a dry and clean round-bottomed double-mouth flask. Add 25 mL of dichloromethane under ice bath conditions, the solution becomes turbid, stirred for 45 minutes. After the solution was clear, compound 7 (4.0 g, 8.27 mmol) and 45 mL of dichloromethane were added. Stirred urgently for 2 h under ice bath conditions. After the solution returned to room temperature, transferred to an oil bath at 45 °C and refluxed for 15 hours. After the reaction was completed, it was extracted with dichloromethane. The crude product was concentrated under vacuum, and the column chromatographic purification was carried out with petroleum ether and ethyl acetate (8:1~4:1) as eluents, and the red solid compound 8C was obtained with a content of 65.1% (4.16g, 5.38mmol). HRMS(ESI) (M+, $C_{43}H_{47}N_7O_5S$): calcd:908.3832; found: 908.3837. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.15 (d, J = 8.0 Hz, 1H，CHO), 8.09 - 8.05 (m, 2H, ArH), 7.97 - 7.92 (m, 3H, ArH), 7.45 - 7.42 (m, 1H, CH), 7.14 - 7.06 (m, 3H,,ArH), 7.01 (d, J = 8.1 Hz, 1H, ArH), 6.96 - 6.92 (m, 2H, CH), 6.60 (s, 1H,CH), 4.53 - 4.39 (m, 2H, OCH_2), 4.38 - 4.33 (m, 2H, OCH_2), 3.65 (m, J = 21.0, 14.7, 8.5, 5.8 Hz, 2H, NCH_2), 2.95 (t, J = 6.5 Hz, 2H, SCH_2), 2.89 - 2.81 (m, 1H, CH), 2.76 (s, 2H, CH_2), 2.50 (s, 2H, CH_2), 2.39 (s, 3H, CH_3), 1.60 (d, J = 27.5 Hz, 2H, CH_2), 1.38 (d, J = 6.8 Hz, 3H, CH_3), 1.31 (d, J = 6.6 Hz, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.06 (s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.64, 165.93, 165.54, 156.46, 151.17, 145.68, 145.12, 144.80, 136.33, 132.71, 131.63, 127.35, 127.07, 126.57, 126.41, 125.79, 124.31, 123.79, 119.03, 118.85, 113.42, 63.54, 63.08, 54.96, 46.64, 43.54, 41.83, 40.03, 33.48, 30.30, 29.84, 28.50, 27.01, 24.96, 20.38, 20.22.

2.6 Synthesis of 8f

Compounds 3,5-bis(propyl-2-yn-1-oxy) benzoic acid (4.57g, 19.85mmol), DMAP (0.24g, 1.98mmol) and EDCI (3.79g, 19.85mmol) were placed in a dry and clean round-bottom double-mouth flask under the atmosphere of Ar. Add 25mL of dichloromethane under ice bath conditions, the solution became turbid, stirred for 45minutes. After the solution was clear, add compound 7 (4.0 g, 8.27 mmol) and 30 mL of dichloromethane. Under ice bath conditions, stirred for 2 hours, and after the solution returned to room temperature, transferred to an oil bath at 45°C for 15 hours. After the reaction was complete, it was extracted with dichloromethane. After vacuum concentration, the crude product was purified by column chromatography with petroleum ether and ethyl acetate (10:1~4:1) as eluting solution, and the red solid compound was obtained by 8d with a yield of 77.5%. (5.82g, 6.41mmol) HRMS(ESI) (M+, $C_{55}H_{57}NO_9S$) calcd:774.3438; found: 774.3432. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.15 (d, J = 8.0 Hz, 1H, CHO), 7.91 (d, J = 16.0 Hz, 1H, CH), 7.44 (d, J = 8.5 Hz, 1H, ArH), 7.32 (d, J = 2.4 Hz, 2H, ArH), 7.20 (d, J = 2.4 Hz, 2H, ArH), 7.09 (d, J = 16.0 Hz, 1H, CH), 7.00 (d, J = 8.0 Hz, 1H, ArH), 6.84 (t, J = 2.4 Hz, 1H, ArH), 6.77 (t, J = 2.4 Hz, 1H, ArH), 6.56 (s, 1H, CH), 4.72 (d, J = 2.4 Hz, 4H, OCH_2), 4.65 (d, J = 2.4 Hz, 4H, OCH_2), 4.47 (m, J = 10.8, 6.5, 5.3, 2.3 Hz, 2H,OCH_2), 4.40 - 4.35 (m, 2H, OCH_2), 2.94 (t, J = 6.7 Hz, 2H, NCH_2), 2.85 (dt, J = 18.3, 5.9 Hz, 1H, CH), 2.79 - 2.73 (m, 2H, CH), 2.55 (t, J = 2.4 Hz, 2H, CH), 2.54 - 2.51 (m, 2H, SCH_2), 2.49 (s, 2H, CH_2), 2.39 (s, 3H, CH_3), 1.77 (dd, J = 13.1, 4.8 Hz, 1H, CH_2), 1.65 (s, 2H, CH_2), 1.56 (t, J = 12.9 Hz, 1H, CH_2), 1.38 (s, 3H, CH_3), 1.33 (d, J = 6.6 Hz, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.05 (d, J = 3.5 Hz, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.66, 166.09, 165.69, 158.69, 158.55, 156.57, 151.08, 145.61, 136.38, 132.73, 132.09, 127.57, 126.99, 126.54, 125.66, 124.23, 123.74, 113.36, 109.19, 109.05, 107.64, 78.08, 76.14, 64.33, 63.17, 56.25, 54.96, 46.65, 43.43, 41.79, 40.03, 33.42, 30.26, 29.85, 28.49, 27.01, 25.03, 20.37, 20.19.

2.7 Synthesis of QLD1

Refer to previous literature.[1]

2.8 Synthesis of QLD2

Refer to previous literature.[1]

2.9 Synthesis of chromophore QLD3

Compounds 8a (4.21g, 5.36mmol) and CF3-TCF receptor (1.86g, 5.89mmol) were dried in a vacuum drying oven for 2 hours and sealed after drying. Add 15 mL of absolute ethanol and 2 mL of tetrahydrofuran in argon and stirred and refluxed at 65 °C for 6 h. After the reaction was completed, concentrated the solution. The crude product was petroleum ether and ethyl acetate (1:8~1:1) as the eluate twice, and the solid QLD3 product was obtained by column chromatography purification, and the yield was 33.2% (3.89g, 3.59mmol). HRMS (ESI) (M+, $C_{59}H_{57}F_3N_6O_9S$): calcd:1083.3938; found: 1083.3937. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (t, J = 17.4 Hz, 2H, CH), 7.58 - 7.51 (m, 5H, CH), 7.50 (s, 1H, CH), 7.42 (d, J = 8.3 Hz, 1H, ArH), 7.28 (d, J = 7.9 Hz, 1H, ArH), 6.75 - 6.57 (m, 4H, CH), 6.52 (d, J = 15.5 Hz, 2H, CH), 4.28 - 4.14 (m, 2H, NCH2), 3.86 (t, J = 7.1 Hz, 2H, OCH2), 3.72 (t, J = 7.1 Hz, 2H, OCH_2), 3.69 - 3.37 (m, 2H, NCH_2), 2.88 (m, J = 20.2, 13.3, 7.0 Hz, 1H, CH), 2.79 (q, J = 6.9 Hz, 2H, SCH_2), 2.68 (t, J = 7.1 Hz, 2H, CH_2), 2.59 - 2.51 (m, 4H, CH_2), 2.41 (s, 3H, CH_3), 2.29 (dt, J = 43.8, 10.8 Hz, 2H, CH_2), 2.05 - 2.01 (m, 2H, CH_2), 1.35 (d, J = 8.4 Hz, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 0.90 (t, J = 4.2 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.41, 147.36, 137.92, 134.36, 131.47, 130.20, 129.80, 128.46, 126.96, 124.66, 123.64, 117.27, 116.04, 63.40, 62.37, 55.30, 46.34, 41.89, 41.28, 34.86, 34.01, 33.78, 33.58, 33.11, 32.85, 32.06, 31.76, 30.50, 29.81, 29.50, 28.76, 28.01, 26.95, 25.16, 22.83, 20.34, 20.21, 14.26.

2.10 Synthesis of chromophore QLD4

According to the synthesis steps of chromophore QLD3, the synthetic chromophore QLD4 was prepared from compound 8b with a yield of 48.7% (2.79g, 2.96mmol), which is a dark green solid. HRMS (ESI) (M+, $C_{59}H_{59}F_3N_4O_7S$): calcd:1025.4235; found: 1025.4233. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (t, J = 24.1 Hz, 2H, CH), 7.54 - 7.45 (m, 6H, ArH), 7.39 (d, J = 12.2 Hz, 1H, CH), 7.28 (t, J = 4.5 Hz, 1H, ArH), 7.23 (s, 2H, CH), 6.50 – 6.44 (m, 2H, CH), 6.23 (m, J = 31.8, 3.1, 1.9 Hz, 2H, CH), 6.04 - 5.87 (m, 2H, CH), 4.27 - 4.12 (m, 2H, OCH_2), 3.63 - 3.31 (m, 2H, OCH_2), 2.97 (t, J = 7.5 Hz, 2H, NCH_2), 2.88 – 2.80 (m, 3H, CH_2), 2.75 (t, J = 6.7 Hz, 2H, SCH_2), 2.67 (t, J = 7.6 Hz, 2H, CH_2), 2.55 - 2.49 (m, 4H, CH_2), 2.37 (d, J = 8.0 Hz, 3H, CH_2), 2.35 - 2.21 (m, 2H, CH_2), 1.74 (dd, J = 13.2, 4.7 Hz, 1H, CH_2), 1.50 (d, J = 13.1 Hz, 1H, CH_2), 1.23 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 0.89 (d, J = 3.0 Hz, 3H, CH_3).^{13}C NMR (151 MHz, $CDCl_3$) δ 177.38, 175.95, 172.48, 172.28, 162.25, 159.42, 154.11, 153.80, 151.13 , 147.40 , 141.54 , 141.25, 134.38, 131.34, 130.41 , 129.82, 128.50 , 128.15, 126.89, 124.48, 116.54, 114.32, 111.71, 111.21, 110.34, 106.01, 105.64, 105.38, 94.90, 66.55, 62.89, 62.57, 44.93, 41.68, 41.42, 34.11, 32.83, 32.64, 32.37, 32.06, 31.55, 30.48, 29.77, 29.49, 29.19, 28.61, 27.95, 23.60, 23.46, 23.29, 22.83, 14.25, 12.88.

2.11 Synthesis of chromophore QLD5

Chromophore QLD5 was synthesized from compound 8c according to the synthesis procedure of chromophore

QLD3, and the yield was 55.1%, was a dark green solid. HRMS (ESI) (M+, $C_{71}H_{63}F_3N_4O_9S$): calcd:1205.4346; found: 1205.4345. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 15.8 Hz, 2H,ArH), 7.57 - 7.47 (m, 6H,ArH), 7.46 - 7.40 (m, 1H, ArH), 7.32 (d, J = 2.4 Hz, 2H, ArH), 7.23 (s, 1H, CH), 7.17 (d, J = 2.3 Hz, 2H, CH), 6.84 (t, J = 2.3 Hz, 1H, ArH), 6.79 (t, J = 2.3 Hz, 1H, ArH), 6.59 (s, 1H, CH), 6.45 (d, J = 14.7 Hz, 1H, CH), 4.72 (d, J = 2.4 Hz, 4H, OCH_2), 4.64 (d, J = 2.4 Hz, 4H, OCH_2), 4.52 - 4.35 (m, 4H, OCH_2), 3.82 - 3.53 (m, 2H, NCH_2), 2.94 (t, J = 6.6 Hz, 2H, SCH_2), 2.86 (dt, J = 11.6, 6.6 Hz, 1H,CH), 2.55 (t, J = 2.4 Hz, 2H, CH_2), 2.52 (t, J = 2.4 Hz, 2H, CH_2), 2.50 (d, J = 19.0 Hz, 2H,CH), 2.41 (s, 3H, CH_3), 2.36 - 2.23 (m, 2H, CH_2), 1.79 (dd, J = 13.2, 4.7 Hz, 1H, CH), 1.40 (s, 3H, CH_3), 1.34 (d, J = 6.6 Hz, 3H, CH_3), 1.26 (d, J = 9.8 Hz, 2H,CH_2), 1.24 (s, 3H,CH_3), 0.99 (d, J = 2.1 Hz, 3H, CH_3), 0.91 (d, J = 5.2 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.79, 166.10, 165.65, 162.75, 158.68, 137.90, 135.61, 131.97, 131.45, 130.19, 129.81, 129.56, 128.39, 126.93, 125.38, 124.68, 123.75, 113.63, 109.25, 107.71, 107.24, 78.03, 76.20, 64.18, 62.98, 56.28, 55.38, 46.44, 41.91, 41.31, 34.21, 30.60, 29.84, 28.79, 27.99, 26.98, 25.31, 20.41, 20.12.

2.12 Synthesis of chromophore QLD6

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 (ESI) (M+, $C_{63}H_{65}NO_5S$): calcd:948.28; found: 948.36. 1H 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.

3. NMR pictures

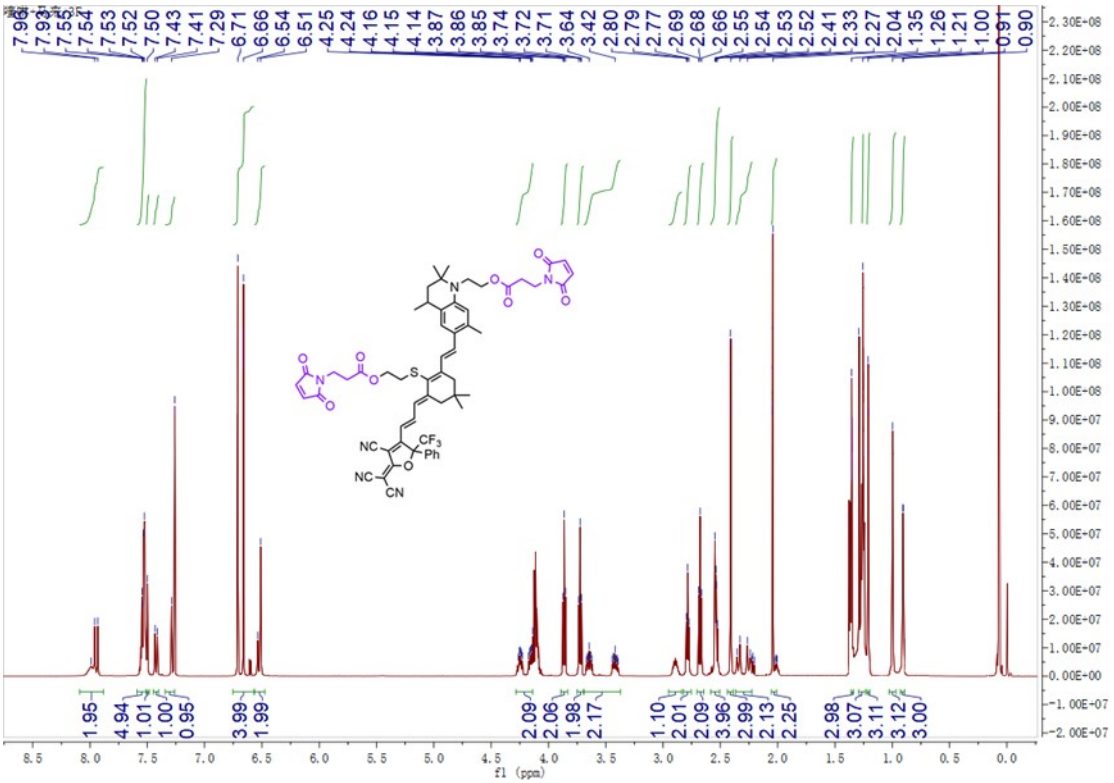


Figure S2. ^{1}H-NMR spectrum of Chromophore QLD3

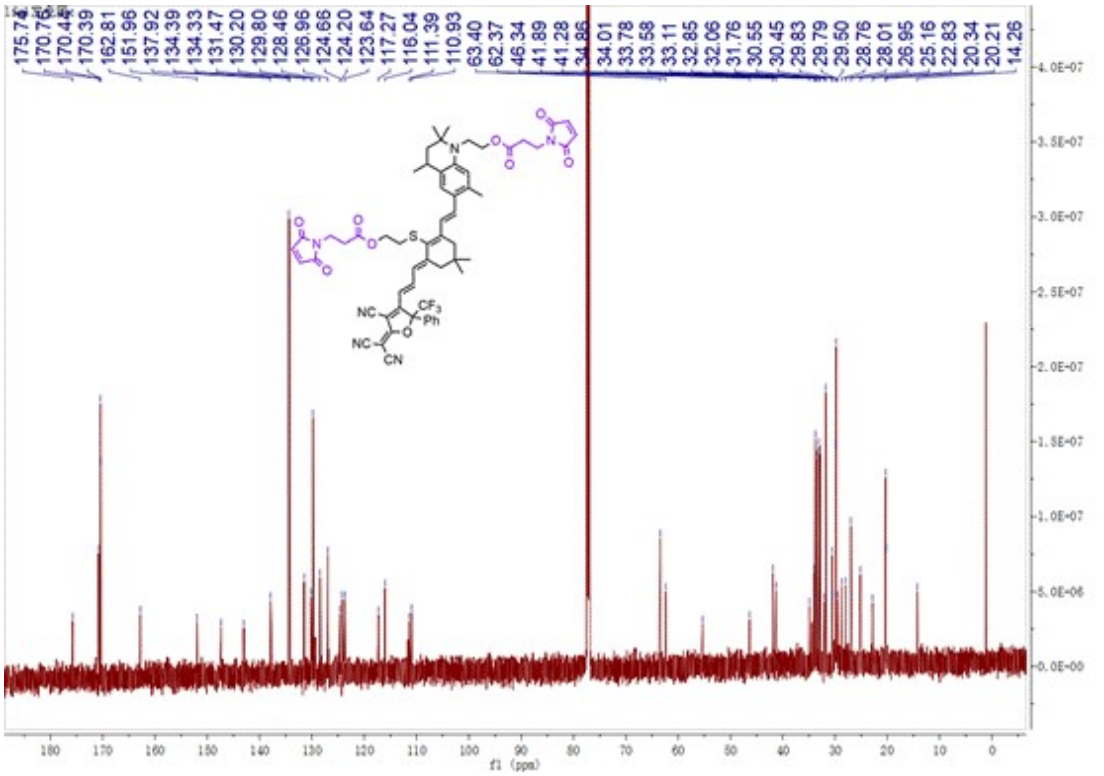


Figure S3. ^{13}C-NMR spectrum of Chromophore QLD3.

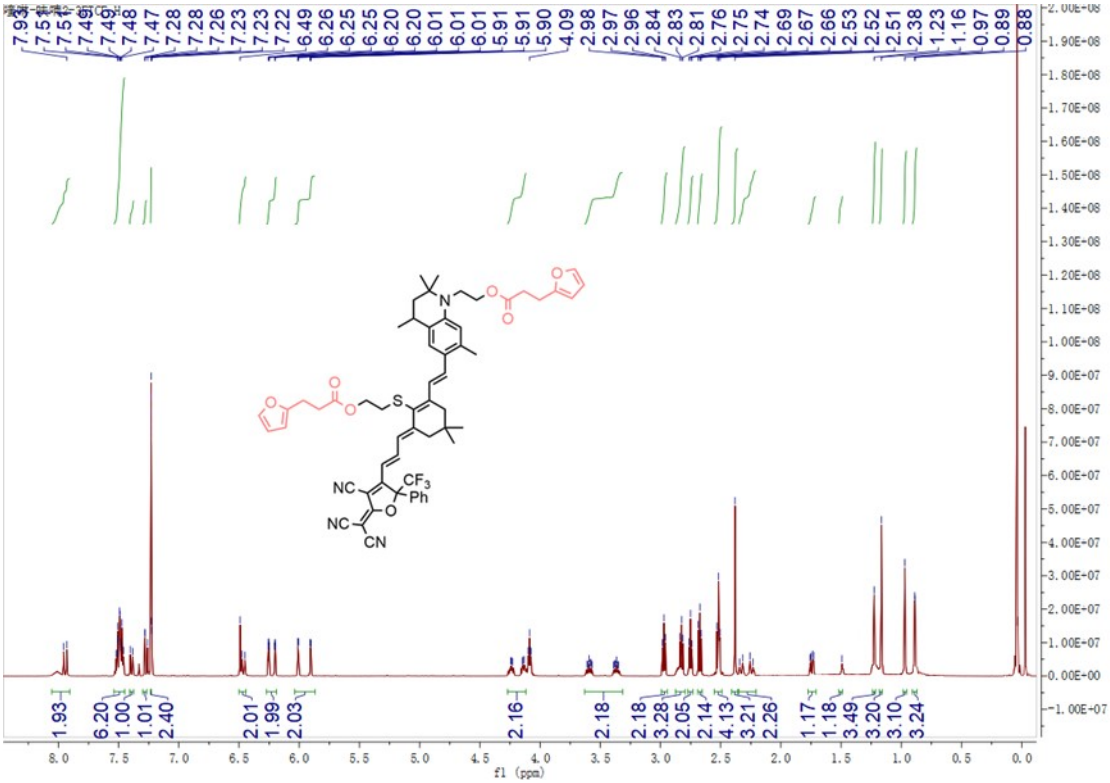


Figure S4. ^{1}H-NMR spectrum of Chromophore QLD4.

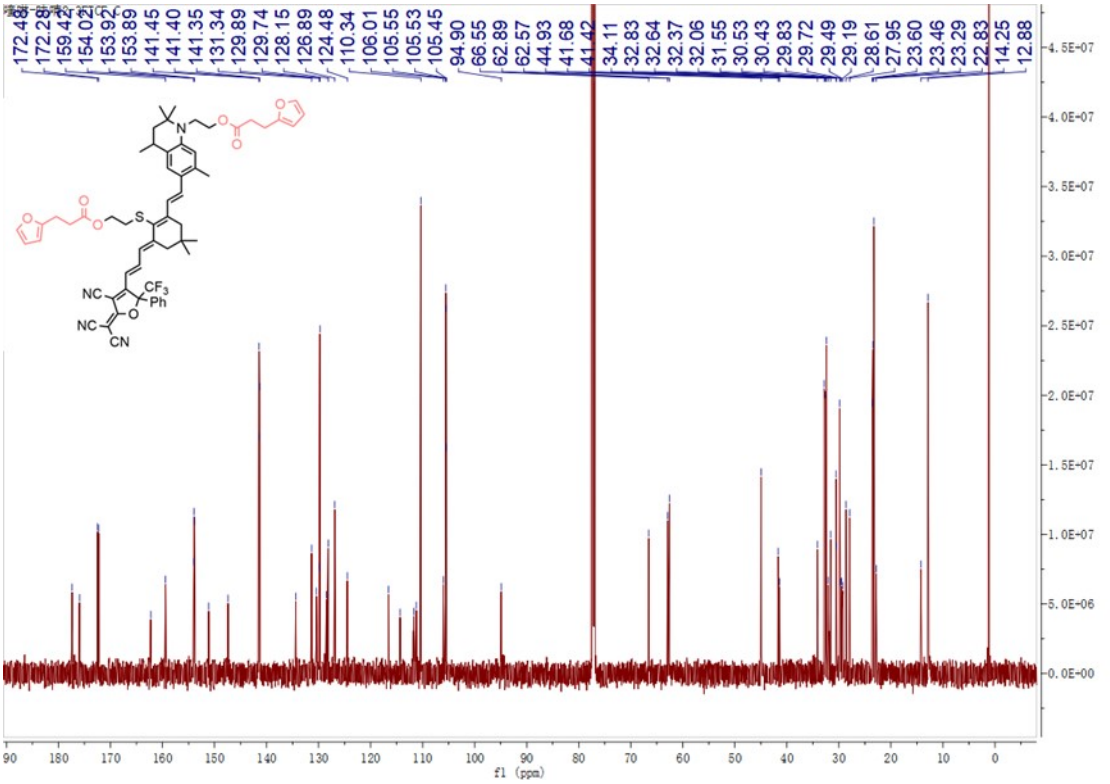


Figure S5. ^{13}C-NMR spectrum of Chromophore QLD4.

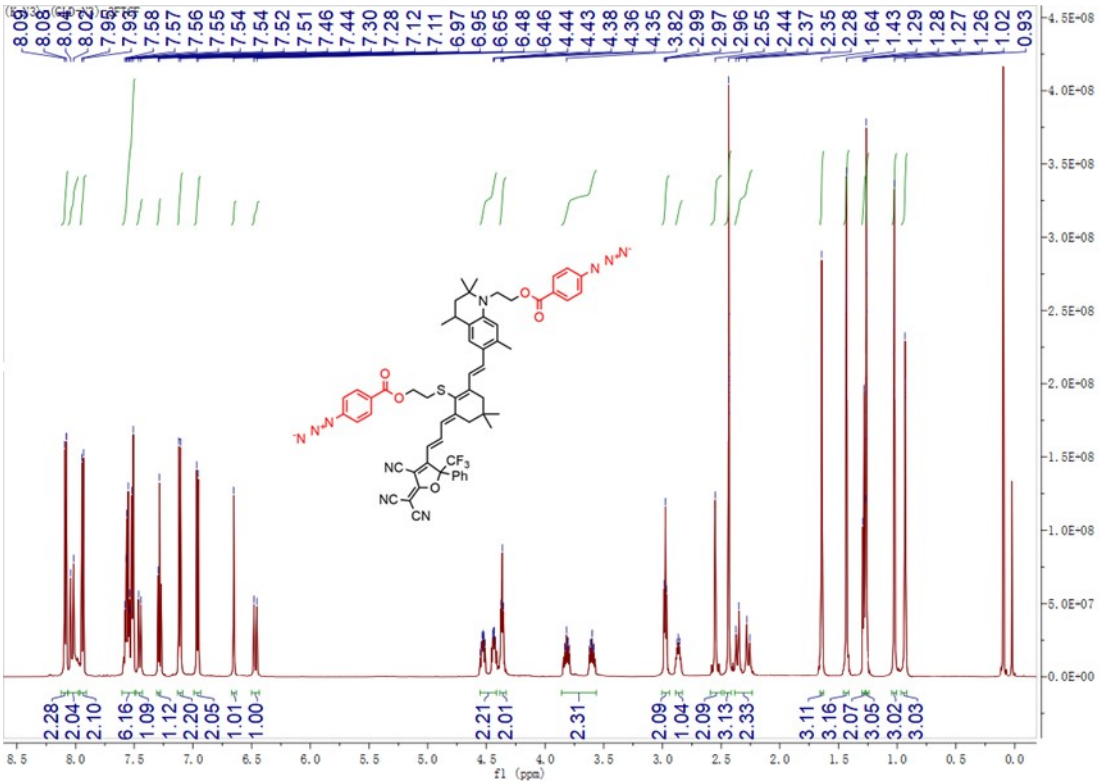


Figure S6. ^{1}H-NMR spectrum of Chromophore QLD5.

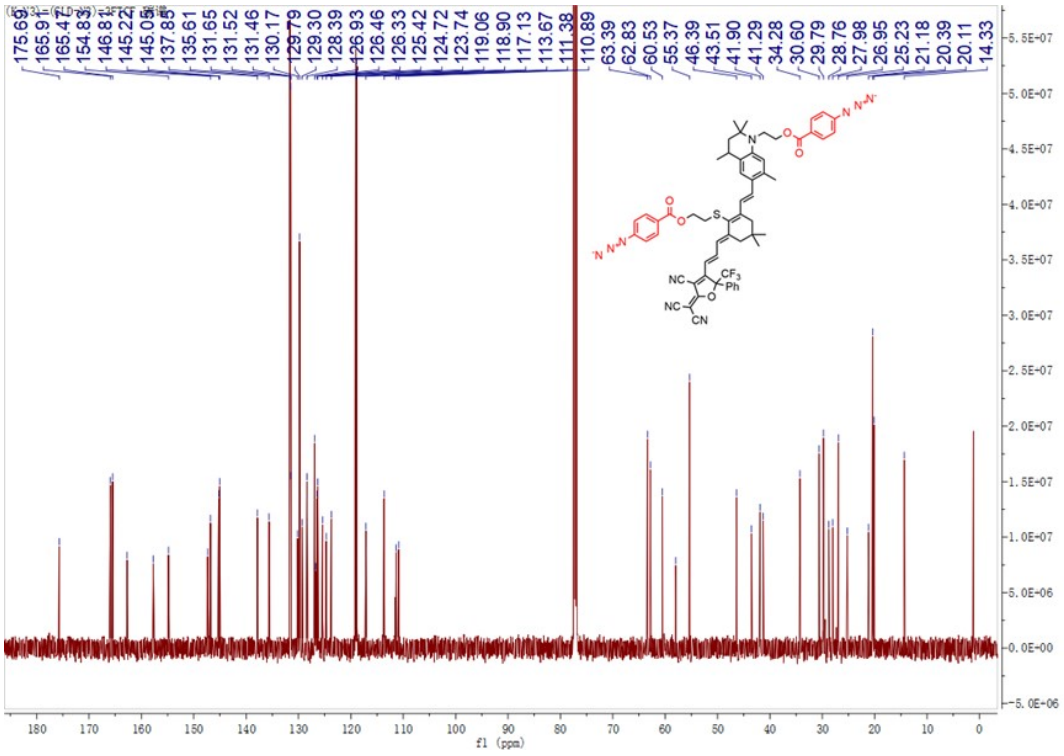


Figure S7. ^{13}C-NMR spectrum of Chromophore QLD5.

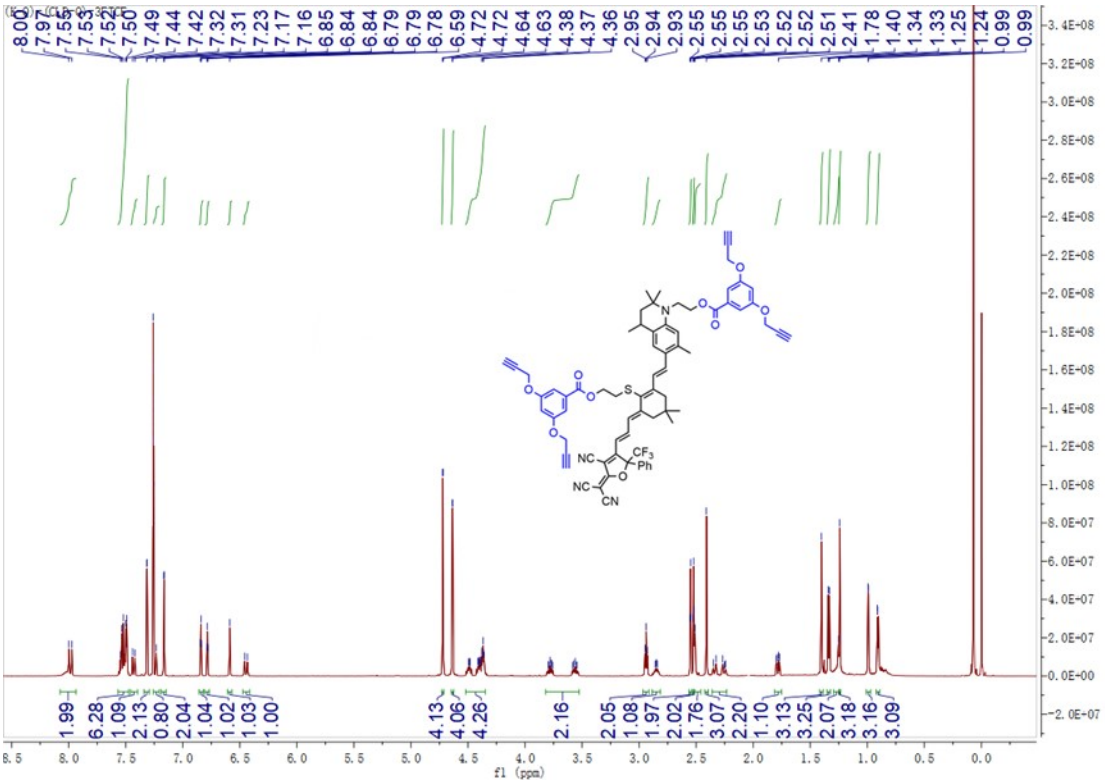


Figure S8. ^{1}H-NMR spectrum of Chromophore QLD6.

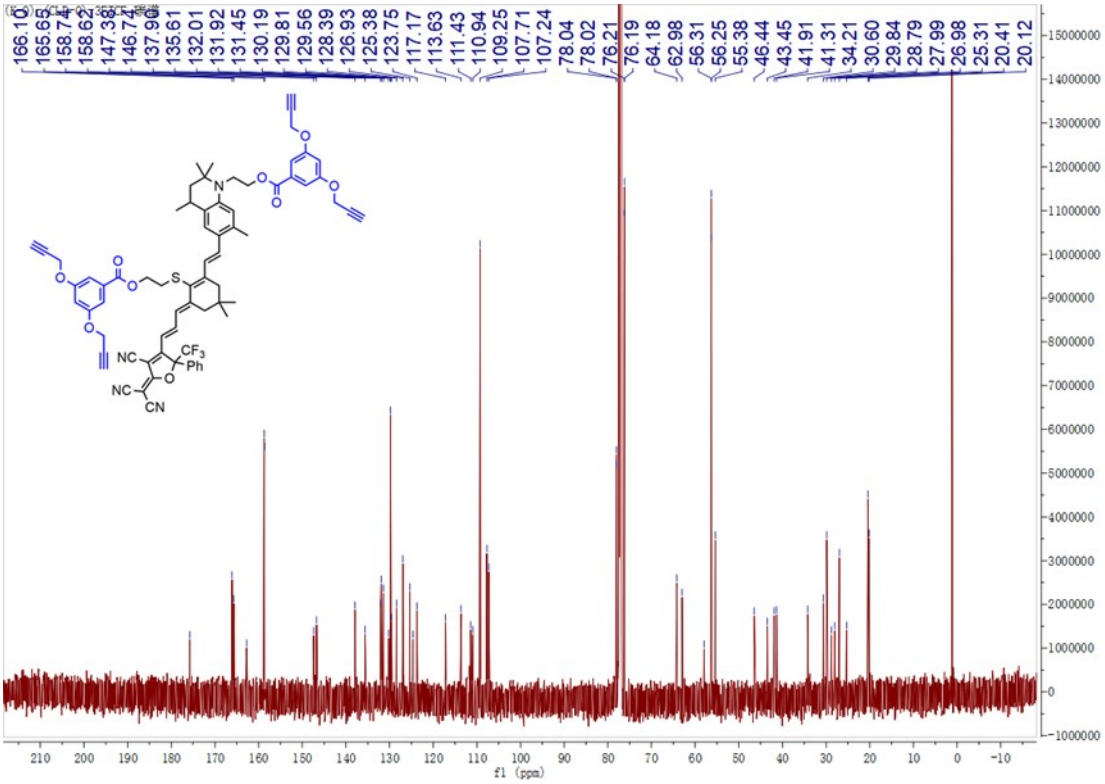


Figure S9. ^{13}C-NMR spectrum of Chromophore QLD6.

4. UV-Vis Absorption Spectroscopy

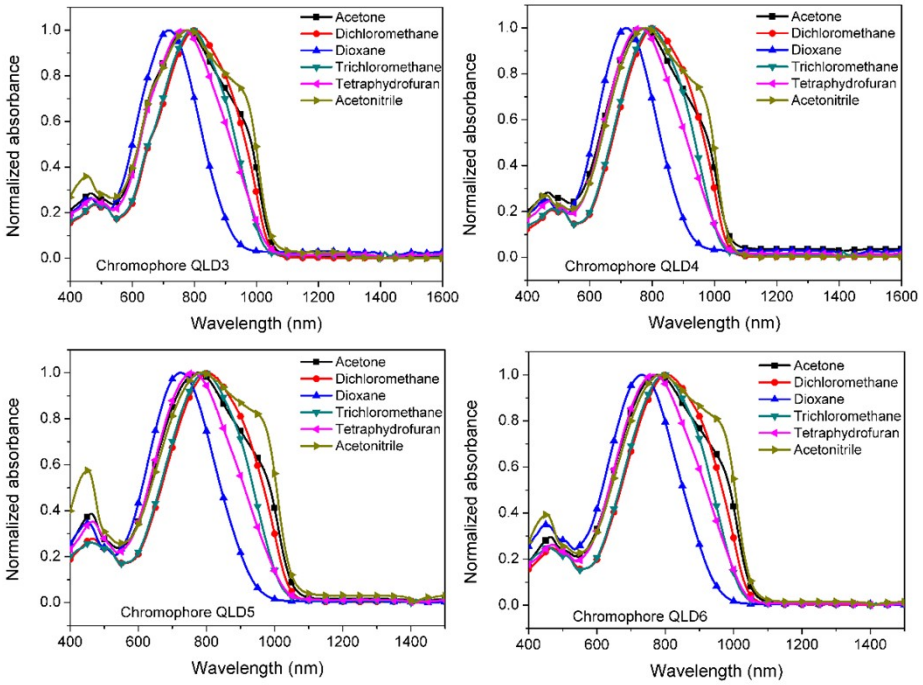


Figure S10. Normalized UV-Vis absorption spectra of chromophores QLD3-6 in seven aprotic solvents with varying dielectric constants (ε).

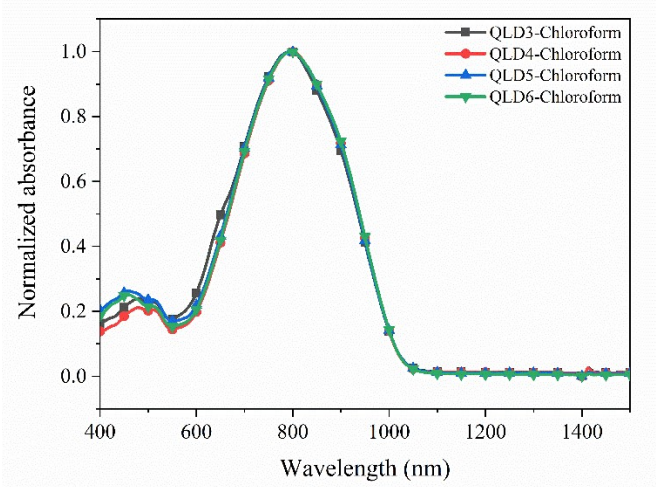
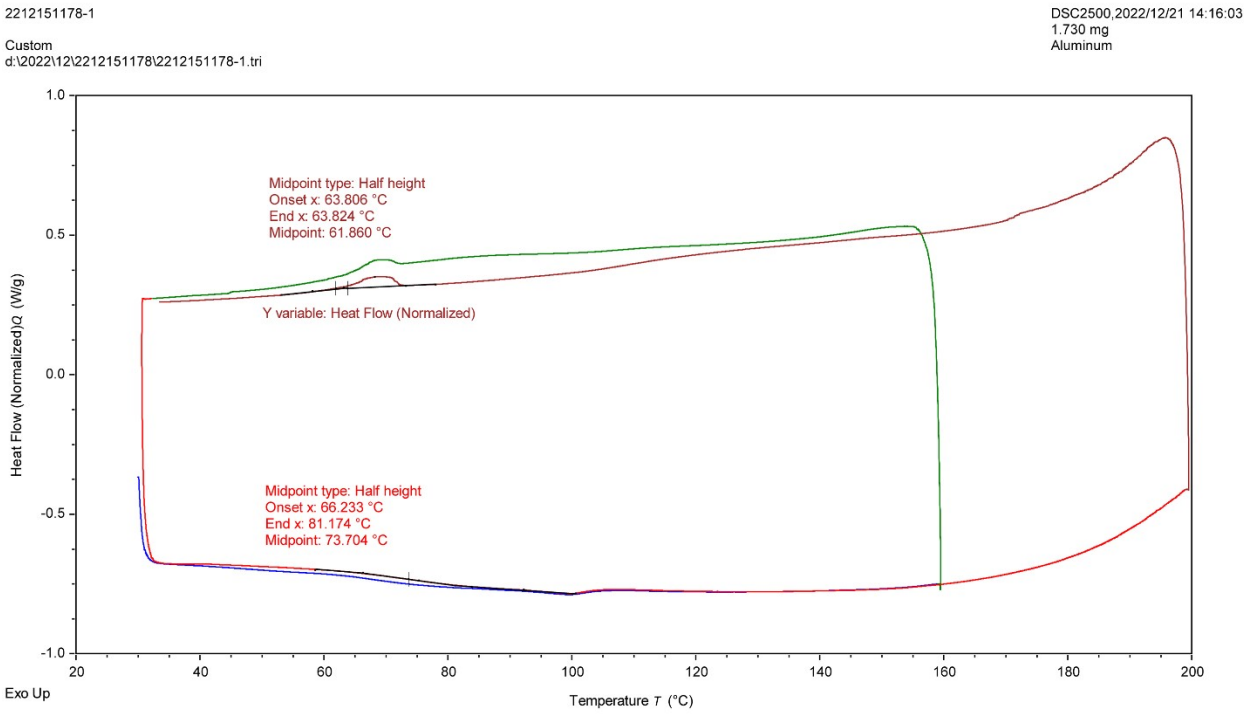
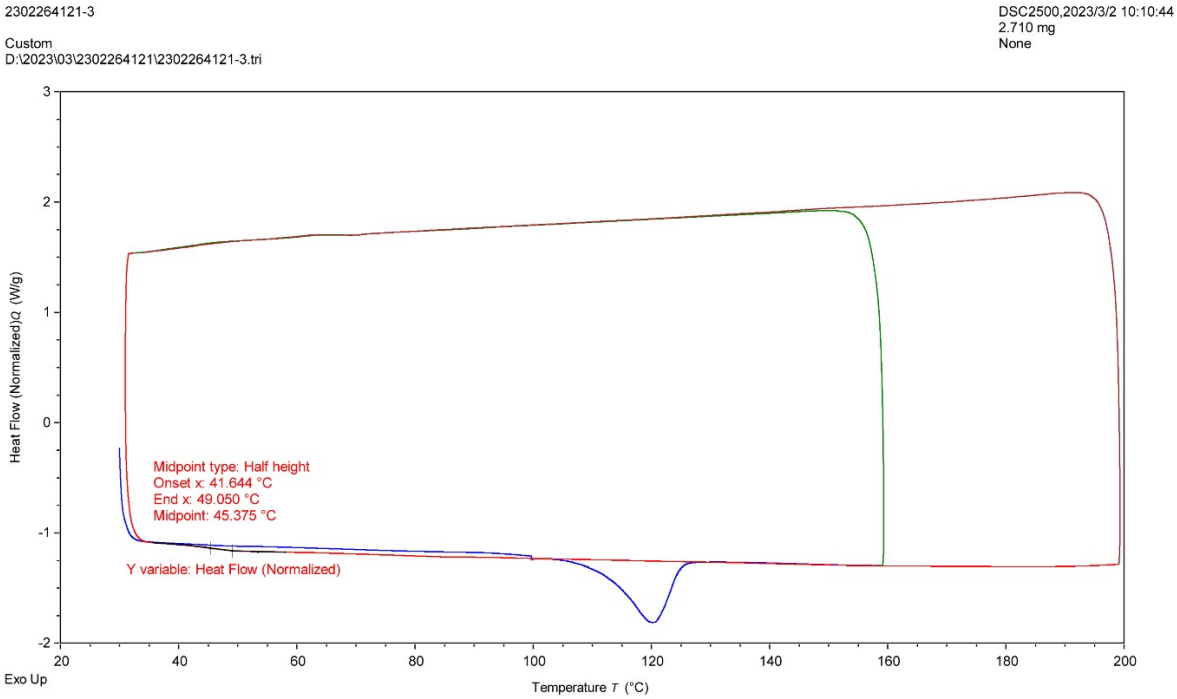


Figure S11. Ultraviolet absorption spectrum of chromophores QLD3-6 in chloroform

5. Differential Scanning Calorimetry testing



234 **Figure S12.** DSC curves for crosslinking chromophores QLD3 before crosslinking



235

236 **Figure S13**. DSC curves for crosslinking chromophores QLD4 before crosslinking

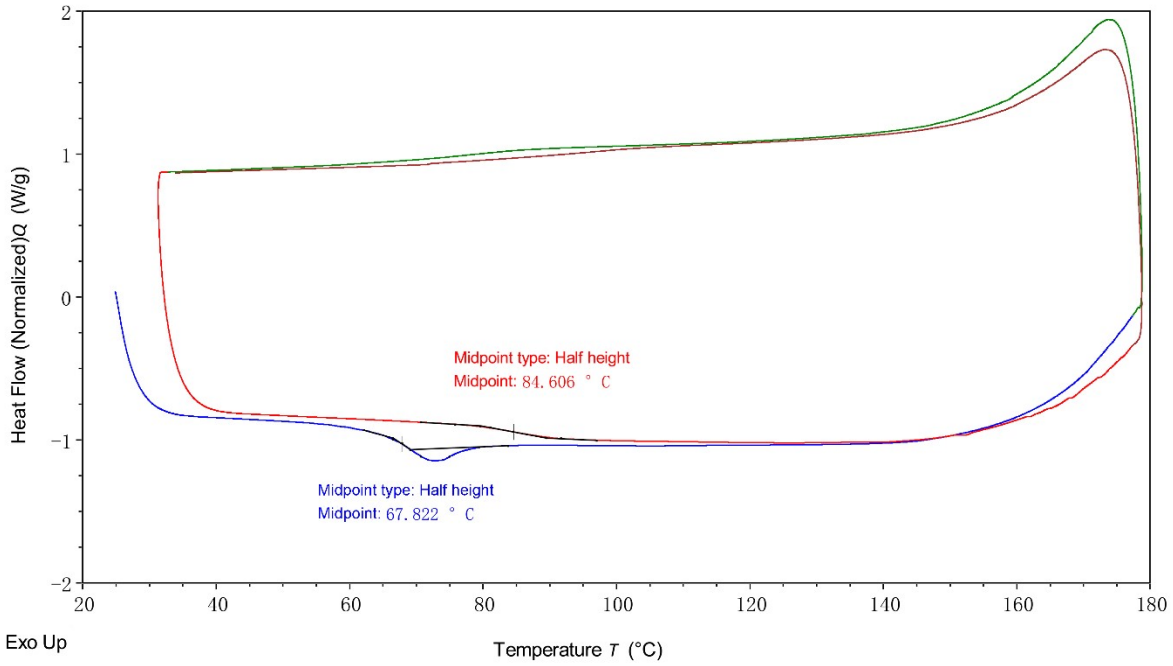


Figure S14. DSC curves for crosslinking chromophores QLD5 before crosslinking

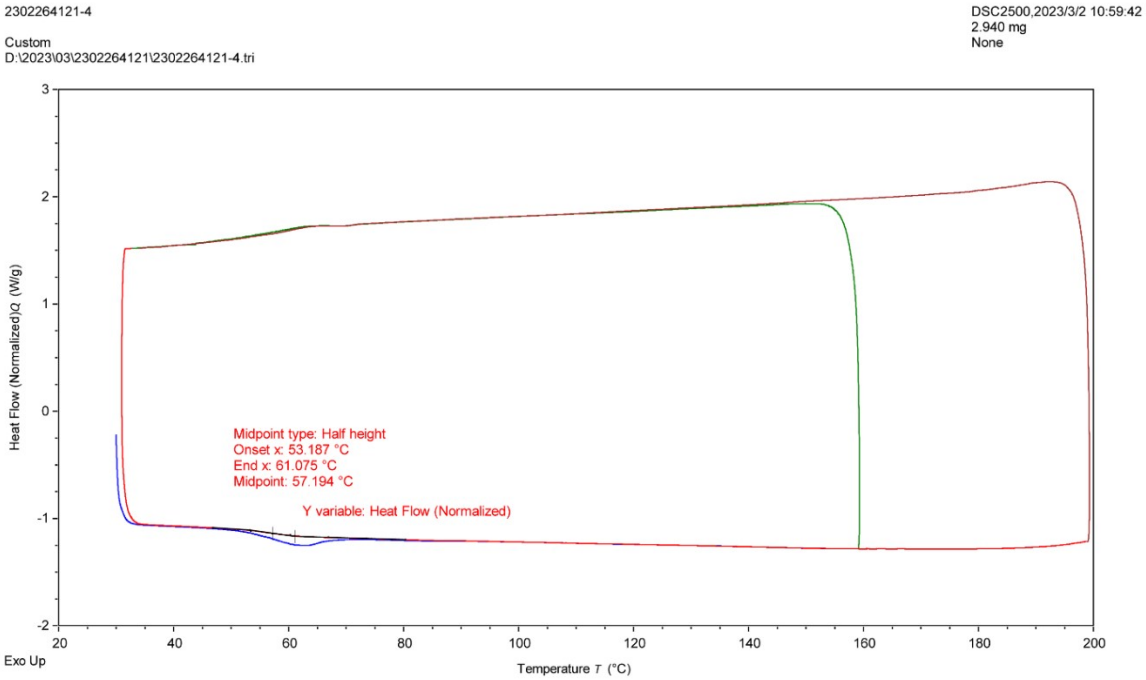


Figure S15. DSC curves for crosslinking chromophores QLD6 before crosslinking

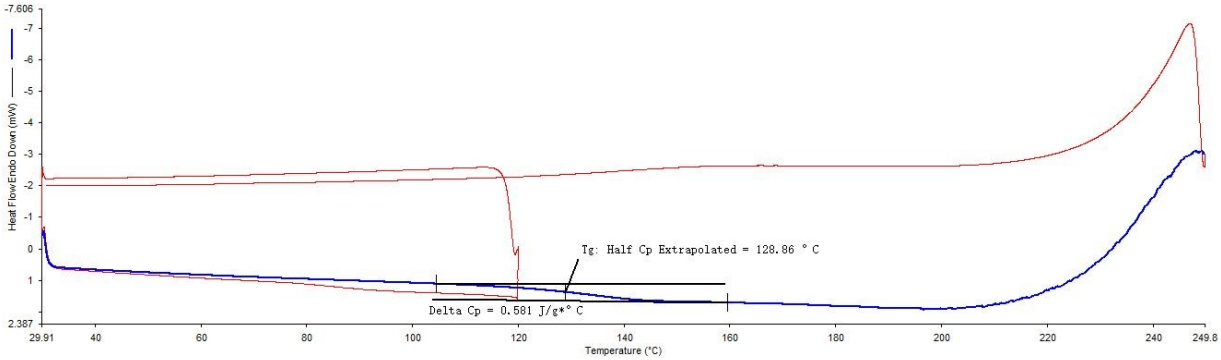


Figure S16. DSC curves for crosslinking chromophores 1：1 QLD1/QLD3 before crosslinking

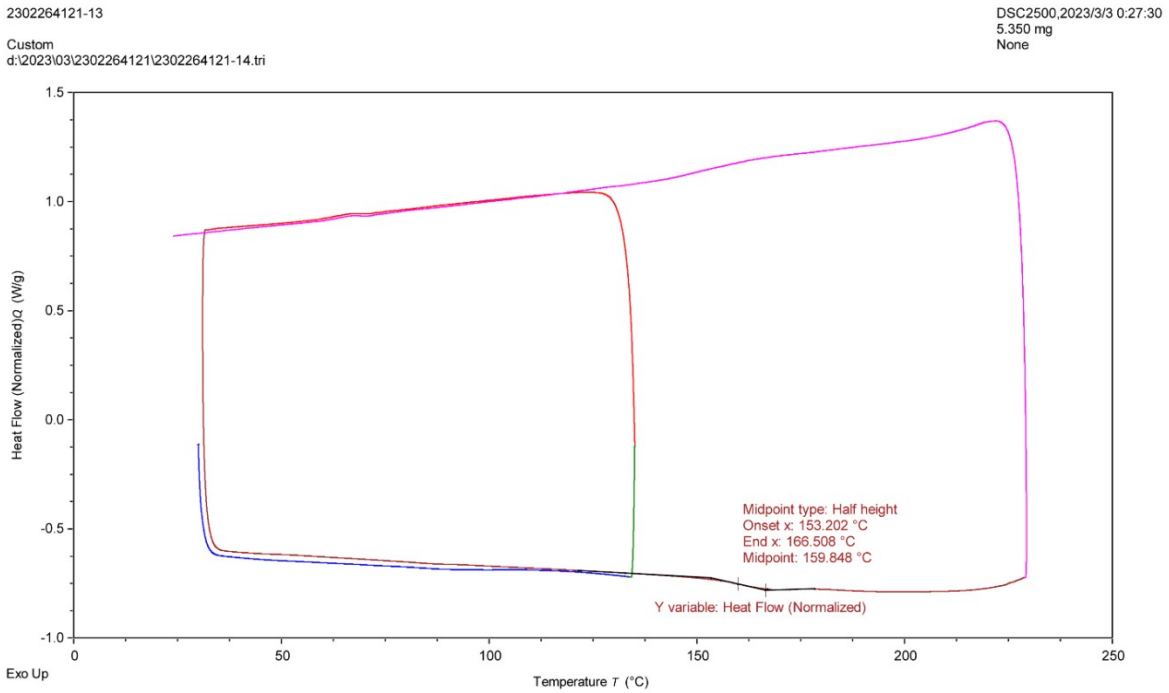
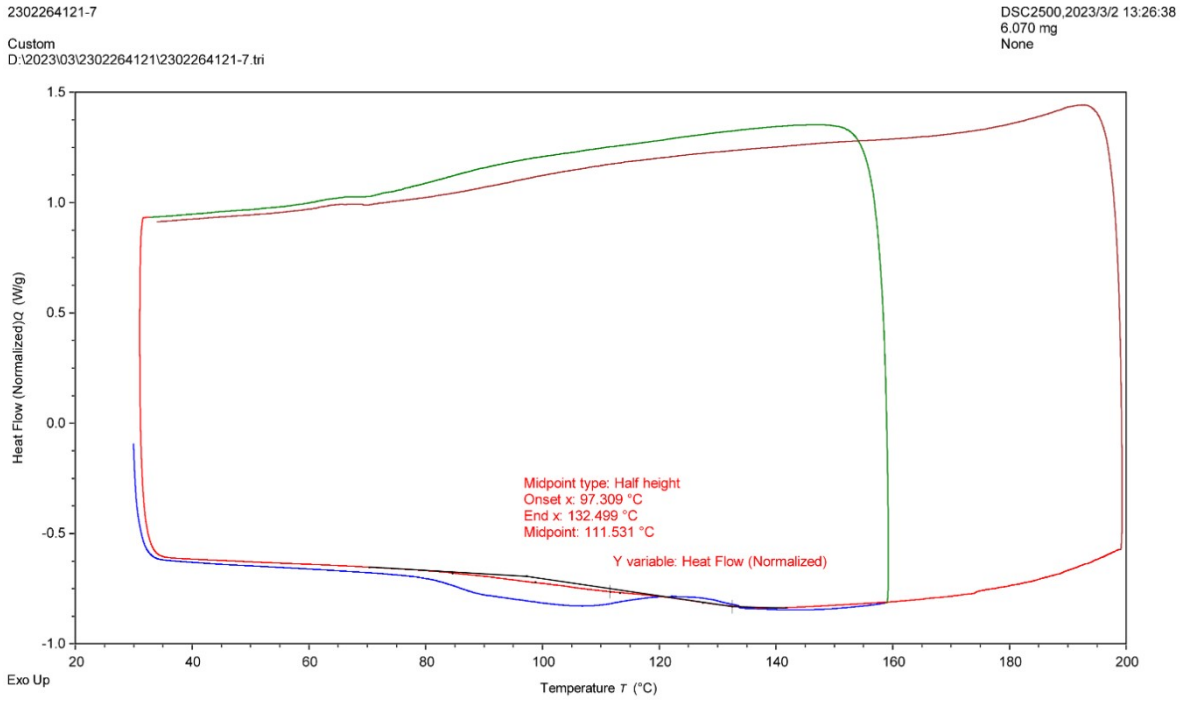
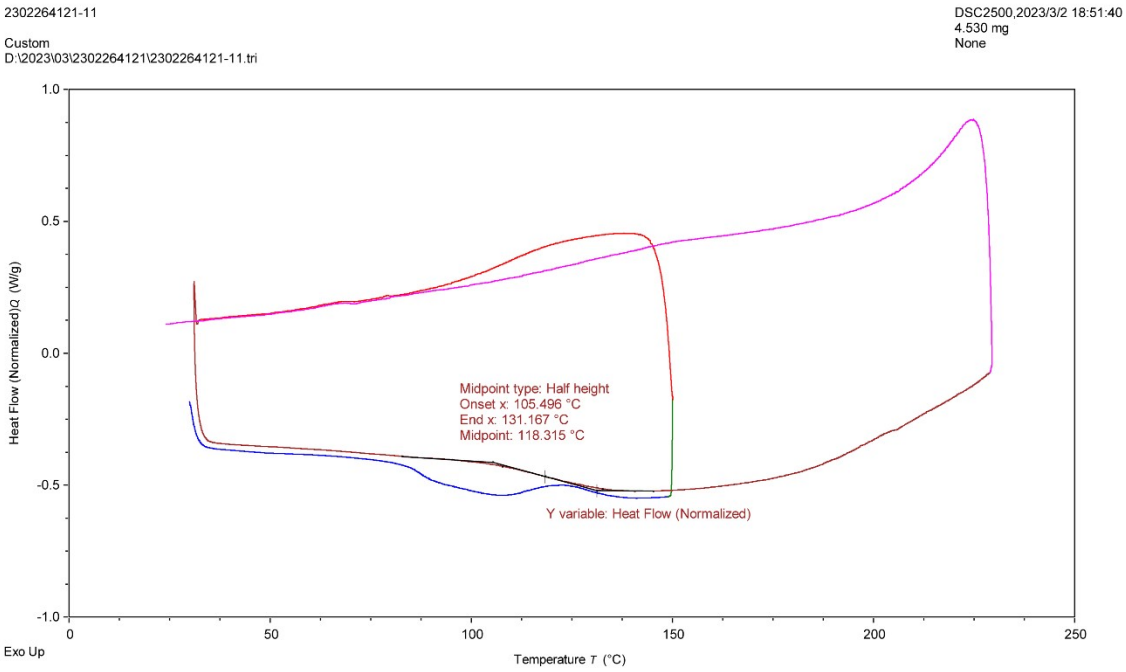


Figure S17. DSC curves for crosslinking chromophores 1：1 QLD1/QLD3 after crosslinking



252 **Figure S18**. DSC curves for crosslinking chromophores 1:1 QLD3:QLD4 before crosslinking



253

254 **Figure S19**. DSC curves for crosslinking chromophores 1:1 QLD3:QLD4 after crosslinking

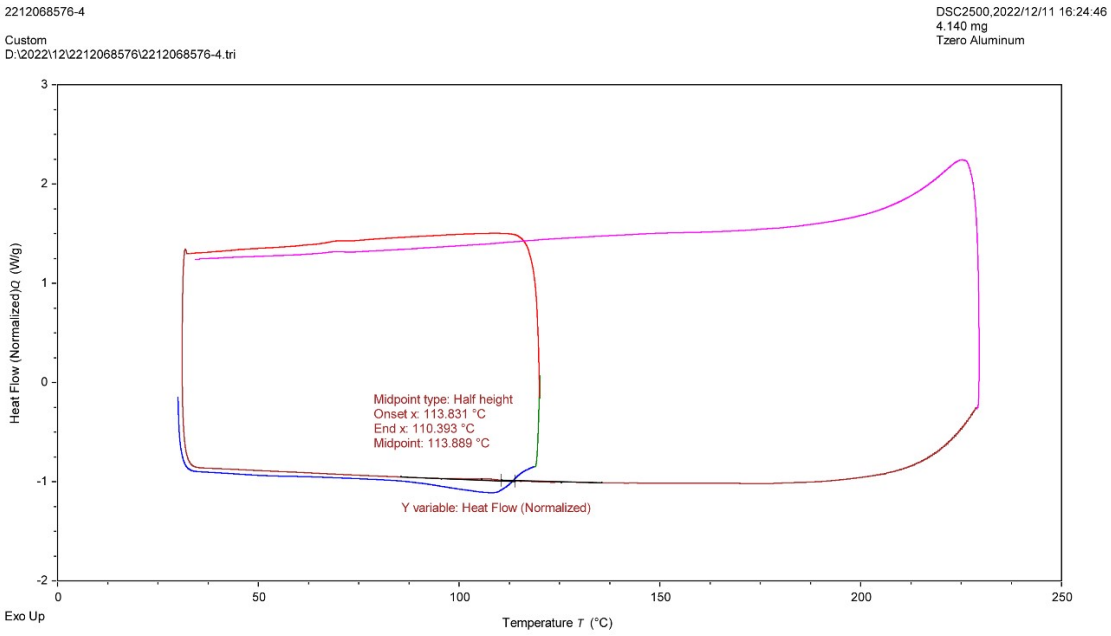


Figure S20. DSC curves for crosslinking chromophores 1:2 QLD5:QLD6 before crosslinking

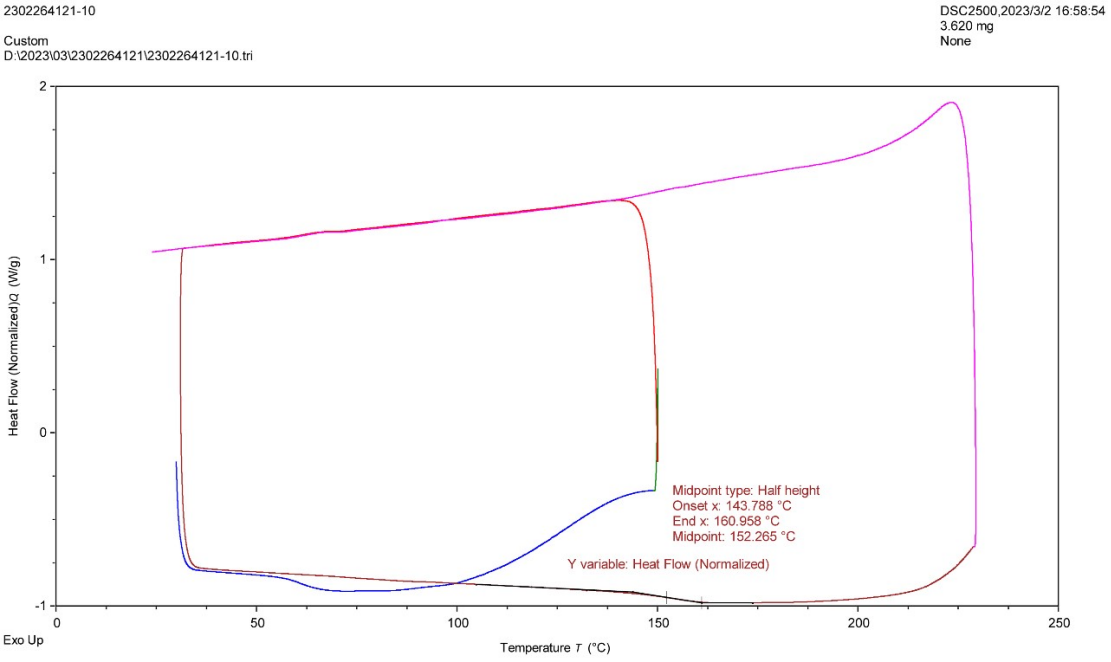


Figure S21. DSC curves for crosslinking chromophores 1:2 QLD5:QLD6 after crosslinking

6. Chemical structure and performance of HLD1-2 and QLD1-2.

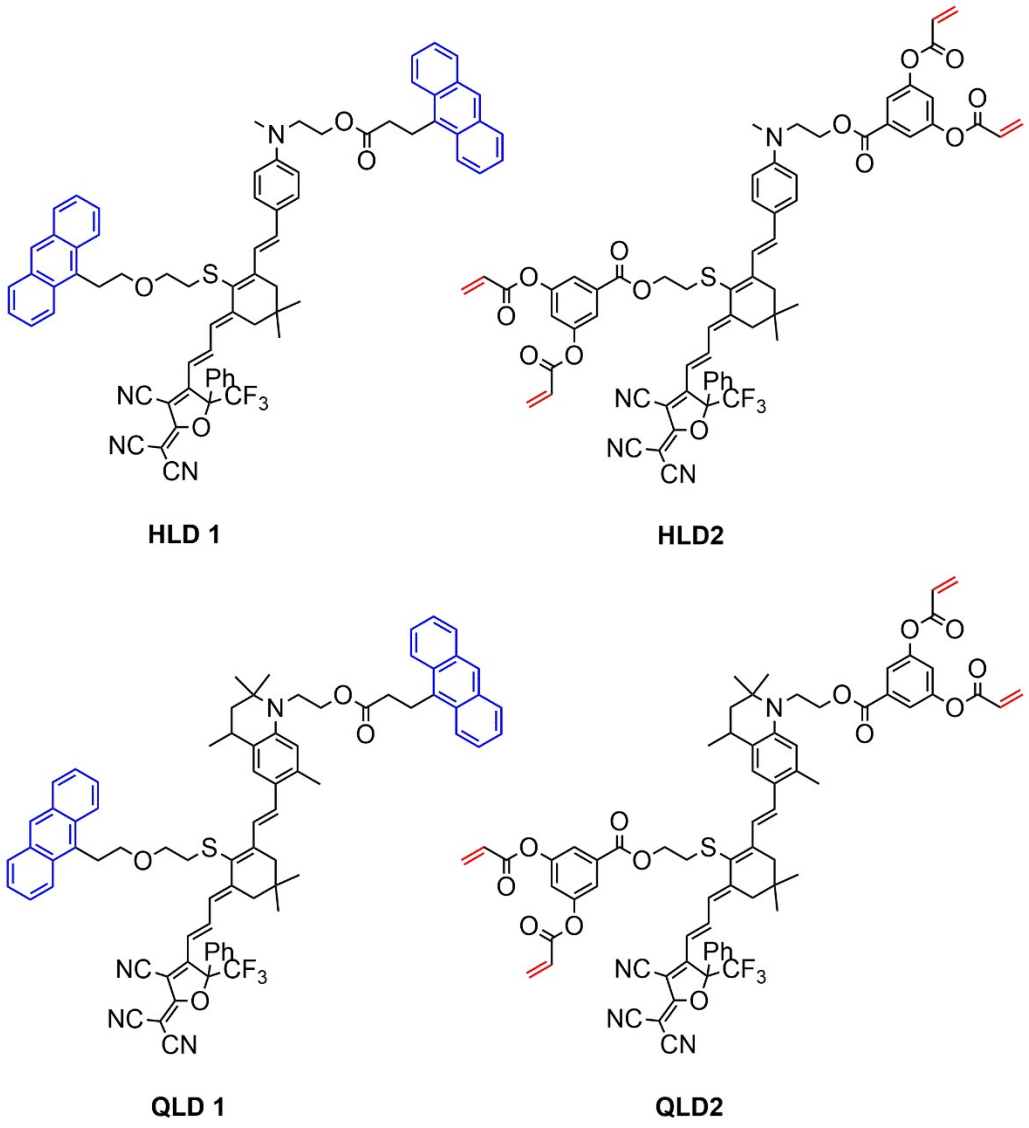


Figure S22. Chemical structure and performance of HLD1-2 and QLD1-2.

7. DFT Calculations

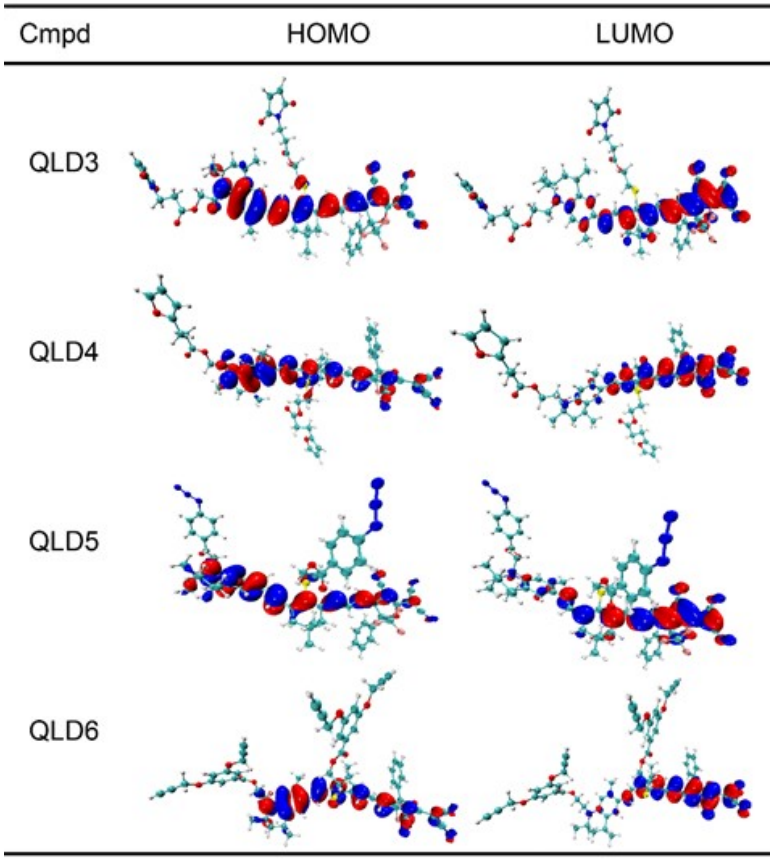


Figure S23. Chemical structures for Truncation A of chromophore QLD3-6 used in DFT calculations.

Table S1 β value of chromophores in solvent

Cmpd	tetrahydrofuran	chloroform	toluene
QLD1	3128	2715	1951
QLD2	3586	3105	2221
QLD3	3223	2793	2001
QLD4	2949	2649	2035
QLD5	3482	3059	2255
QLD6	3095	2721	2016
HLD1	2576	2234	1603
HLD2	2745	2384	1713

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

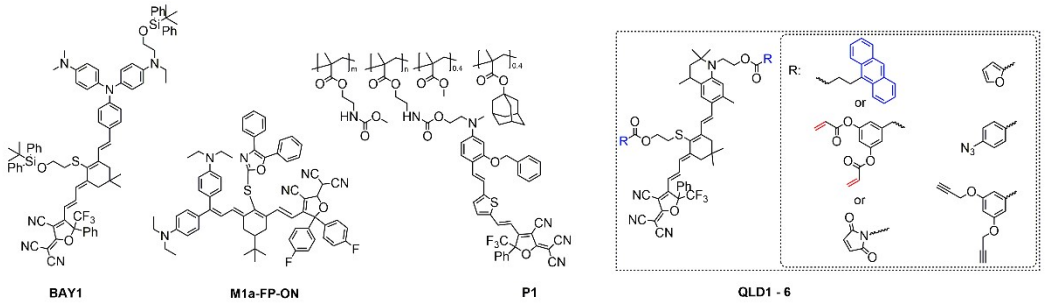


Figure S24. Chemical structures of the state-of-the-art organic EO materials.

Table S2 Properties of the state-of-the-art organic EO materials[2-4]

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
QLD1-6	205-317	128-185	1128-1188	260-351

[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 stand out in terms of the high-temperature stability and EO efficiency in a well-balanced manner.

9. Reference

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2. G.-W. Lu, J. Hong, F. Qiu, A. M. Spring, T. Kashino, J. Oshima, M.-a. Ozawa, H. Nawata and S. Yokoyama, *Nature Communications*, 2020, **11**, 4224.
3. D. Zhang, J. Zou, W. Chen, S.-M. Yiu, M.-K. Tse, J. Luo and A. K. Y. Jen, *Chemistry of Materials*, 2022, **34**, 3683-3693.
4. H. Xu, D. L. Elder, L. E. Johnson, Y. de Coene, S. R. Hammond, W. Vander Ghinst, K. Clays, L. R. Dalton and B. H. Robinson, *Advanced Materials*, 2021, **33**, 2104174.