Supporting Information

Optimization of donor, acceptor and bridge for novel organic electro-optic materials

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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 tetrahydrofura n(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 ABCD 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(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 (Tg) was measured by DSC8000(Perkin Elmer)with a heating rate of 10 °C min^{-1} under the protection of nitrogen.

2 Experimental

(1)The synthesis of A1, A3, A5, C1, D1 and acceptor was shown in the references. [1-5]

(2) Synthesis of compound 3 (Figure 2)

Imidazole (4.47 g, 65.7 mmol) and tert-butyldimethylchlorosilane (9.86 g, 65.7 mmol) were slowly added to compound 2 (10.0 g, 26.30 mmol) dissolved in 50 mL DMF under nitrogen atmosphere. React at room temperature for 3h, then pour into 100 ml water. The organic phase is extracted with ethyl acetate, washed in brine and dried in magnesium sulfate. After the solvent was removed in vacuum, the crude product was purified by silica gel chromatography and eluted with ethyl acetate/hexane (1:15 to 1:10). The oil compound 3 (15.2 g, 25.0 mmol) was obtained with a yield of 95%.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 -- 7.65 (m, 4H), 7.02 -- 6.60 (m, 4H), 3.79 (dq, J = 9.7, 4.Hz, 4H), 3.69 (dt, J = 12.7,3. Hz, 2 h), 2.91 (DDD, J = 13.0, 11.2, 2 Hz, 2 h), 2.85 (dd, J = 13.4, 10 Hz, 2 h), 2.01 (dd, J = 9.1, 4 Hz, 2 h),1.92 1.79 (m, 2 h), 1.69 1.57 (m, 2 h), 1.56 1.47 (m, 2 h), 0.93 (s, 18 h), 0.12 (d, J = 5 Hz,12H).^{13}C NMR (151 MHz, $CDCl_3$) δ 193.70, 153.32, 132.16, 127.83, 113.38, 67.36, 55.63, 47.85, 34.14, 25.85, 22.92,18.12, -4.57, -4.64.

(3)Synthesis of compound 4 (Figure 2)

Diethyl cyanomethylphosphate (16.12 mL, 26.25 g, 148.0 mmol) was slowly added to a flask containing sodium hydride (5.92 g, 148.0 mmol) and 40 mL of dried tetrahydrofuran. Compound 3 (15 g, 24.6 mmol) in THF (90 mL) was then added and the mixture was returned overnight.After the removal of THF by rotary evaporation, the residue was purified by silica gel column chromatography and eluted with ethyl acetate/hexane (1:15 to 1:10) to obtain yellow oily compound 4 (10.89 g, 17.2 mmol) with a yield of 70%.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, J= 8.Hz, 2H), 7.22 (d, J= 8.Hz, 2H), 6.91 (d, J= 8.Hz, 2H), 6.84 (d,J = 9.0 Hz, 2 h), 5.43 (s, 1 h), 3.81 (TDD, J = 13.5, 9.0, 4 Hz, 2 h), 3.76 3.68 (m, 2 h), 3.67 3.57 (m, 2 h),2.89 2.80 (m, 2 h), 2.77 (td, J = 12.3, 9. Hz, 2 h), 2.00 (td, J = 9.2, 4 Hz, 2 h), 1.84 (DDD, J = 12.5, 8.7, 3. Hz,2 h), 1.69 1.55

(m, 2 h), 1.52 1.41 (m, 2 h), 0.93 (d, J = 9 Hz, 18 h), 0.13 (dd, J = 10.0, (3) Hz,^{13}C NMR (151 MHz, $CDCl_3$) δ 171.02, 162.59, 152.33, 152.07, 131.26, 130.13, 128.83, 126.88, 119.69, 114.56,114.48, 88.46, 67.69, 67.47, 60.35, 56.13, 55.96, 48.29, 48.15, 34.12, 34.06, 29.74, 25.89, 25.85, 23.22, 22.98, 21.03,18.14, 18.11, 14.24, -4.55, -4.57, -4.60, -4.64.

(4)Synthesis of compound 5 (Figure 2)

Compound 4 (10.0 g, 15.8 mmol) was slowly added to toluene solution of diisobutylaluminum hydride (1.0 M, 31.69 mL, 31.69 mmol) at -78 ℃. After the reaction was maintained at -78℃ for 2 hours, wet silica gel (8.0 g) containing 80.0 mL H2O was added to quench the reaction. The reaction continues at 0 ℃ for 2 hours, the mixture is poured into water, extracted with ethyl acetate, and then concentrated in a vacuum. The oil compound 5 (7.04 g, 11.1 mmol) was obtained by silica gel column chromatography and elution with ethyl acetate/hexane (1:15 to 1:10), with a yield of 70.1%.^{1}H NMR (600 MHz, $CDCl_3$) δ 9.49 (d, J = 8.Hz, 1H), 7.30 (d, J = 9.0Hz, 2H), 7.21 (d, J = 8.Hz, 2H), 6.92 (d,J = 8.7 Hz, 2 h), 6.84 (d, J = 9.0 Hz, 2 h), 6.45 (d, J = 8 Hz, 1 h), 3.83 (DDD, J = 13.6, 9.0, 4 Hz, 1 h), 3.78 (DDD,J = 13.4, 9.0, 4 Hz, 1 h), 3.72 (dd, J = 12.2, 4 Hz, 2 h), 3.66 3.60 (m, 2 h), 2.91 2.82 (m, 2 h), 2.78 (DDD,J = 12.1, 9.0, 6. Hz, 2 h), 2.00 (td, J = 13.4, (3) Hz, 2 h), 1.91 1.73 (m, 2 h), 1.71 1.56 (m, 2 h), 1.47 (td, J = 16.3, 8.4, 4.1, 2. Hz, 2H), 0.92 (d, J = 10.Hz, 18H), 0.12 (dd, J = 12.8, 3. Hz, 12H). ^{13}C NMR (151 MHz,$CDCl_3$) δ 193.79, 162.91, 152.48, 151.98, 132.58, 130.65, 129.26, 126.84, 123.65, 114.58, 114.31, 67.72, 67.43, 60.38,56.28, 55.78, 48.45, 47.99, 34.07, 34.03, 25.87, 25.84, 23.14, 22.96, 21.05, 18.14, 18.11, 14.22, 4.55, 4.58, 4.62,4.65.

(5) Synthesis of compound 6 (Figure 2)

The metallic sodium (0.33 g, 13.7 mmol) was slowly dissolved in ethanol (30 mL) and added to a nitrogen-protected flask. Then 2-mercaptoethanol (1.03 g, 1.72 mL, 13.2 mmol) was added to the above solution. After the reaction at room temperature for 20 minutes,4, 4, 6-trimethyl-7-oxabicyclic [4.1.0] heptane-2-one (2.04 g, 13.2 mmol) was added.Before adding compound 5 (7.0 g, 11.0 mmol), stir the mixture at room temperature for another 1 h. After overnight reaction at 65 ℃, concentration in vacuum. The crude product was purified by column chromatography, and compound 6 (7.39 g, 9.18 mmol) was obtained at 80% yield using ethyl acetate and hexane (1:10 to 1:4) as eluents.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, J = 15.Hz, 1H), 7.24 (d, J = 8.Hz, 2H), 7.16 (d, J = 8.Hz, 2H), 7.04 (dd, J = 15.3, 11. Hz, 1 h), 6.95 (d, J = 8 Hz, 2 h), 6.81 (dd, J = 10.1, 4 Hz, 3 h), 3.84 (DDD, J = 13.7, 9.1, 4 Hz, 1 h),3.78 (DDD, J = 13.8, 9.2, 4 Hz, 1 h), 3.74 3.65 (m, 2 h), 3.62 (dd, J = 12.7, 8 Hz, 2 h), 3.59 3.53 (m, 6 h),2.83 (t, J = 5 Hz, 2 h), 2.82 2.78 (m, 3 h), 2.78 2.74 (m, 1 h), 2.74 2.67 (m, 2 h), 2.04 1.95 (m, 3 h),1.87 (DDD, J = 14.6, 7.1, 3. Hz, 1 h), 1.84 1.75 (m, 1 h), 1.73 1.58 (m, 2 h), 1.03 (s, 6 h), 0.91 (d, J = 10 Hz,18H), 0.11 (dd, J = 13.4, 2. Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.35, 196.87, 166.86, 160.24, 151.24, 151.01,149.47, 138.06, 131.98, 131.88, 130.60, 129.56, 129.50, 128.69, 127.45, 124.78, 115.18, 114.92, 67.95, 67.65, 60.36,60.29, 56.72, 56.35, 51.54, 48.82, 48.52, 48.12, 41.22, 38.87, 37.91, 34.10, 34.00, 32.65, 32.30, 28.29, 28.10, 25.88,25.86, 24.54, 23.30, 23.18, 18.17, 18.14, 4.57, 4.61, 4.63.

(6) Synthesis of compound 7 (Figure 2)

Imidazole (0.86 g, 12.6 mmol) and tert-butyldimethylchlorosilane (1.89 g, 12.6 mmol) were slowly added to compound 6 (7.0 g, 8.43 mmol) in a solution of 20 mL DMF. Continue the

reaction at room temperature for 3h, then pour into 100ml water. The organic phase is extracted with ethyl acetate, washed in brine and dried on magnesium sulfate. After the solvent was removed in vacuum, the crude product was purified by silica gel column and eluted with ethyl acetate/hexane (1:15 to 1:10) to obtain 7 (7.16 g, 7.59 mmol) oily compound with 90% yield.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, J = 15.Hz, 1H), 7.21 (d, J = 8.Hz, 2H), 7.14 (d, J = 8.Hz, 2H), 7.00 -- 6.90 (m,3 h), 6.79 (dd, J = 12.2, 10 Hz, 3 h), 3.84 (DDD, J = 13.7, 9.1, 4 Hz, 1 h), 3.77 (DDD, J = 13.7, 9.2, 4 Hz, 1 h),3.66 (dt, J = 18.5, 7 Hz, 5 h), 3.58 (dd, J = 22.7, 12 Hz, 2 h), 2.87 (2 h, t, J = 7.0 Hz), 2.83 2.78 (m, 2 h),2.70 (DDD, J = 28.9, 12.0, 9. Hz, 3 h), 2.22 (s, 2 h), 2.03 1.93 (m, 2 h), 1.90 1.82 (m, 1 h), 1.82 1.76 (m, 1 h),1.72 1.56 (m, 2 h), 1.50 1.37 (m, 2 h), 1.00 (d, J = 5 Hz, 6 h), 0.90 (dd, J = 9.8, 5 Hz, 6 h), 0.10 (dd, J = 13.0,3. Hz, 27H), 0.04 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.67, 195.28, 163.50, 157.46, 151.06, 150.87, 148.26, 136.46,132.25, 131.82, 131.32, 129.70, 129.39, 129.24, 128.72, 125.03, 115.23, 115.00, 67.92, 67.64, 62.87, 62.82, 56.79,56.44, 52.01, 51.81, 48.87, 48.59, 48.02, 41.18, 36.40, 35.72, 34.12, 34.03, 32.60, 32.21, 28.30, 28.12, 26.90, 25.98,25.92, 25.90, 25.89, 25.77, 24.48, 23.29, 23.18, 18.31, 18.28, 18.14, 18.11, 18.02, 3.45, 4.51, 4.54, 4.59, 4.61,-5.17, -5.21.

(7) Synthesis of compound 8 (Figure 2)

Diethyl cyanomethyl phosphate (6.98 mL, 7.89 g, 44.4 mmol) was slowly added to a flask containing sodium hydride (1.77 g, 44.4 mmol) and 20 mL dry THF was added under nitrogen protection. Compound 7 (7.0 g, 7.41 mmol) dissolved in THF (40 mL) was then added and the mixture was returned overnight. After removal of THF in vacuum, the residue was purified directly by silica gel column chromatography and eluted with ethyl acetate/hexane (1:15 to 1:10) to obtain yellow oily compound 8 (4.81 g, 4.94 mmol) at 65% yield.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, J= 15.Hz, 1H), 7.21 (d, J= 8.Hz, 2H), 7.14 (d, J= 8.Hz, 2H), 7.00 -- 6.90 (m,3 h), 6.79 (dd, J = 12.2, 10 Hz, 3 h), the delta 6.26 (s, 1 h), 3.84 (DDD, J = 13.7, 9.1, 4 Hz, 1 h), 3.77 (DDD, J = 13.7, 9.2,4. Hz, 1 h), 3.66 (dt, J = 18.5, 7 Hz, 5 h), 3.58 (dd, J = 22.7, 12 Hz, 2 h), 2.87 (2 h, t, J = 7.0 Hz), 2.83 2.78 (m,2 h), 2.70 (DDD, J = 28.9, 12.0, 9. Hz, 3 h), 2.22 (s, 2 h), 2.03 1.93 (m, 2 h), 1.90 1.82 (m, 1 h), 1.82 1.76 (m,1 h), 1.72 1.56 (m, 2 h), 1.50 1.37 (m, 2 h), 1.00 (d, J = 5 Hz, 6 h), 0.90 (dd, J = 9.8, 5 Hz, 6 h), 0.10 (dd,J = 13.0, 3. Hz, 27H),0.04 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.38, 157.91, 153.80, 150.97, 150.79, 149.05,146.80,134.26, 132.61, 131.91, 131.77, 129.95, 129.24, 126.87, 125.42, 125.02, 119.23, 118.72, 115.32, 115.13, 95.05, 94.98,68.03, 67.75, 62.27, 62.24, 56.87, 56.57, 48.96, 48.73, 48.20, 43.49, 43.45, 41.47, 37.85, 36.78, 34.13, 34.04, 30.63,30.12, 27.96, 27.81, 27.78, 25.93, 25.89, 25.88, 24.34, 23.40, 23.28, 18.35, 18.32, 18.18, 18.16, 4.53, 4.57, 4.60,-4.63, -5.22, -5.27.

(8) Synthesis of compound 9 (Figure 2)

Compound 8 (4.0 g, 4.13 mmol) was slowly added to diisobutylaluminum hydride in hexane (1.0 M, 8.27 mL, 8.48 mmol) under nitrogen. After the reaction was maintained at -78 ℃ for 2 hours, wet silica gel (4.0 g) containing 40.0 mL H2O was added. The reaction continues at 0 ℃ for 2 hours, the mixture is poured into water, extracted with ethyl acetate, and then concentrated in a vacuum.The residue was purified by silica gel column chromatography and eluted with ethyl acetate/hexane (1:15 to 1:10) to obtain oil compound 9 (2.80 g, 2.89 mmol) with a yield of 70.1%.^{1}H NMR (600 MHz, $CDCl_3$) δ 10.14 (d, J = 8.0Hz, 1H), 7.69 (d, J = 14.Hz, 1H), 7.25 (d, J = 8.Hz, 2H), 7.18 (d,J = 8 Hz, 2 h), 6.99 (dd, J = 28.1, 8 Hz, 3 h), 6.90 6.78 (m, 4 h), 3.87 (DDD, J

= 13.7, 9.1, 4 Hz, 1 h), 3.81 (DDD,J = 13.8, 9.2, 4 Hz, 1 h), 3.76 3.65 (m, 4 h), 3.61 (dd, J = 25.7, 12 Hz, 2 h), 2.87 2.57 (m, 8 h), 2.35 2.19 (m,2 h), 2.10 1.95 (m, 2 h), 1.88 (DDD, J = 14.6, 7.2, 3. Hz, 1 h), 1.85 1.77 (m, 1 h), 1.76 1.57 (m, 2 h),1.54 1.42 (m, 2 h), 0.99 (s, 6 h), 0.93 (dd, J = 15.8, 8 Hz, 27 h), 0.13 (dd, J = 13.7, (3) Hz, 12 h), 0.08 (s,6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 191.71, 191.40, 156.27, 150.95, 150.77, 150.01, 146.80, 134.17, 132.65, 132.62,131.81, 130.00, 129.26, 129.24, 127.17, 125.58, 115.31, 115.12, 68.00, 67.72, 62.49, 56.90, 56.58, 48.94, 48.71,48.20, 41.52, 39.92, 39.77, 37.61, 34.16, 34.08, 30.54, 29.99, 28.28, 28.09, 26.95, 26.00, 25.94, 25.93, 25.80, 24.88,23.37, 23.26, 18.36, 18.33, 18.18, 18.16, 4.47, 4.51, 4.54, 4.57, 5.15, 5.19.

(9) Synthesis of chromophore B1

Compound 9 was prepared in a dry double necked flask under nitrogen protection. After adding the receptor, it was refluxed with ethanol as the solvent at 65 ℃ for 3 hours. After spin drying, it was purified twice in a silica gel column with ethyl acetate/petroleum ether (2:1), yielding a blue-green product (0.30 g, 0.26 mmol) with a yield of 70.8%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (t, 1H, J=14.) CH), 7.71 (d, J=15.0 Hz, 1H), 7.53 (d, J=12 Hz, 1H, 7.27-7.24 (m, 2H, ArH), 7.20-7.15 (m, 2H, ArH), 6.97 (s, 1H), 6.97-6.92 (m, 2H, ArH), 6.87-6.84 (d, 2H, J=2.7Hz, ArH), 6.83 (s, 1H, CH), 6.39 (d, 1H, J=14 Hz CH, 3.86 (m, 1H, OCH), 3.80 (m, 1H, OCH), 3.76-3.68 (m, 4H, NCH), 3.63 (m, 2H, OCH_2), 2.86-2.79 (m, 2H, SCH_2), 2.78-2.69 (m, 4H, NCH_2), 2.46 (s, 2H, CH_2), 2.33 (s, 2H, CH_2), 2.08-1.96 (m, 2H, CH_2), 1.94-1.80 (m, 2H, CH_2), 1.71 (s, 6H), CH_3), 1.47 (m, 2H, CH2), 1.34-1.25 (m, 2H, CH2), 0.98 (s, 6H, CH_3), 0.94 (s, 9H, CH_3), 0.93 (s, 18H, CH_3), 0.14 (s, 6H, CH_3), 0.12 (d, 6H, CH_3), 0.10 (s, 6H, CH_3), 0.08 (s, 6H, CH_3) ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.19, 173.28, 154.30, 151.57, 151.13, 150.95, 148.31, 144.65, 135.88, 132.74, 132.29, 131.94, 130.69, 129.72, 129.53, 128.27, 125

(10) Synthesis of chromophore B3

Compound 9 was prepared in a dry double necked flask under nitrogen protection. After adding the receptor, it was refluxed with ethanol as the solvent at 65 ℃ for 3 hours. After spin drying, it was purified twice in a silica gel column with ethyl acetate/petroleum ether (2:1), yielding a blue-green product (0.42 g, 0.33 mmol) with a yield of 67.8%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.77-7.67 (m, 1H), 7.56 (q, J=1 Hz, 1H), 7.54 (d, J=3 Hz, 1H, 7.53 (d, J=5.0 Hz, 2H), 7.51-7.49 (m, 1H), 7.26 (d, J=8 Hz, 2H), 7.18 (d, J=8 Hz, 2H, 7.02 (dd, J=15.2, 11.5 Hz, 1H), 6.96 (d, J=8 Hz, 2H, 6.88-6.80 (m, 3H), 6.56-6.46 (m, 1H), 3.86 (tt, J=9.1, 4 Hz, 1H), 3.80 (tt, J=9.1, 4 Hz, 1H), 3.76-3.67 (m, 4H), 3.67-3.59 (m, 2H), 2.89-2.81 (m, 2H), 2.82-2.74 (m, 2H), 2.71 (t, J=6 Hz, 2H), 2.31 (d, J=4 Hz, 2H), 2.02 (ddt, J=20.0, 12.8, 4 Hz, 2H), 1.87 (ddt, J=37.2, 13.4, 3 Hz, 2H, 1.53-1.43 (m, 2H), 1.28 (s, 4H), 0.94 (d, J=3 Hz, 12H), 0.92 (s, 9H), 0.90 (s, 9H), 0.86 (s, 3H), 0.14 (s, 6H), 0.12 (d, J=2.7 Hz, 6H), 0.06 (d, J=2 Hz, 6H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.68, 162.49, 157.75, 153.96, 151.35, 151.14, 150.01, 147.13, 137.79, 132.71, 132.11, 13

(11) Synthesis of chromophore B5

Compound 9 was prepared in a dry double necked flask under nitrogen protection. After adding the receptor, it was refluxed with ethanol as the solvent at 65 ℃ for 3 hours. After spin drying, it was purified twice in a silica gel column with ethyl acetate/petroleum ether (2:1), yielding a blue-green product (0.38 g, 0.29 mmol) with a yield of 67.8%. ^{1}H NMR (600 MHz,

$CDCl_3$) δ 7.76 (s, 1H, CH), 7.69 (d, 1H, J=15.0 Hz, CH), 7.46 (d, 1H, J=12 Hz, CH), 7.28-7.22 (m, 2H, CH), 7.20-7.14 (m, 2H, ArH), 7.02-6.93 (m, 3H, ArH), 6.87-6.80 (m, 3H, ArH), 6.38 (d, 1H, J=14 Hz, CH), 3.86 (m, 1H, J=9.1, 4 Hz, OCH), 3.79 (m, 1H, OCH), 3.75-3.67 (m, 4H, NCH_2), 3.67-3.59 (m, 2H, NCH_2), 2.87-2.80 (m, 2H, NCH_2), 2.79-2.72 (m, 2H, SCH_2), 2.70 (t, 2H, J=6 Hz, OCH_2), 2.32 (s, 2H), 2.19 (s, 2H, CH_2), 2.06-1.97 (m, 2H, CH_2), 1.93-1.80 (m, 2H, CH_2), 1.75-1.63 (m, 2H, CH_2), 1.60 (s, 3H, CH_3), 1.52-1.42 (m, 2H, CH_2), 0.97 (s, 3H, CH_3), 0.94 (s, 9H, CH_3), 0.92 (s, 9H, CH_3), 0.90 (s, 9H, CH_3), 0.80 (s, 9H, CH_3), 8 (s, 3H, CH_3), 0.14 (s, 6H, CH_3), 0.11 (s, 6H, CH_3), 0.06 (s, 6H, CH_3) ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.62, 169.47, 155.82, 152.91, 151.26, 151.05, 149.33, 144.73, 137.01, 132.63, 132.04, 132.02, 130.82, 129.70, 1

(12) Synthesis of compound 2a (Figure 4)

Under the protection of argon gas, 9-aldehyde-8-hydroxy-1,1,7,7-tetramethyljiuluonidine (2.73 g, 10 mmol) and tert butyl (2-chloroethoxy) dimethylsilane (2.92 g, 15 mmol) were mixed and dissolved in 90 mL of dichloromethane before being added to a double necked flask. Anhydrous potassium carbonate (2.4 g, 15 mmol) was then injected into the flask. Mix at 90 ℃ for 12 hours and then pour into water. The organic phase was extracted with ethyl acetate and then dried with magnesium sulfate. The crude product was purified by silica gel chromatography after solvent removal under reduced pressure. It was eluted with a solution of acetone to n-hexane at a ratio of 1:10 to obtain a yellow solid compound 2a (3.91 g, 9.07 mmol) with a yield of 90.7%. MS (MALDI) (M^+, $C_{25}H_{41}NO_3$ Si): calcd: 431.29 found: 431.36; ^1H NMR (300 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.58 (s, 1H), 4.06-3.99 (m, 4H), 3.32-3.26 (m, 2H), 3.25-3.20 (m, 2H), 1.74-1.57 (m, 4H), 1.44 (s, 6H), 1.26 (s, 6H), 0.91 (s, 9H), 0.11 (m, 6H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.72, 161.44, 148.29, 126.10125.73, 120.91, 117.04, 79.10, 62.48, 47.49, 47.45, 46.86, 46.83, 39.38, 35.69, 32.56, 32.04, 29.87, 26.03, 25.90, 18.37, − 5.12

(13) Synthesis of compound 3a (Figure 4)

Under the protection of argon gas, lithium perchlorate (3.19 g, 30 mmol) and compound 1b (6.47 g, 18 mmol) were added to the two-mouth flask, and compound 2a (6.47 g, 15 mmol) was slowly dissolved in 30 ml of tetrahydrofuran and injected into the flask.Then N, n-dimethyltrimethylsilamine (5.25 g, 30 mmol) was added. The solution was stirred overnight at room temperature, then concentrated with a rotary evaporator, extracted three times with 70mL ethyl acetate, and dried in vacuum with machine layer. The solution of ethyl acetate and petroleum ether was 1:10 to 1:6 as eluent, and the crude product was purified by silica gel column. The red viscous compound 3a (7.92g, 11.75mmol) was obtained with a yield of 78%.MS (MALDI)(M^+, $C_{44}H_{55}NO_3Si$): calcd: 674.01;found: 674.13. ^1H NMR(600 MHz, $CDCl_3$) 7.95 (d, J = 7.Hz, 2H, ArH), 7.76 (d, J = 7.6Hz, 2H, ArH), 7.61-7.55 (m, 2H,ArH), 7.52 7.42 (m, 3 h, ArH, CH), 7.30 (d, J = 16 Hz, 1 h, CH), 7.06 (d, J = 16 Hz, 1 h, CH), 6.65 (s, 1 h, ArH),3.98 3.94 (m, 4 h, OCH_2), 3.44 (t, J = 4.6 Hz, 2 h, NCH_2), 3.36 (t, J = 4 Hz, 2 h, NCH_2), 3.22 (s, 2 h, CH_2), 3.01 (s, 2 h,CH_2), 1.96 1.85 (m, 4 h, CH_2), 1.60 (s, 6 h and CH_3), 1.50 (s, 6 h and CH_3), 1.02 (s, 9 h and CH_3), 0.12 (s, 6 h,CH_3).^{13}C NMR (126 MHz, $CDCl_3$) d 198.08, 156.76, 156.53, 150.18, 144.19, 139.33, 133.33,127.80, 127.54, 126.61,125.53, 123.52, 123.30, 123.13, 122.16, 120.02, 116.20, 75.80, 62.12, 50.78, 47.21, 46.68, 46.49, 39.81,36.24,35.50, 32.55, 32.10, 30.84, 29.98, 25.77, 18.24, 5.55.

(14) Synthesis of compound 4a (Figure 4)

In argon protection, sodium hydride (0.8 g, 20.0 mmol) was added to a two-mouth flask and placed at 0 degrees. After cooling, diethyl cyanomethyl phosphate (3.54 g, 20.0 mmol) and 30 mL tetrahydrofuran were slowly added into the flask. After the reaction, 10 mL tetrahydrofuran and compound 3a (2.76 g, 5.0mmol) were added to the solution and stirred at 66 ℃ overnight. Then concentrated in a rotary evaporator and extracted three times with 70 mL ethyl acetate; The bonded organic layer is dried in a vacuum.Using ethyl acetate and petroleum ether (1:15 ~ 1:10) as eluents, the crude product was purified by silica gel column. Compound 4a (2.78 g, 4.0 mmol) was obtained, and the product was red oil with a yield of 79%.MS (MALDI) (M^+, $C_{46}H_{56}N_2O_2Si$): calcd: 697.05;found: 697.15. 1H NMR (600 MHz, $CDCl_3$) 7.95 (d, J = 7.Hz,2H, ArH), 7.64 (d, J = 7.Hz,2H, ArH), 7.61 -- 7.56 (m, 3H, ArH,CH), 7.53 7.46 (m, 2 h, ArH), 7.35 (s, 1 h, ArH), 7.17 (d, J = 16 Hz, 2 h, CH), 5.01 (s, 1 h, CH), 4.02 3.96 (m, 4 h,OCH_2), 3.42 (t, J = 4 Hz, 2 h, NCH_2), 3.34 (t, J = 4 Hz, 2 h, NCH_2), 3.11 (s, 2 h, CH_2), 2.88 (s, 2 h, CH_2), 1.99 1.88 (m,4H, CH_2), 1.62 (s, 6H,CH_3), 1.56 (s, 6H,CH_3), 1.03 (s, 9H, CH_3), 0.12 (s, 6H,CH_3). ^{13}C NMR (126 MHz,$CDCl_3$) d 156.39, 156.04, 150.01, 146.32, 143.45, 139.29, 129.68, 127.60,127.38, 126.55, 124.61, 123.24,122.55, 121.99, 119.75, 117.55,116.74, 91.16, 75.36, 62.02, 48.72, 47.09, 46.55, 40.42, 39.86, 36.32,34.83,34.45, 32.39, 32.00, 30.93, 29.98, 25.64, 25.07, 18.06, 5.68.

(15) Synthesis of compound 5a (Figure 4)

Under the protection of argon, diisobutyl aluminum hydride solution in n-hexane (2.72 mL, 4.0 mmol) was slowly added to compound 4a (1.15 g, 2.0 mmol) and 20.0 mL ultra-dry toluene in a cooling solution at -78 ℃. And the reaction continues at this temperature for 2 hours. When the reaction is over, slowly add 10 mL of water to quench the reaction. After the reaction continues at 0℃ for 2 hours, the solution is poured into water, extracted with methylene chloride, and then concentrated in vacuum. The crude product was eluted by silica gel column chromatography with ethyl acetate ratio of petroleum ether 1:8 to 1:5, and the red solid compound 5a(0.84 g, 1.46 mmol) was obtained by spin distillation with a yield of 73%.MS (MALDI) (M^+, $C_{36}H_{55}NO_3Si$): calcd: 577.93;found: 577.83. ^1H NMR (600 MHz, $CDCl_3$) 10.04 (d, J = 8.Hz, 1H, CHO), 7.31 -- 7.18 (m, 1H, CH), 7.09 -- 6.91 (m, 1H, CH),6.78 6.61 (m, 1 h, CH), 6.30 (s, 1 h, ArH), 5.91 (d, J = 8 Hz, 1 h), 4.01 (t, J = 5 Hz, 2 h, OCH_2), 3.90 (t, J = 5 Hz,OCH_2, 2 h), 3.20 3.16 (m, 2 h, NCH_2), 3.13 3.10 (m, 2 h, NCH_2), 2.68 (s, 2 h, CH_2), 2.36 (s, 2 h, CH_2), 1.79 1.65 (m, 4 h, CH_2),1.43 (s, 6H,CH_3), 1.29 (s, 6H,CH_3), 1.06 (s, 6H,CH_3), 0.94 (s, 9H, CH_3), 0.14 (s, 6H,CH_3). ^{13}C NMR (126 MHz,$CDCl_3$) d 190.46, 157.14,156.09, 147.31, 147.16, 143.53, 129.06, 127.47, 126.73, 125.88, 125.79, 125.64, 123.76, 122.76,122.32, 120.32, 117.30, 75.51, 62.49, 47.32, 46.80, 40.11, 39.24, 38.91, 36.55, 32.68, 32.22, 31.17, 31.13, 31.07,30.23, 28.38,28.24, 25.96, 18.44, 5.19.

(16) Synthesis of chromophore C3

Compound 9 (0.40 g, 0.5 mmol) and receptor Ph-3F-TCF (0.19 g, 0.6 mmol) were added to a three necked flask and placed in a vacuum drying oven for 1 hour. Add 10mL of ethanol to dissolve the solid, then heat it in a microwave reactor to 65 ℃ and reflux for 1 hour. The crude product was concentrated by rotary evaporation and purified by silica gel on a chromatographic column. It was eluted with a solution of petroleum ether to ethyl acetate in a ratio of 1:10 to 1:1 to obtain a green solid chromophore C3 (0.29 g, 0.26 mmol) with a yield of 52%. HRMS (ESI) ($[M^+H]^+$, $C_{68}H_{73}F_3N_5O_2SSi$): calcd: 1108.5206 found: 1108.5210; ^1HNMR (600 MHz, Acetone) δ 7.93 (s, J=13.) Hz, 1H, CH), 7.77 (d, J=14 Hz, 1H, CH), 7.73-7.71 (m, 2H, ArH), 7.68-7.66 (m,

4H, ArH), 7.61-7.59 (m, 3H, ArH), 7.55 (d, J=13 Hz, 1H, CH), 7.46-7.41 (m, 2H, ArH), 7.38 (m, 4H, ArH, CH), 7.32-7.28 (m, 1H, ArH), 7.26 (d, J=8 Hz, 4H, ArH), 6.95 (d, J=12.0 Hz, 1H, CH), 6.81 (d, J=8 Hz, 4H, ArH), 6.51 (d, J=13 Hz, 1H, CH), 3.83-3.72 (m, 2H, OCH_2), 3.61-3.49 (m, 8H, NCH_2), 2.81 (t, J=6 Hz, 2H, SCH_2), 2.36 (s, 2H, CH_2), 2.34-2.21 (m, 2H, CH_2), 1.23 (t, J=7.0 Hz, 12H, CH_3), 1.05 (s, 9H, CH_3), 0.88 (s, 3H, CH_3), 0.80 (s, 3H, CH_3) ^{13}C NMR (151 MHz, Acetone) δ 175.33, 156.68, 149.06, 143.75, 142.11, 134.84, 132.86, 132.29, 130.82, 130

(17) Synthesis of chromophore C5

Add compound 9 (0.40 g, 0.5 mmol) and receptor ArF-TCF (0.21 g, 0.6 mmol) to a three necked flask and place them in a vacuum drying oven for 1 hour. Add 10mL of ethanol to dissolve the solid, then heat it in a microwave reactor to 65 ℃ and reflux for 1 hour. The crude product was concentrated by rotary evaporation and purified by silica gel on a chromatographic column. It was eluted with a solution of petroleum ether to ethyl acetate in a ratio of 1:10 to 1:1 to obtain a green solid chromophore C5 (0.36 g, 0.32 mmol) with a yield of 64%. HRMS (ESI) ($[M^+H]^+$, $C_{68}H_{71}F_5N_5O_2SSi$): calcd: 1144.5018 found: 1144.5016; ^1H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J=6 Hz, 1H, ArH), 7.57-7.49 (m, 6H, ArH), 7.35 (d, J=12 Hz, 1H, CH), 7.30 (d, J=7 Hz, 2H, ArH), 7.27-7.24 (m, 3H, ArH, CH), 7.16 (d, J=10 Hz, 2H, ArH), 7.07 (d, J=8.0 Hz, 2H, ArH), 7.03-6.98 (m, 1H, CH), 6.66 (d, J=11 Hz, 1H, CH), 6.63 (d, J=8 Hz, 2H, ArH), 6.51 (d, J=8 Hz, 2H, ArH), 6.14 (d, J=14 Hz, 1H, CH), 3.63 (t, J=6 Hz, 2H, OCH_2), 3.41-3.30 (m, 8H, NCH_2), 2.64 (t, J=6 Hz, 2H, SCH_2), 2.22 (s, 2H, CH_2), 2.03 (s, 2H, CH_2), 1.18-1.10 (m, 15H, CH_3), 0.96 (s, 9H, CH_3), 0.82 (s, 3H, CH_3), 0.75 (s, 3H, CH_3) ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.85, 168.08, 155.98, 153.41, 150.94, 147.43, 147.10, 145.83, 143.87, 14

(18) Synthesis of chromophore D3

Compound 5a (0.58 g, 1 mmol) and Ph-3F-TCF (0.42 g, 1.2 mmol) receptors were added to a three-mouth flask and vacuum dried in a vacuum drying oven for 1 hour. After the solid was dissolved by adding 10mL of ethanol, it was heated to 65 ℃ using a microwave reactor and reflow for 1 hour. The crude product was purified on the chromatographic column by spinning concentration and silica gel. The green solid chromophore D3 (0.49 g, 0.48 mmol) was obtained by elution with a ratio of ethyl acetate to ethane of 1:6 to 1:4. The yield was 48%.HRMS (ESI) ($[M^+ H]^+$, $C_{62}H_{64}F_3N_4O_3Si$):calcd: 997.4700 found:997.4705;^1H NMR (600 MHz, Acetone) δ 7.90 (d, J = 7.Hz, 2H, ArH), 7.69 (d, J = 14.Hz, 2H, CH), 7.59 -- 7.53 (m, 3H, ArH),7.48 (d, J = 7.Hz, 1H, ArH), 7.45 -- 7.40 (m, 4H, ArH), 7.41 -- 7.35 (m, 2H, ArH, CH), 7.34 -- 7.18 (m, 3H, ArH, CH),7.02 (d, J = 23 Hz, 1 h, CH), 6.62 (d, J = 10 Hz, 1 h, ArH), 6.30 (d, J = 12 Hz, 1 h, CH), 3.88 3.80 (m, 4 h, OCH_2),3.47 (d, J = 47.Hz, 4H, NCH_2), 2.86 (s, 4H, CH_2), 1.76 -- 1.72 (m, 4H, CH_2), 1.37 -- 1.25 (m, 12H, CH_3), 0.78 (s, 9H,CH_3), -0.11 (s, 6H, CH_3).^{13}C NMR (151 MHz, Acetone) δ 175.69, 150.68, 150.59, 139.64, 139.61, 131.68, 130.76, 129.26, 127.94, 127.92,127.64, 127.57, 126.56, 123.55, 120.14, 120.11, 113.68, 113.16, 112.57, 77.04, 62.23, 59.66, 49.25, 47.95, 47.28,38.74, 35.85, 35.19, 32.41, 32.00, 29.35, 29.26, 29.22, 29.10, 28.97, 28.84, 28.71, 28.58, 25.38, 18.05,-6.09.

(19) Synthesis of chromophore D5

Compound 5a (0.58 g, 1 mmol) and acceptor ArF-TCF (0.38 g, 1.2 mmol) were added into a three-mouth flask and vacuum dried for 1 hour in a vacuum drying oven. After the solid was

dissolved by adding 10 mL of ethanol, it was heated to 65 ℃ using a microwave reactor and reflow for 1 hour. The crude product was purified on the chromatographic column by spinning concentration and silica gel. Then the chromophore D5 (0.7 g, 0.68 mmol) with a yield of 68% was obtained by elution with ethyl acetate ratio of 1:6 to 1:4 of ethane.HRMS (ESI) ([M^+ H]$^+$, $C_{62}H_{62}F_5N_4O_3Si$):calcd: 1033.4511 found:1033.4508.;^{1}H NMR (600 MHz,$CDCl_3$) δ 7.68 (d, J = 6.Hz, 2H, ArH), 7.32 -- 7.26 (m, 3H, ArH), 7.21 -- 7.15 (m, 2H, ArH),7.10 (d,J = 5.Hz, 2H, ArH), 7.02 -- 6.78 (m, 3H, CH), 6.68 (s, 1H, CH), 6.36 (d, J = 11.Hz, 1H, CH), 6.20 (d, J = 12.Hz,1H, CH), 3.67 (s, 4H, NCH_2), 3.18 (s, 2H, OCH_2), 3.09 (s, 2H, OCH_2), 2.91-2.57 (m, 4H, CH_2), 1.93 (d, J = 21.0Hz,3H, CH_3), 1.64 -- 1.58 (m, 4H, CH_2), 1.25 -- 1.16 (m, 9H, CH_3), 0.67 (s, 12H, CH_3), -0.23 (s, 6H, CH_3). ^{13}C NMR (126 MHz,$CDCl_3$) δ 174.58, 170.04, 167.98, 156.50, 154.25, 149.22, 149.02, 144.15, 142.21, 138.59, 138.42, 132.26,129.08, 126.99, 126.89, 126.63, 126.53, 126.21, 123.83, 122.23, 121.44, 119.17, 119.10, 115.97, 113.44,111.23, 110.49, 92.58, 92.26, 75.28, 61.20, 54.65, 47.98,46.48, 45.92, 38.63, 35.24, 35.03, 34.64, 31.61,31.18, 29.55, 28.86, 24.82, 17.32, -6.50.

3. NMR pictures

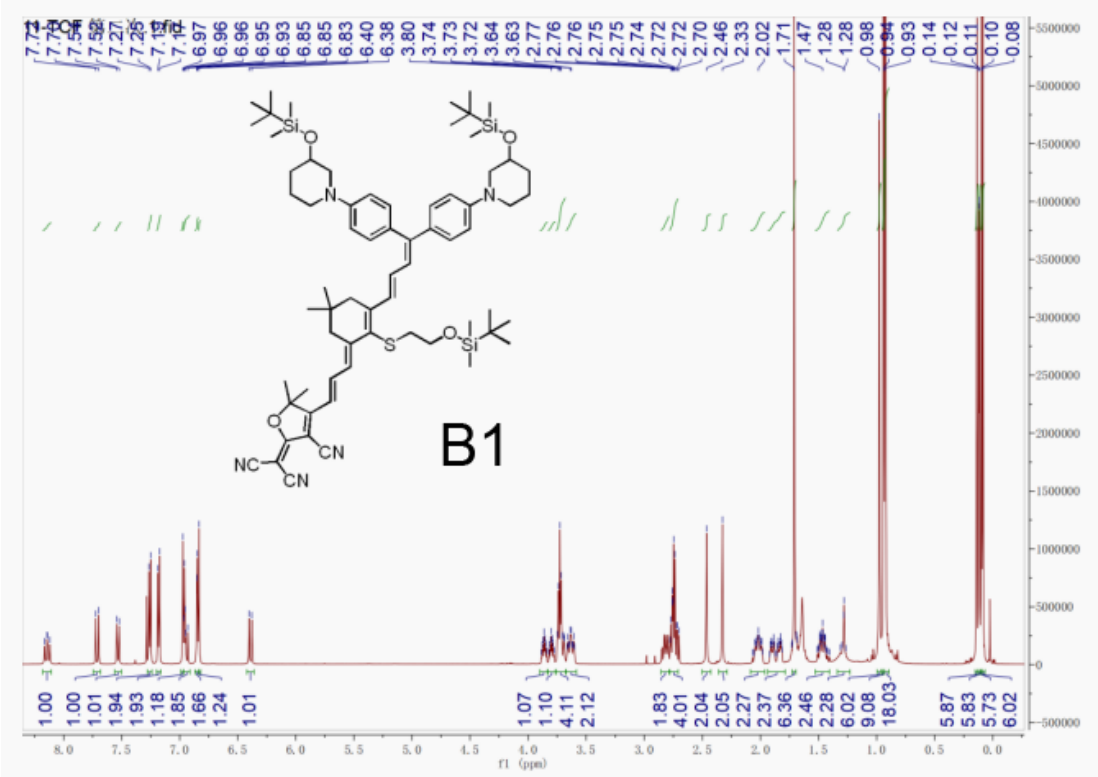


Figure S1. ^{1}H-NMR spectrum of Chromophore B1

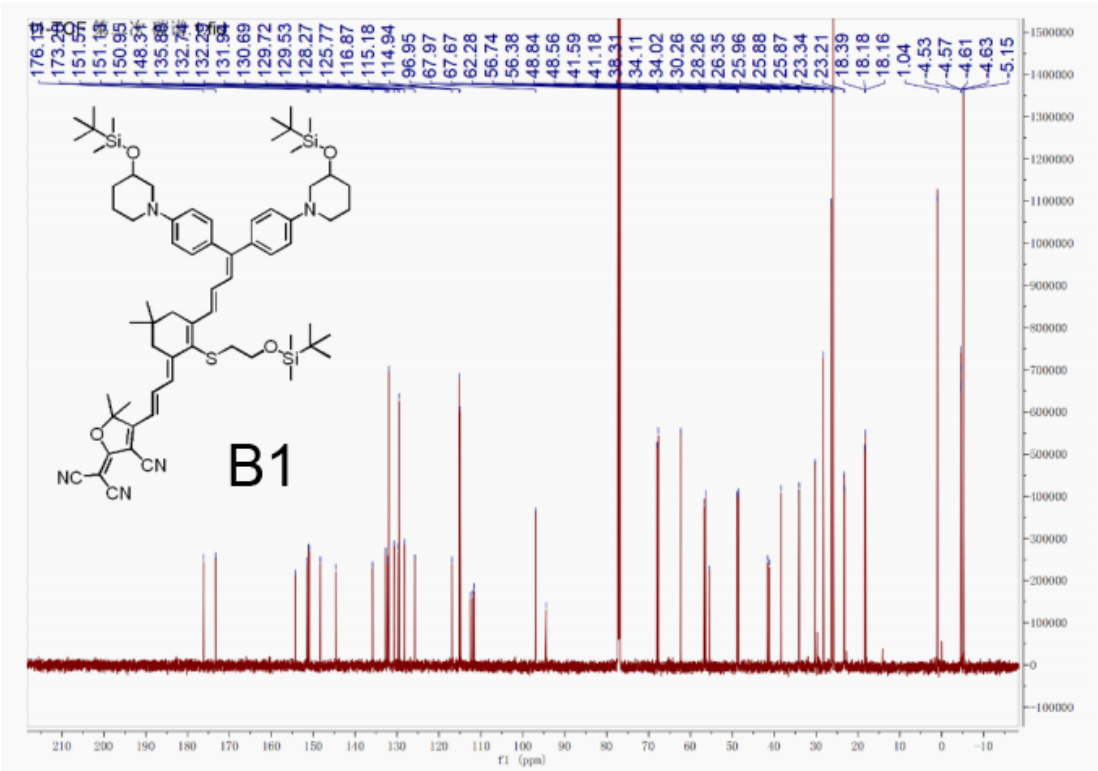


Figure S2. ^{13}C-NMR spectrum of Chromophore B1

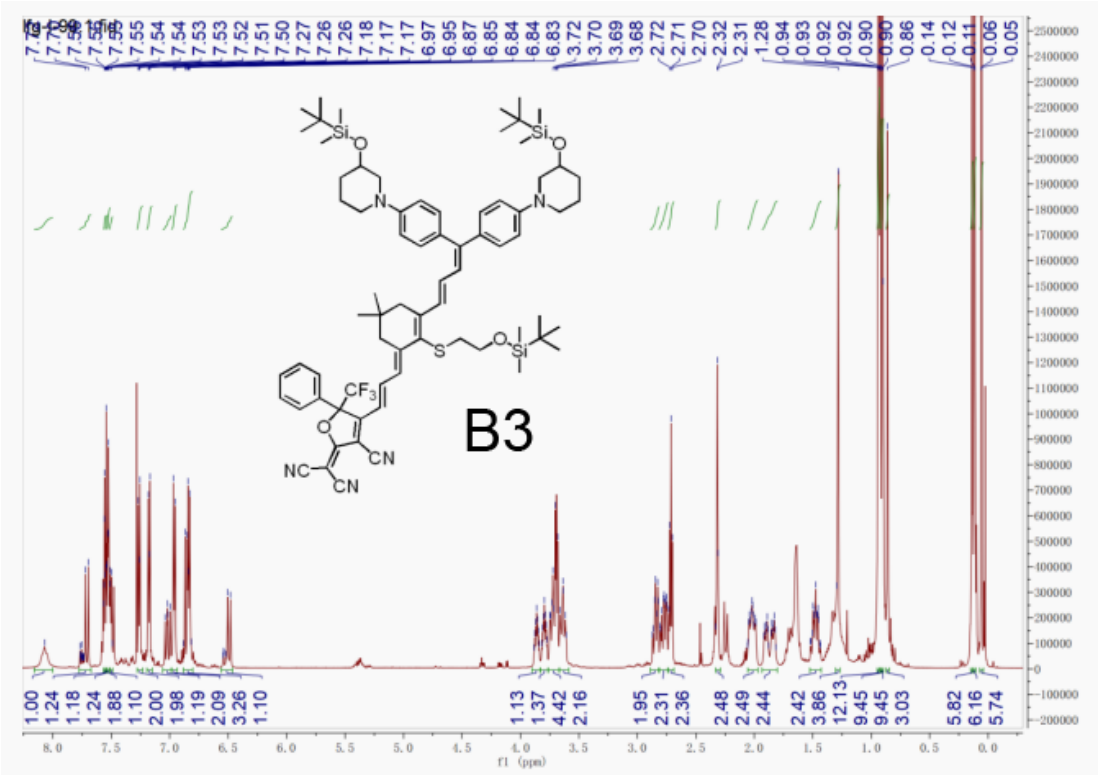


Figure S3. ^{1}H-NMR spectrum of Chromophore B3

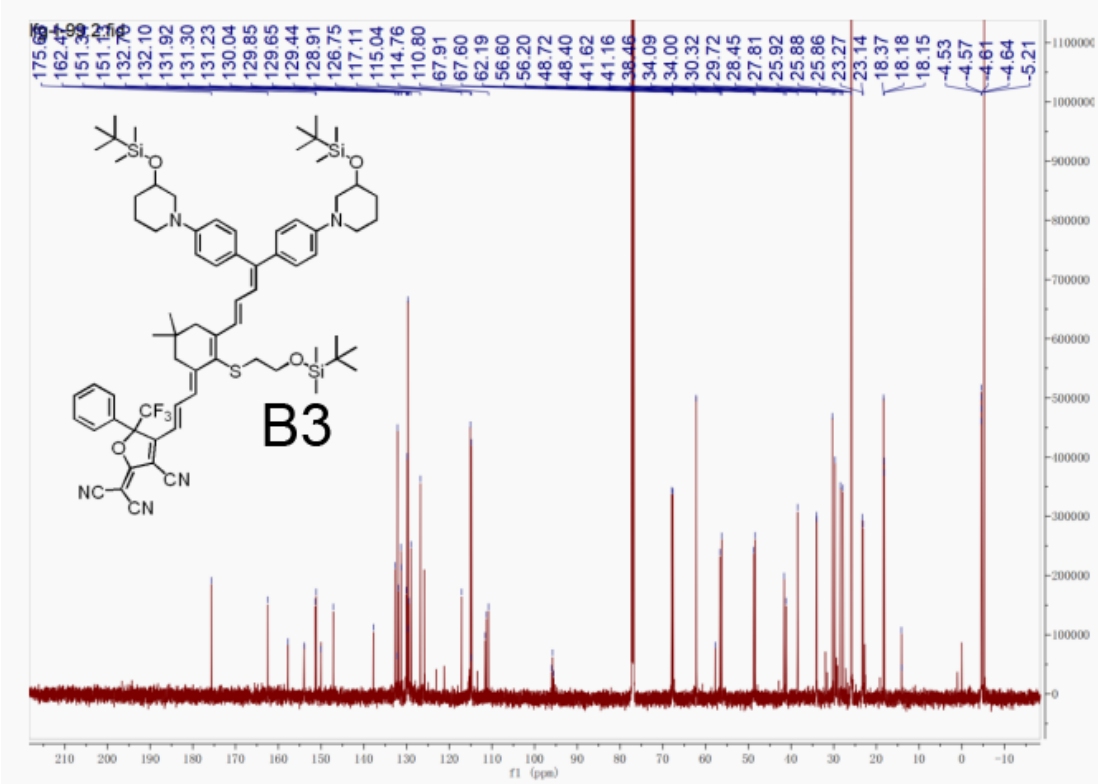


Figure S4. ^{13}C-NMR spectrum of Chromophore B3

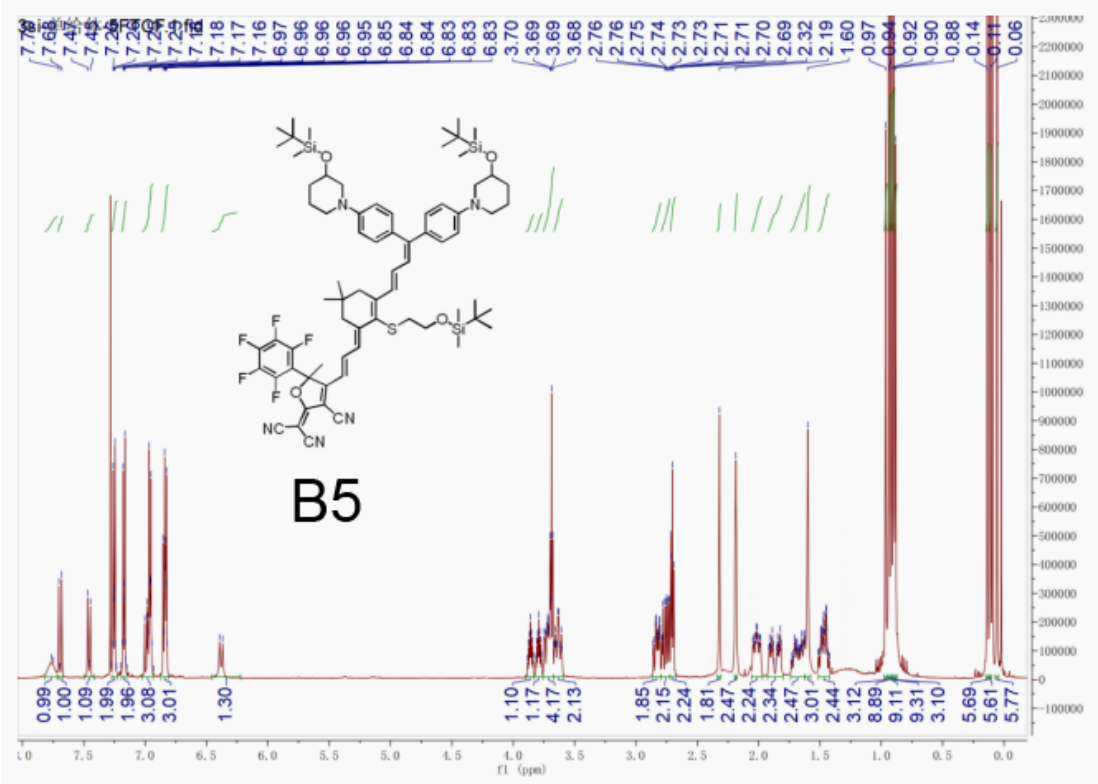


Figure S5. ^{1}H-NMR spectrum of Chromophore B5

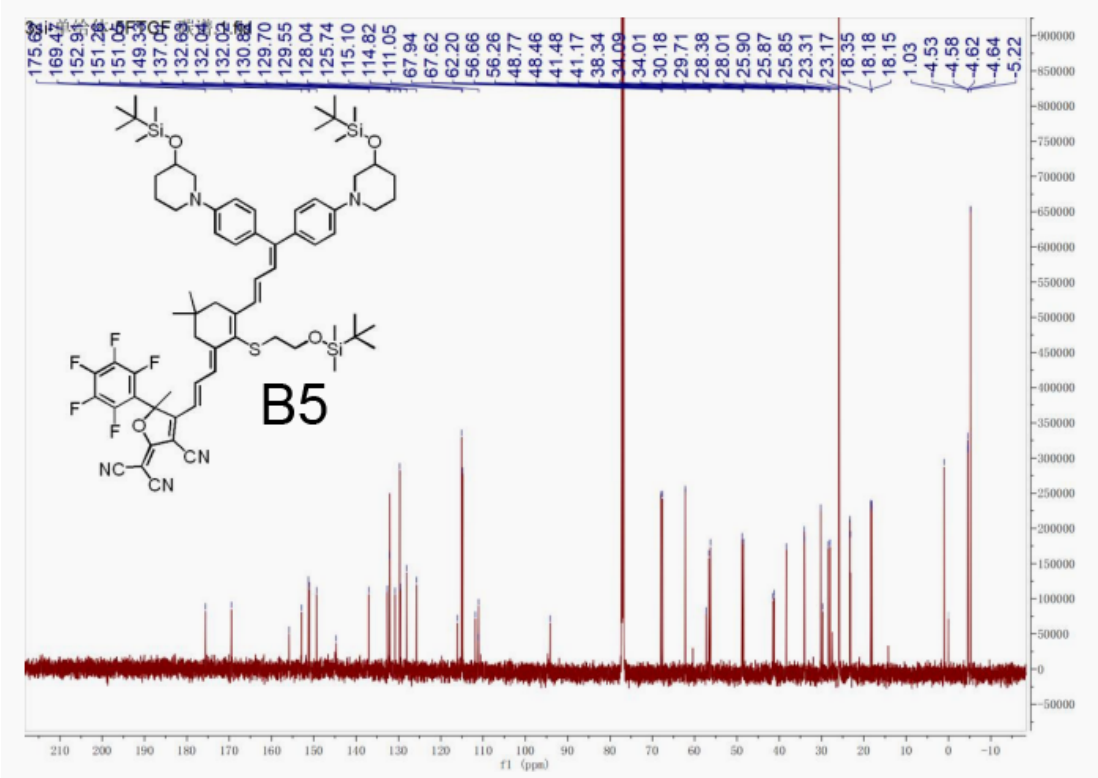


Figure S6. ^{13}C-NMR spectrum of Chromophore B5

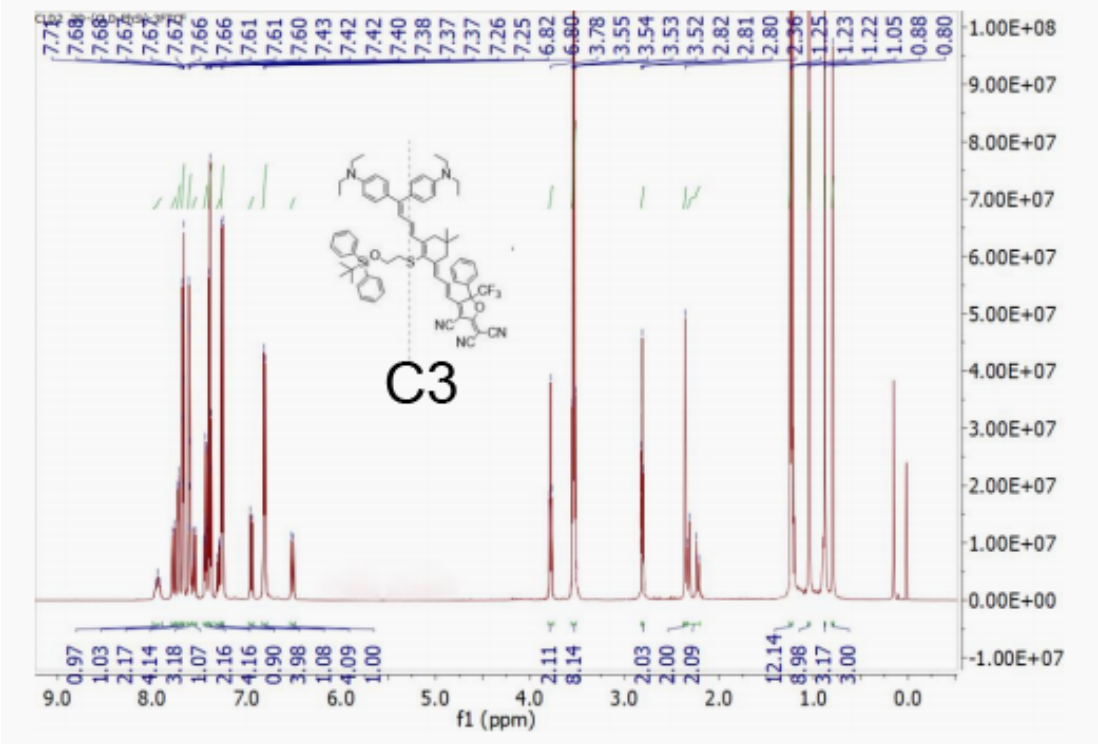


Figure S7. ^{1}H-NMR spectrum of Chromophore C3

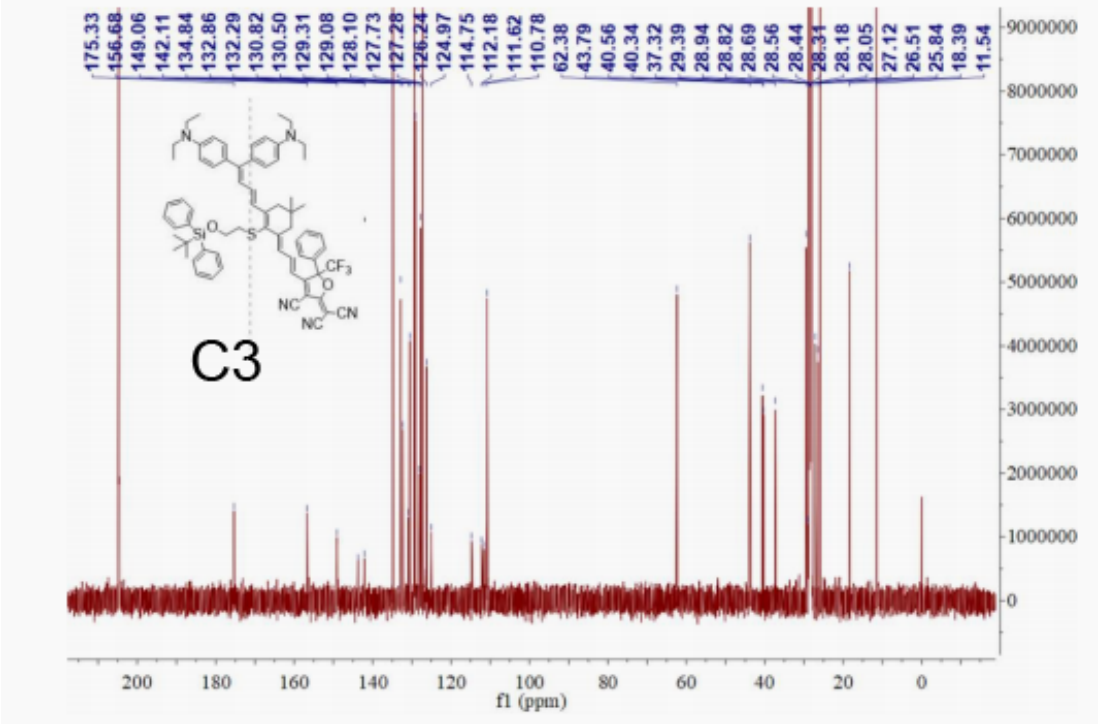


Figure S8. ^{13}C-NMR spectrum of Chromophore C3

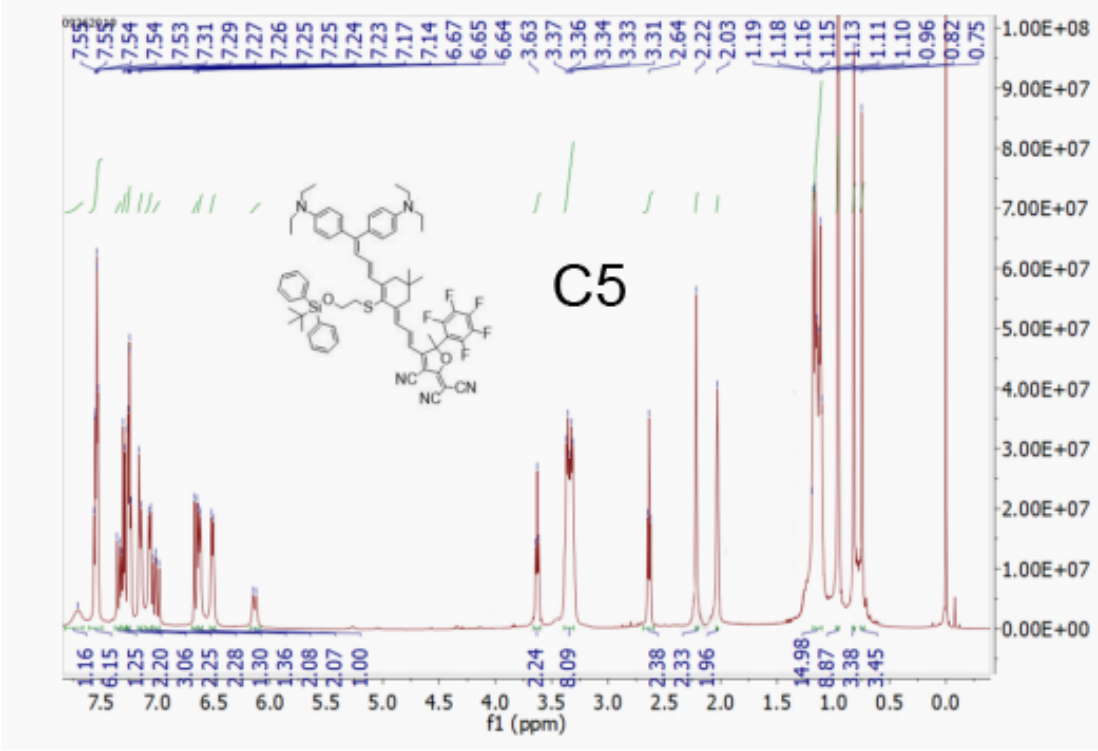


Figure S9. ^{1}H-NMR spectrum of Chromophore C5

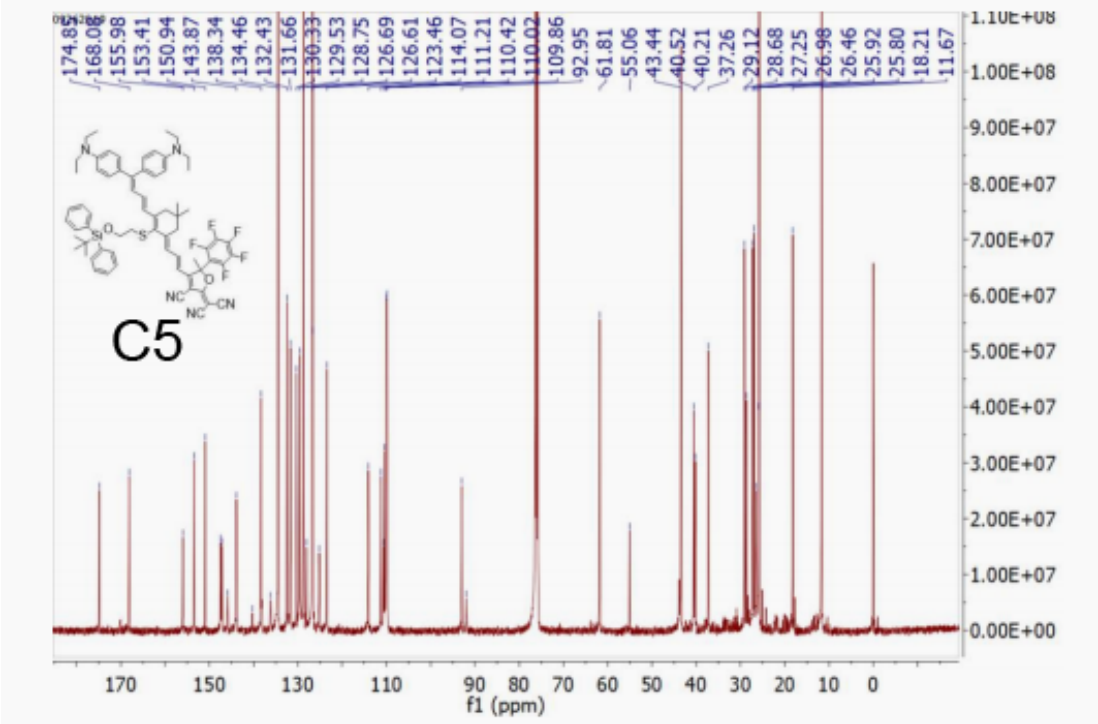


Figure S10. ^{13}C-NMR spectrum of Chromophore C5

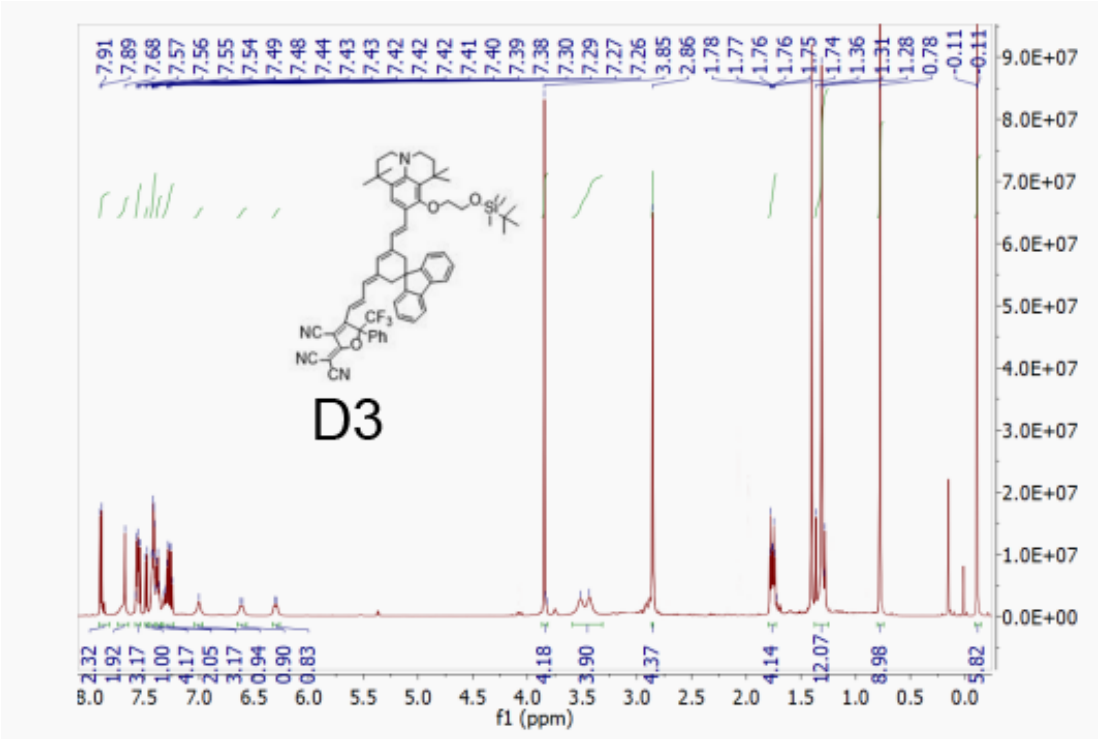


Figure S11. ^{1}H-NMR spectrum of Chromophore D3

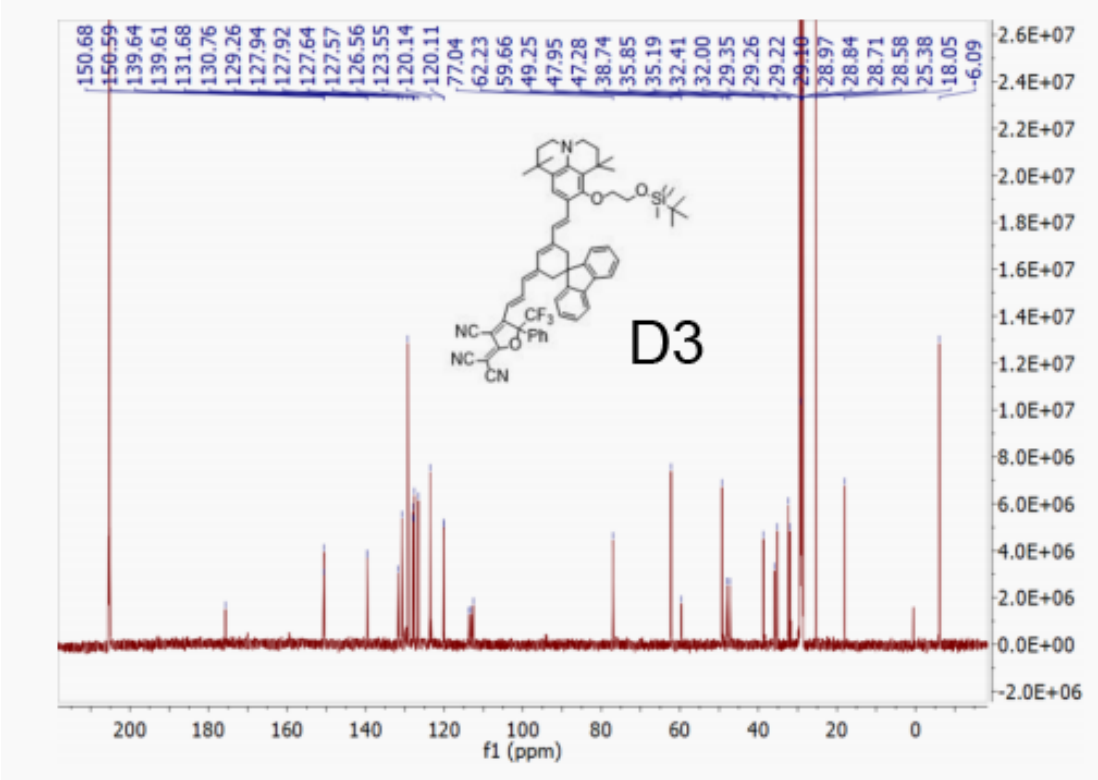


Figure S12. ^{13}C-NMR spectrum of Chromophore D3

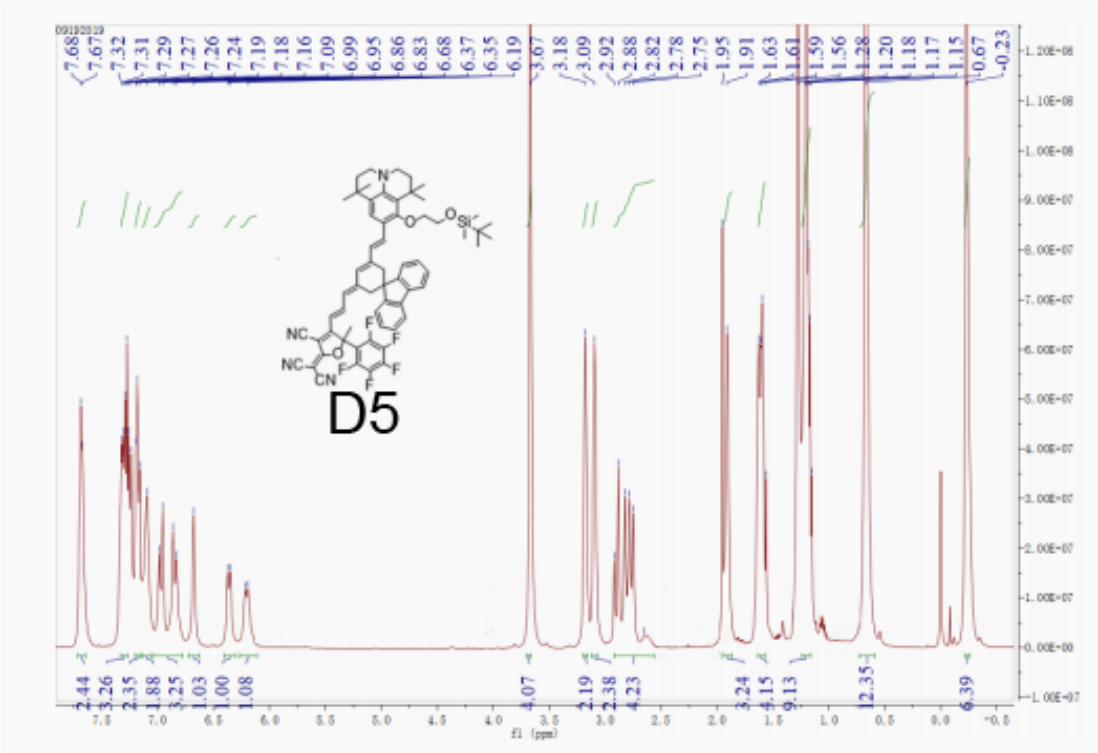


Figure S13. ^{1}H-NMR spectrum of Chromophore D5

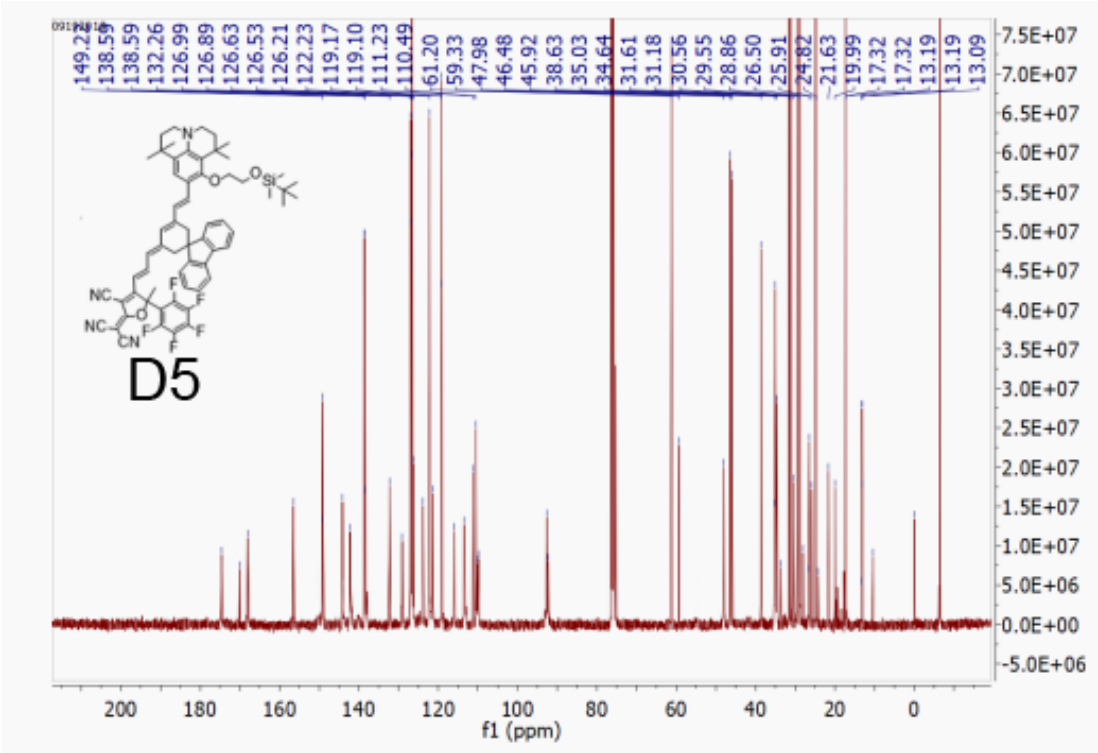
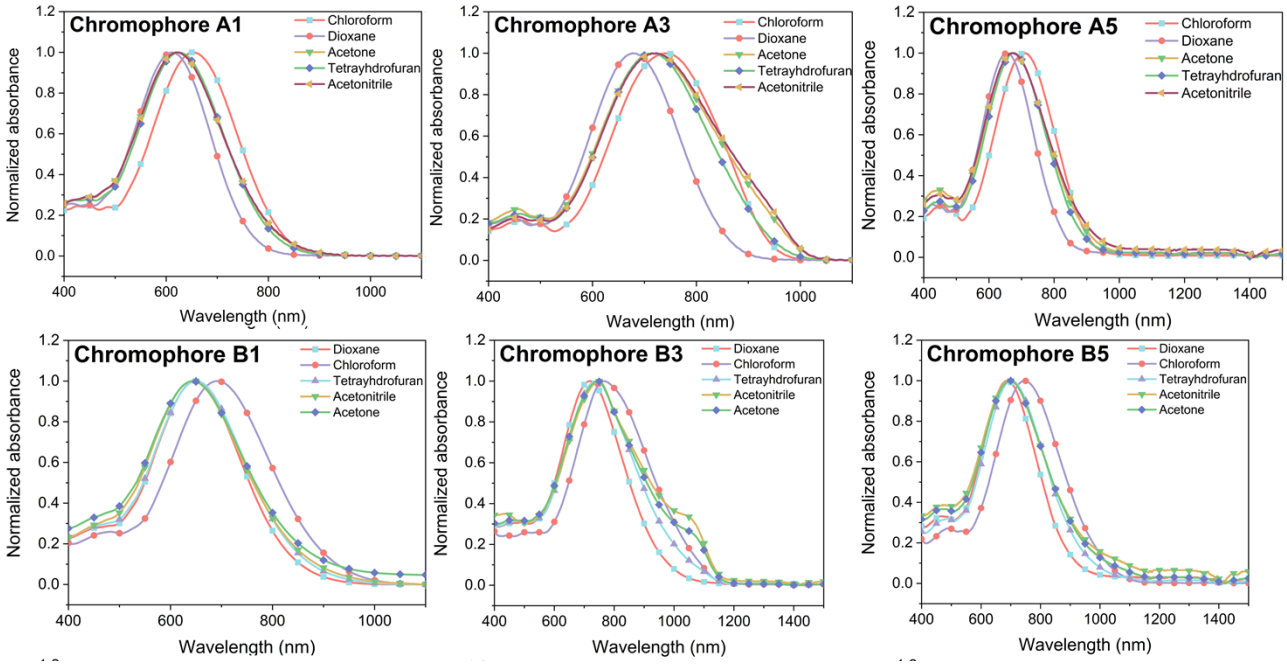


Figure S14. ^{13}C-NMR spectrum of Chromophore D5

4. UV-Vis Absorption Spectroscopy



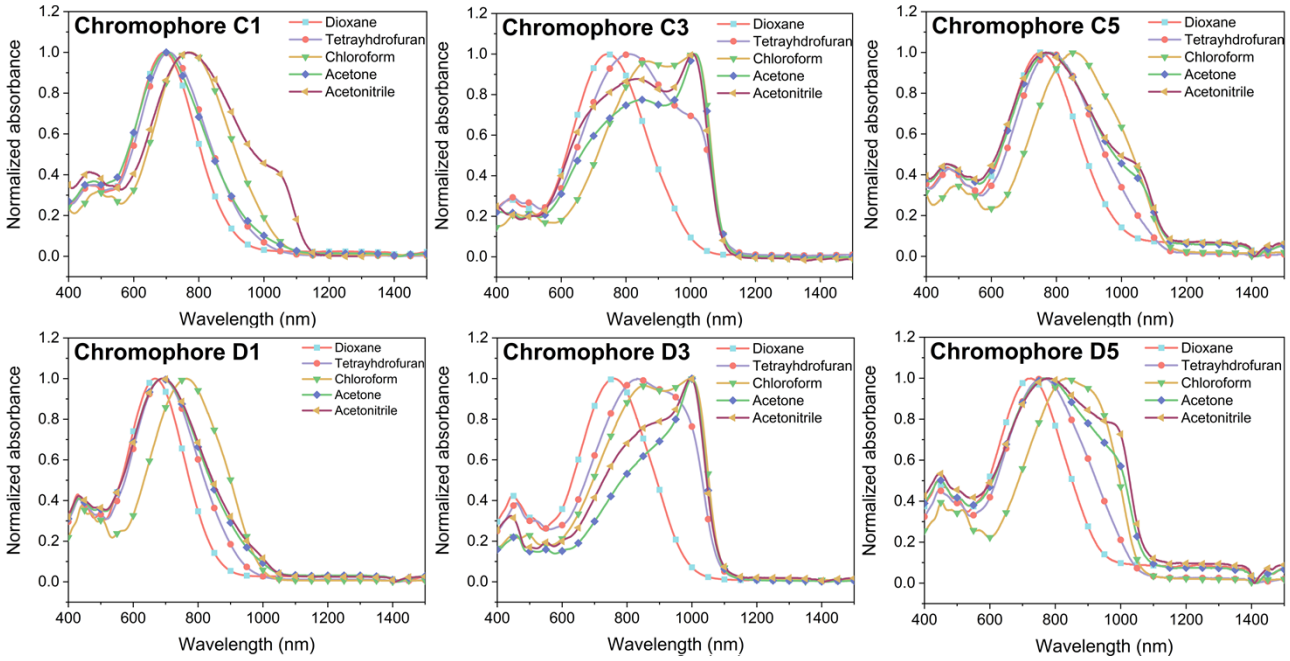


Figure S15. Normalized UV-Vis absorption spectra of chromophores ABCD in five aprotic solvents

5. DFT Calculations

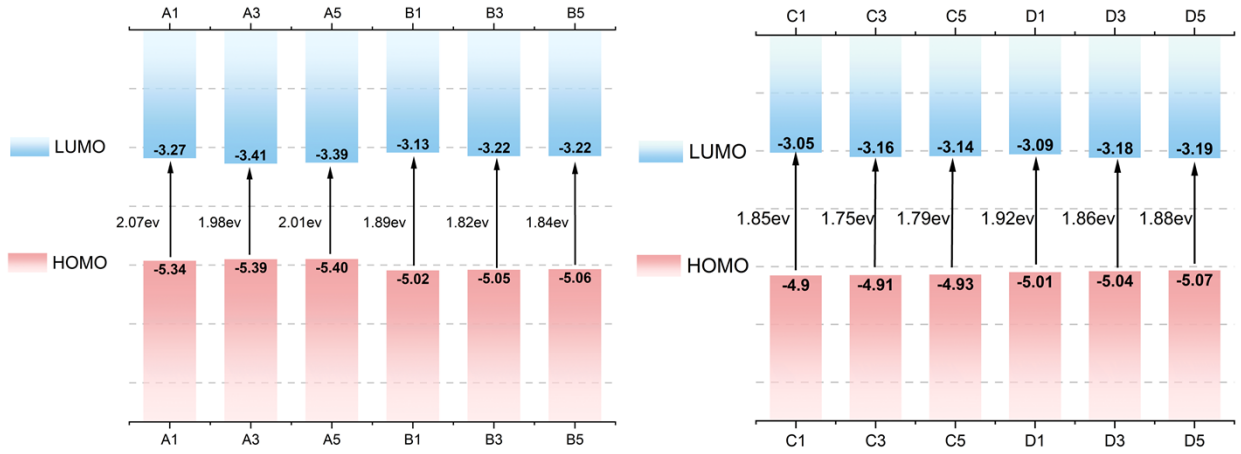
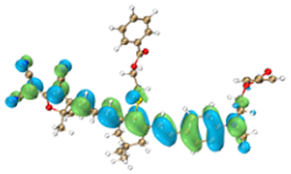
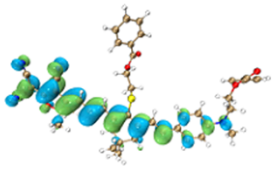
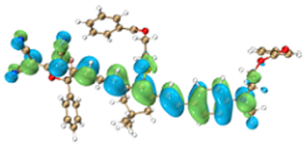
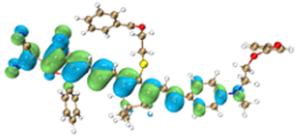
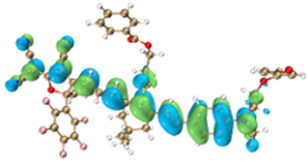
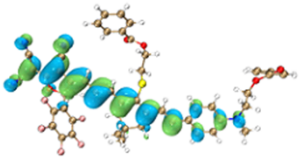
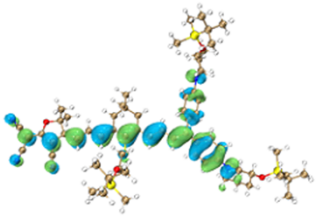
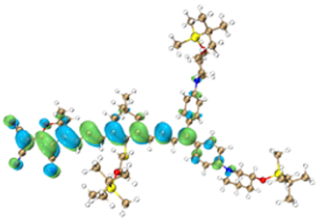
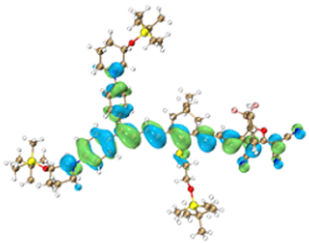
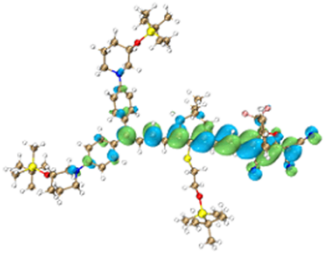
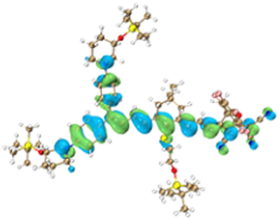
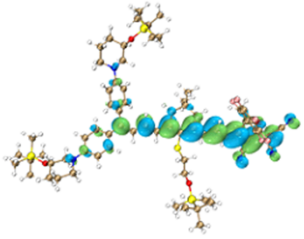


Figure S16. HOMO and LUMO energy gaps, in eV.

	HOMO	LUMO
A1		
A3		
A5		
B1		
B3		
B5		

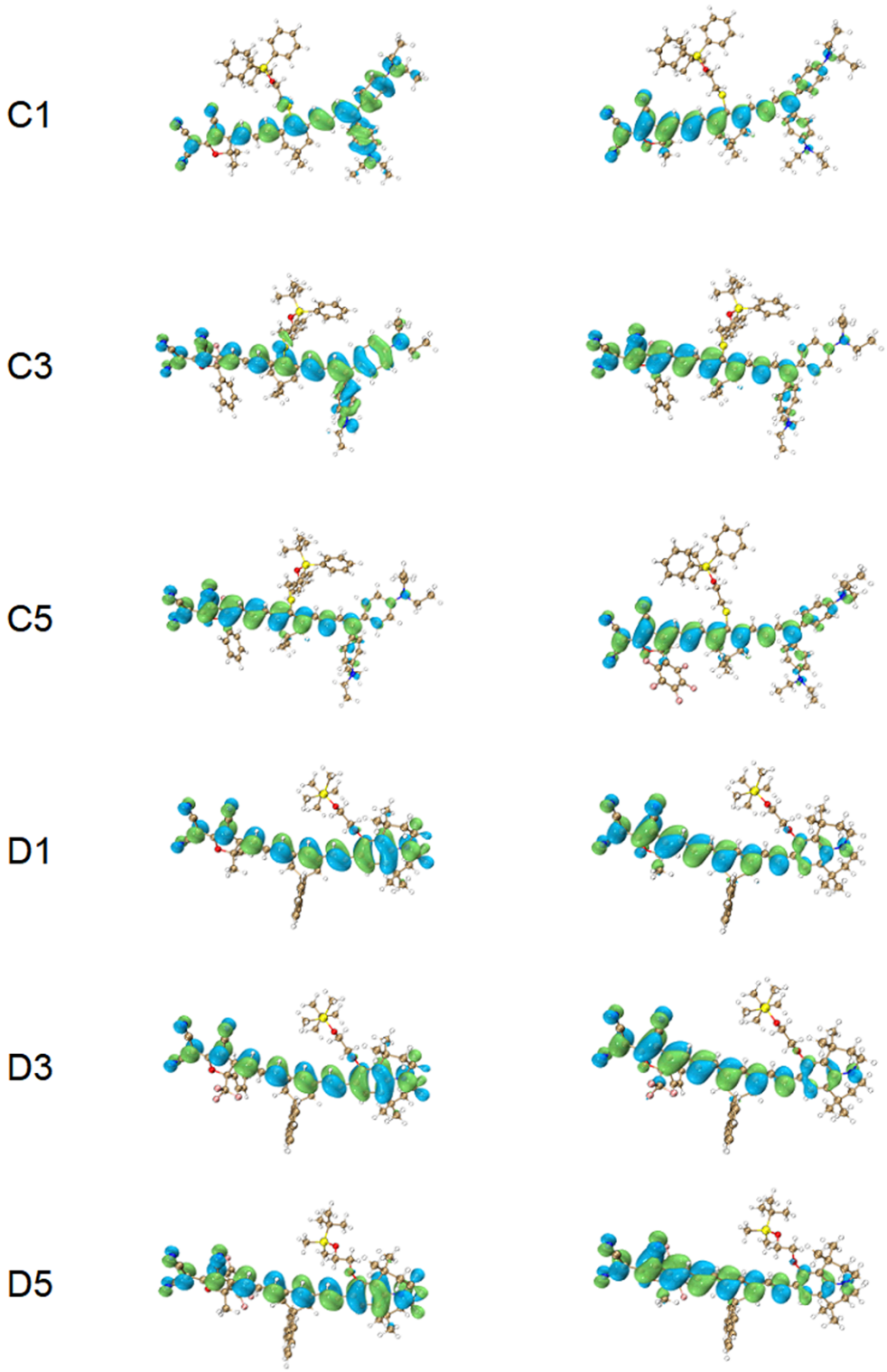


Figure S17. Frontier molecular orbitals HOMO and LUMO of chromophores ABCD

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