Supporting Information

Novel D–A–π–A Type Organic Dyes Containing a Ladder-Like Dithienocyclopentacarbazole Donor for Effective Dye-Sensitized Solar Cells

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Content

Measurements. ^{1}H NMR and ^{13}C NMR spectra of samples were recorded on a Bruker Avance 400 instrument (400 MHz) using tetramethylsilane as the internal standard. Matrix-assisted laser desorption/ionization time of Flight mass spectrometry (MALDITOF-MS) was performed on Bruker Autoflex III instrument. UV-vis absorption spectra of the dyes in a chloroform solution and on dye-soaked TiO_2 films were obtained on a Perkin-Elmer Lambda 25 spectrometer. The photoluminescence (PL) spectra were measured by using Perkin-Elmer LS-50 luminescence spectrometer. Cyclic voltammetry (CV) experiments were carried out on an electrochemical workstation (CHI660A, Chenhua, Shanghai) by using a conventional three-electrode system, which is composed of a Pt working electrode, a Pt wire counter electrode, an Ag/AgCl reference electrode in a saturated KCl solution. 0.1 M tetrabutylammonium hexafluorophosphate($TBAPF_6$) in $CHCl_3$ was used as the supporting electrolyte. The photocurrent density-voltage (*J*–*V*) curves were obtained by recording the generated photocurrent upon applying an external potential bias to the cell using a Keithley model 2400 digital source meter under standard global AM 1.5G illumination condition (100 mW cm^{-2}) using a Si solar cell as a reference. The action spectrum of monochromatic incident photo-to-current conversion efficiency (IPCE) was recorded on a DC Power Meter (Model 2931-C equipped with a 300W xenon arc lamp, Newport Co.) under irradiation with a motorized monochromator (Oriel). The electrochemical impedance spectroscopy (EIS) was conducted on a CHI660E electrochemical workstation, which was performed in complete darkness with a forward bias of –0.70 V and a frequency region at 0.01−100 KHz, respectively.

Fabrication Procedure for DSSCs. The DSSCs were fabricated on the basis of a previously reported procedure.[1] Before the deposition of the TiO_2 paste, fluorine-doped SnO_2 conducting glass (FTO, 2.2 mm thickness, 7–8 Ω/□) were cleaned and immersed in a solution of $TiCl_4$ (40 mM) at 70 ℃ for 30 min, then washed with water and ethanol. The photoanodes (thickness 16 mm; area 0.25 cm^2) were prepared using the screen printing technique containing a 12 μm layer of mesoporous TiO_2 (18NR-T, Dyesol) and a 4 μm scatter layer (18NR-AO, Dyesol). The TiO_2-coated FTO glass was calcined under airflow at 325 ℃ for 5 min, 375 ℃ for 5 min, 450 ℃ for 15 min, and 500 ℃ for 1h. After cooling to room temperature, they were treated with $TiCl_4$ (40 mM) solution at 70 ℃ for 30 min again, and then annealed at 500 ℃ for 30 min. After cooling again, the obtained TiO_2 films were

immersed in a dye solution (0.3 mM in CH_2Cl_2/C_2H_5OH = 1:1 mix solvents) and maintained in the dark for 16 h at room temperature. The sensitized electrodes were washed with CH_2Cl_2 and dried in air. The Pt counter electrode was prepared by spreading a 10 mM solution of H_2PtCl_6 in isopropyl alcohol onto the FTO glass (2.2 mm thickness, 7–8 Ω/□) with a small hole to allow the injection of the liquid electrolyte under vacuum, followed by heating at 400 ℃ for 30 min. The dye-covered TiO_2 electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot–melt gasket of 25 μm thickness made of the ionomer Surlyn 1702 (DuPont). The electrolyte is composed of 0.6 M dimethylpropyl imidazolium iodide, 0.1 M lithium iodide, 0.03 M iodine, 0.5 M tert-butylpyridine in acetonitrile/3-methoxypropionitrile (1:1, v/v). The effective area of the DSSCs is ca. 0.2823 cm^2.

Detailed synthetic procedures for the dyes C1–C3.

All the starting chemicals were purchased from Chem Greatwall and Alfa Aesar, and used without any further purification. Tetrahydrofuran (THF) was distilled from a blue solution of sodium and diphenylmethanone prior to use. The materials 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (6), 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (7) and 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*c*]-pyridine (8) were purchased from Chemical Greatwall. 9-octyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lan-2-yl)-9*H*-carbazole (1),[2] ethyl 2-bromothiophene-3-carboxylate (2),[3] ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (5)[4] were synthesized according to the previous reported literatures.

Synthesis of Compound 3. In a dried 250 mL three-neck round-bottom flask, 9-octyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole 1 (2.71 g, 5.1 mmol), ethyl 2-bromothiophene -3-carboxylate 2 (3.6 g, 15.3 mmol), anhydrous K_2CO_3 (13.8 g, 100 mmol), Aliquant 336 (2 drops), and $Pd(PPh_3)_2Cl_2$ (0.4 g, 0.57 mmol) were dissolved in deoxygenated toluene/H_2O (150 mL, 2:1, v/v). The reaction mixture was refluxed at 90 ℃ for 24 h and then extracted with dichloromethane. The collected organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent (petroleum ether/ethyl acetate, v/v = 20/1) as the eluent and then recrystallized by petroleum ether to give a light yellow product (2.25 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.08 (d, 2H),

7.54 (dd, 4H), 7.36 (dd, 2H), 7.27 (s, 1H), 7.24 (s, 1H), 4.29 (t, 2H), 4.19 (q, 4H), 1.84–1.90 (m, 2H), 1.22–1.39 (m, 10H), 1.13 (t, 6H), 0.83 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 163.59, 151.79, 140.60, 131.04, 130.08, 128.41, 124.02, 122.76, 121.29, 119.87, 110.26, 60.49, 43.29, 31.81, 29.38, 29.19, 29.06, 27.31, 22.62, 14.11, 14.07; MS (MADI-TOF): m/z $[M]^+$ calcd for ($C_{34}H_{37}NO_4S_2$): 587.216; found: 587.182.

Synthesis of Compound 4 (DTCC). To a stirred solution of 1-bromo-4-(octyloxy)benzene (4.85 g, 17 mmol) in dry THF (100 mL) was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (6 mL, 15 mmol) at –78 ℃ under a nitrogen atmosphere. After being stirred at –78 ℃ for 2 h, compound 2 (1.0 g, 1.7 mmol) in dry THF (15 mL) was then added to the mixture by syringe. The mixture was stirred for 30 min at –78 ℃ and then refluxed at 70 ℃ overnight. After cooling to room temperature, the mixture was extracted with dichloromethane. The collected organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the brown crude product was obtained and then used in the next step without further purification. To a stirred solution of the brown crude product mentioned above was added 120 mL of acetic acid dropwise 1.0 mL of concentrated H_2SO_4. The reaction mixture was stirred at 85 ℃ for 4 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane. The collected organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent as the eluent (petroleum ether/ethyl acetate, v/v = 20/1) to give a pale yellow solid (1.59 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.80 (s, 2H), 7.37 (s, 2H), 7.28 (d, 2H), 7.18 (d, 8H), 7.01 (d, 2H), 6.74 (d, 8H), 4.32 (t, 2H), 3.88 (t, 8H), 1.92 (t, 2H), 1.69–1.76 (m, 12H), 1.26–1.47 (m, 46H), 0.85–0.88 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 157.87, 156.93, 145.84, 141.45, 140.67, 137.66, 135.04, 129.04, 127.53, 123.17, 121.28, 117.66, 114.16, 99.43, 67.93, 61.53, 43.43, 31.91, 31.85, 29.47, 29.39, 29.36, 29.26, 29.08, 27.38, 26.11, 22.68, 14.13; MS (MADI-TOF): m/z $[M]^+$ calcd for ($C_{86}H_{109}NO_4S_2$): 1283.780; found: 1284.368.

Synthesis of Compound 9. In a 250 mL three-necked round-bottom flask, ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3.0 g, 10.86 mmol), 4,7-dibromobenzo[*c*]-[1,2,5]thiadiazole (3.3 g, 11.23 mmol), anhydrous K_2CO_3 (11.0 g, 79.7 mmol), Aq336 (1 drop), and $Pd(PPh_3)_2Cl_2$ (0.4 g, 0.57 mmol) were dissolved in deoxygenated THF/H_2O (150 mL, 2:1, v/v). The

reaction mixture was refluxed at 90 ℃ for 0.5 h and then extracted with dichloromethane. The collected organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent (petroleum ether/ethyl acetate, v/v = 20/1) as the eluent, and then recrystallized by petroleum ether and dichloromethane to give a luminous yellow product (2.75 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.21 (dd, 2H), 7.95–7.99 (m, 3H), 7.64 (d, 1H), 4.43 (q, 2H), 1.43 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 166.29, 153.92, 152.93, 140.85, 132.89, 132.22, 130.54, 129.92, 129.15, 128.75, 114.23, 61.19, 14.41.

Synthesis of Compound 10. In a 100 mL three-necked round-bottom flask, ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (0.84 g, 3.03 mmol), 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (1.0 g, 3.03 mmol), anhydrous K_2CO_3 (4.15 g, 30.0 mmol), Aq336 (1 drop), and $Pd(PPh_3)_2Cl_2$ (0.15 g, 0.21 mmol) were dissolved in deoxygenated toluene /H_2O (45 mL, 2:1, v/v). The reaction mixture was refluxed at 90 ℃ for 0.5 h and then extracted with dichloromethane. The collected organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent (petroleum ether/dichloromethane, v/v = 5/1) as the eluent, and then recrystallized by ethyl alcohol and dichloromethane to give a ivory white product (0.87 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.23 (dd, 2H), 7.85 (dd, 2H), 4.44 (q, 2H), 1.43 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 165.99, 153.49, 153.29, 151.52, 151.33, 150.92, 149.95, 149.07, 148.99, 148.74, 133.92, 131.22, 130.43, 129.69, 118.50, 118.36, 99.33, 99.11, 61.25, 14.34.

Synthesis of Compound 11. In a 100 mL three-necked round-bottom flask, ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (0.92 g, 3.32 mmol), 4,7-dibromo-[1,2,5]-thiadiazolo[3,4-*c*]pyridine (1.0 g, 3.4 mmol), anhydrous K_2CO_3 (11.0 g, 79.7 mmol), Aq336 (1 drop), and $Pd(PPh_3)_2Cl_2$ (0.15 g, 0.21 mmol) were dissolved in deoxygenated THF /H_2O (120 mL, 2:1, v/v). The reaction mixture was refluxed at 90 ℃ for 0.5 h and then extracted with dichloromethane. The collected organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent (petroleum ether/ethyl acetate, v/v = 20/1) as the eluent, and then recrystallized by petroleum ether and dichloromethane to give a bright yellow product (0.82 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$), δ

(ppm): 8.87 (s, 1H), 8.67 (d, 2H), 8.24 (d, 2H), 4.44 (q, 2H), 1.44 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 166.15, 156.71, 151.37, 149.36, 145.74, 139.79, 132.20, 129.78, 129.74, 110.71, 100.00, 61.28, 14.36.

Synthesis of Compound 12. In a 100 mL three-necked round-bottom flask, compound 4 (1.22 g, 0.94 mmol), compound 9 (0.34 g, 0.93 mmol), Cesium Carbonate (0.73 g, 2.24 mmol), PivOH (0.06 g, 0.59 mmol), tris(2-methoxyphenyl)phosphine (0.34 g, 0.96 mmol), Palladium acetate (0.12 g, 0.53 mmol) were stirred in toluene (50 mL) at 110 ℃ for 4 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane. The collected organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent (petroleum ether/ethyl acetate, v/v = 20/1) as the eluent, and then recrystallized by ethyl alcohol and dichloromethane to give a deep red product (0.56 g, 38%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.20 (d, 2H), 8.09 (s, 1H), 8.05 (d, 1H), 7.95 (d, 1H), 7.84 (d, 1H), 7.76 (d, 1H), 7.46 (s, 1H), 7.38 (s, 1H), 7.28–7.30 (m, 8H), 7.19 (d, 3H), 7.01 (d, 1H), 6.77 (dd, 8H), 4.43 (q, 2H), 4.32 (t, 2H), 3.87–3.90 (m, 8H), 1.93 (t, 3H), 1.69–1.76 (m, 9H), 1.25–1.45 (m, 48H), 0.84–0.89 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 166.42, 158.01, 157.89, 156.98, 153.75, 152.45, 145.78, 144.10, 141.57, 141.43, 140.85, 140.75, 137.65, 137.46, 130.75, 129.95, 129.80, 129.17, 129.05, 129.01, 127.91, 114.28, 114.16, 99.85, 99.45, 67.97, 62.01, 61.53, 61.06, 43.36, 31.92, 31.83, 29.51, 29.38, 29.36, 29.25, 26.10, 22.67, 14.41, 14.15, 14.11; MS (MADI-TOF): m/z $[M]^+$ calcd for ($C_{101}H_{119}N_3O_6S_3$): 1565.826; found: 1566.414.

Synthesis of Compound 13. In a 100 mL three-necked round-bottom flask, compound 4 (1.0 g, 0.78 mmol), compound 9 (0.31 g, 0.79 mmol), Cesium Carbonate (0.6 g, 1.84 mmol), PivOH (0.04 g, 0.39 mmol), tris(2-methoxyphenyl)phosphine (0.28 g, 0.79 mmol), Palladium acetate (0.09 g, 0.4 mmol) were stirred in toluene (60 mL) at 110 ℃ for 4 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane. The collected organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent (petroleum ether/ethyl acetate, v/v = 20/1) as the eluent, and then recrystallized by ethyl alcohol and dichloromethane to give a deep red product (0.51 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.30 (s, 1H), 8.23 (d,

2H), 7.91 (d, 2H), 7.85 (d, 2H), 7.51 (s, 1H), 7.39 (s, 1H), 7.29–7.31 (m, 6H), 7.19 (d, 3H), 7.01 (d, 1H), 6.77 (dd, 8H), 4.44 (q, 2H), 4.34 (t, 2H), 3.87–3.91 (m, 8H), 1.94 (t, 3H), 1.71–1.75 (m, 9H), 1.25–1.45 (m, 51H), 0.84–0.89 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 166.17, 158.03, 157.90, 157.05, 146.02, 141.39, 140.94, 140.72, 137.61, 137.36, 135.49, 134.25, 130.70, 130.60, 129.59, 129.13, 129.05, 127.80, 122.38, 121.08, 117.76, 114.28, 114.17, 100.18, 99.47, 67.96, 62.00, 61.53, 61.19, 43.39, 31.93, 31.84, 29.74, 29.52, 29.39, 29.36, 29.26, 26.11, 22.68, 14.39, 14.12; MS (MADI-TOF): m/z $[M]^+$ calcd for ($C_{101}H_{117}F_2N_3O_6S_3$): 1601.807; found: 1602.335.

Synthesis of Compound 14. In a 100 mL three-necked round-bottom flask, compound 4 (1.0 g, 0.78 mmol), compound 9 (0.28 g, 0.79 mmol), Cesium Carbonate (0.6 g, 1.84 mmol), PivOH (0.05 g, 0.49 mmol), tris(2-methoxyphenyl)phosphine (0.28 g, 0.79 mmol), Palladium acetate (0.1 g, 0.45 mmol) were stirred in toluene (60 mL) at 110 ℃ for 4 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane. The collected organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent (petroleum ether/ dichloromethane, v/v = 2/1) as the eluent, and then recrystallized by ethyl alcohol and dichloromethane to give a deep purple product (0.45 g, 37%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.01 (s, 1H), 8.72 (d, 2H), 8.23 (d, 2H), 8.18 (s, 1H), 7.84 (d, 2H), 7.44 (s, 1H), 7.36 (s, 1H), 7.28–7.30 (m, 6H), 7.19 (d, 3H), 7.01 (d, 1H), 6.78 (dd, 8H), 4.44 (q, 2H), 4.29 (t, 2H), 3.87–3.91 (m, 8H), 1.90–1.92 (m, 2H), 1.69–1.76 (m, 8H), 1.26–1.46 (m, 53H), 0.84–0.88 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 166.38, 158.08, 157.92, 157.66, 156.89, 154.61, 149.40, 145.91, 145.75, 141.47, 140.83, 140.62, 138.70, 137.70, 137.36, 134.23, 131.44, 129.66, 129.48, 129.19, 129.09, 122.44, 120.97, 114.30, 114.15, 100.01, 99.49, 67.98, 67.94, 62.00, 61.51, 61.20, 43.16, 31.97, 31.86, 29.57, 29.41, 29.38, 29.28, 27.39, 26.13, 22.70, 14.42, 14.15; MS (MADI-TOF): m/z $[M]^+$ calcd for ($C_{100}H_{118}N_4O_6S_3$): 1566.821; found: 1567.336.

Synthesis of C1. In a 100 mL three-necked round-bottom flask, compound 12 (0.39 g, 0.25 mmol) and KOH (0.28 g, 5.0 mmol) were dissolved in a mixed solvent of THF/H_2O (60 mL, 3/1, v/v) under a nitrogen atmosphere. The reaction mixture was refluxed at 80 ℃ for 12 h and then extracted with dichloromethane. The collected organic layer was washed with brine over three times, and then dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was

purified by column chromatography on silica gel using a mixture solvent (chloroform/methanol=10/1, v/v) as the eluent to give a deep red product (0.28 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.23 (d, 2H), 8.06 (d, 2H), 7.90 (d, 1H), 7.84 (d, 2H), 7.72 (d, 1H), 7.32 (d, 8H), 7.21 (d, 4H), 7.00 (d, 1H), 6.79 (dd, 8H), 4.16 (br, 2H), 3.87–3.91 (m, 8H), 1.85 (br, 3H), 1.70–1.76 (m, 9H), 1.26–1.41 (m, 48H), 0.84–0.88 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 171.61, 158.09, 157.92, 153.50, 152.19, 149.81, 145.76, 144.94, 143.35, 141.64, 140.56, 137.84, 137.70, 134.67, 130.30, 129.29, 129.15, 128.83, 127.80, 122.94, 121.76, 120.90, 117.20, 114.32, 114.18, 103.00, 99.84, 99.42, 68.01, 61.88, 61.46, 42.96, 31.87, 29.43, 29.39, 29.28, 29.25, 26.15, 26.11, 22.70, 22.66, 14.13, 14.10; MS (MADI-TOF): m/z $[M]^+$ calcd for ($C_{99}H_{115}N_3O_6S_3$): 1537.795; found: 1538.413.

Synthesis of C2. In a 100 mL three-necked round-bottom flask, compound 13 (0.44 g, 0.27 mmol) and KOH (0.3 g, 5.4 mmol) were dissolved in a mixed solvent of THF/H_2O (60 mL, 3/1, v/v) under a nitrogen atmosphere. The reaction mixture was refluxed at 80 ℃ for 12 h and then extracted with dichloromethane. The collected organic layer was washed with brine over three times, and then dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent (chloroform/methanol=10/1, v/v) as the eluent to give a deep red product (0.39 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.31 (s, 1H), 8.28 (d, 2H), 7.95 (d, 2H), 7.85 (d, 2H), 7.52 (s, 1H), 7.39 (s, 1H), 7.29–7.31 (m, 6H), 7.19 (d, 3H), 7.01 (d, 1H), 6.78 (dd, 8H), 4.34 (br, 2H), 3.89 (br, 8H), 1.94 (br, 3H), 1.69–1.75 (m, 9H), 1.26–1.43 (m, 48H), 0.84–0.89 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 171.18, 158.04, 157.89, 156.89, 145.83, 141.47, 140.79, 140.52, 137.70, 137.47, 135.42, 134.15, 130.62, 130.05, 129.16, 129.06, 122.97, 120.84, 117.48, 114.26, 114.12, 106.55, 100.17, 99.41, 67.97, 67.94, 61.88, 61.44, 31.93, 31.81, 29.70, 29.55, 29.37, 29.35, 29.26, 29.23, 29.10, 29.00, 27.36, 26.08, 24.74, 22.65, 22.64, 14.11, 14.09, 14.08; MS (MADI-TOF): m/z $[M]^+$ calcd for ($C_{99}H_{113}F_2N_3O_6S_3$): 1573.776; found: 1574.311.

Synthesis of C3. In a 100 mL three-necked round-bottom flask, compound 14 (0.33 g, 0.21 mmol) and KOH (0.24 g, 4.2 mmol) were dissolved in a mixed solvent of THF/H_2O (60 mL, 3/1, v/v) under a nitrogen atmosphere. The reaction mixture was refluxed at 80 ℃ for 12 h and then extracted with dichloromethane. The collected organic layer was washed with brine over three times, and then dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was

purified by column chromatography on silica gel using a mixture solvent (chloroform/methanol=10/1, v/v) as the eluent, and then recrystallized by acetone and dichloromethane to give a deep purple product (0.27 g, 84%). ^{1}H NMR (400 MHz, CD_2Cl_2), δ (ppm): 8.72 (s, 1H), 8.56 (d, 2H), 8.06 (d, 2H), 7.96 (s, 1H), 7.90 (d, 2H), 7.43 (d, 4H), 7.27 (d, 4H), 7.21 (s, 1H), 6.99 (s,1H), 6.90 (d, 4H), 6.81 (d, 6H), 3.92 (br, 8H), 3.46 (br, 2H), 1.72–1.74 (m, 9H), 1.22–1.42 (m, 51H), 0.83–0.87 (m, 15H); ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 158.25, 158.06, 156.63, 156.20, 153.29, 148.77, 145.45, 141.66, 140.43, 140.26, 137.80, 137.57, 129.80, 129.23, 129.06, 122.59, 121.96, 121.65, 120.45, 116.78, 114.27, 114.06, 100.00, 99.43, 68.09, 68.03, 61.72, 61.33, 31.98, 31.84, 31.82, 29.65, 29.40, 29.36, 29.32, 29.26, 29.25, 28.76, 27.24, 26.06, 22.69, 22.67, 22.65, 13.90, 13.88, 13.86; MS (MADI-TOF): m/z $[M]^+$ calcd for ($C_{98}H_{114}N_4O_6S_3$): 1538.790; found: 1539.198.

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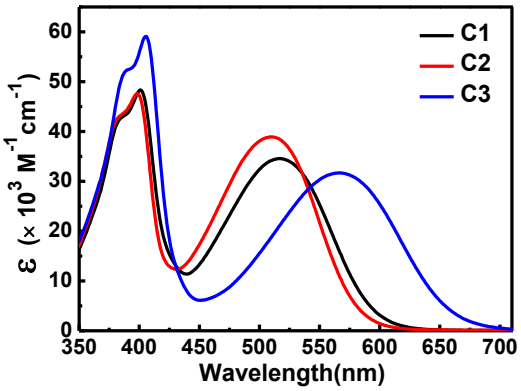

Figure S1. UV-vis absorption spectra and the corresponding molar extinction coefficient (ε) of the dyes C1–C3 in $CHCl_3$ solution (10^{-5} M).

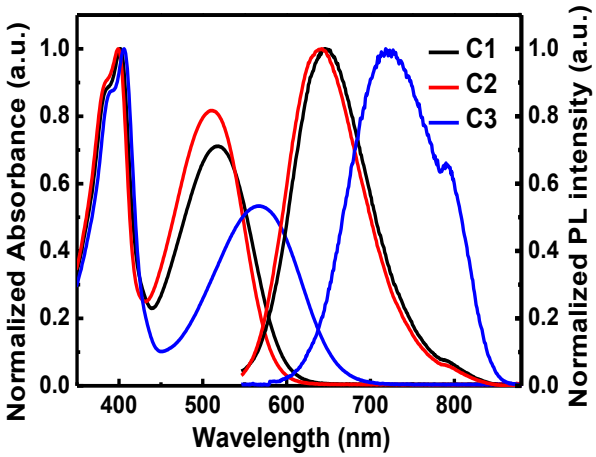

Figure S2. Normalized UV-vis absorption spectra and normalized PL spectra of the dyes C1–C3.

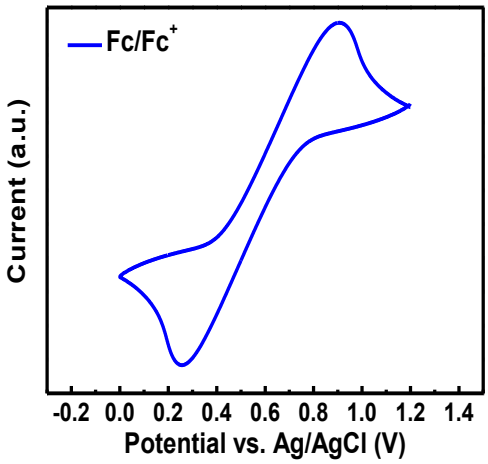

Figure S3. The CV curve of Fc/Fc^{+} in $CHCl_3$ solution.

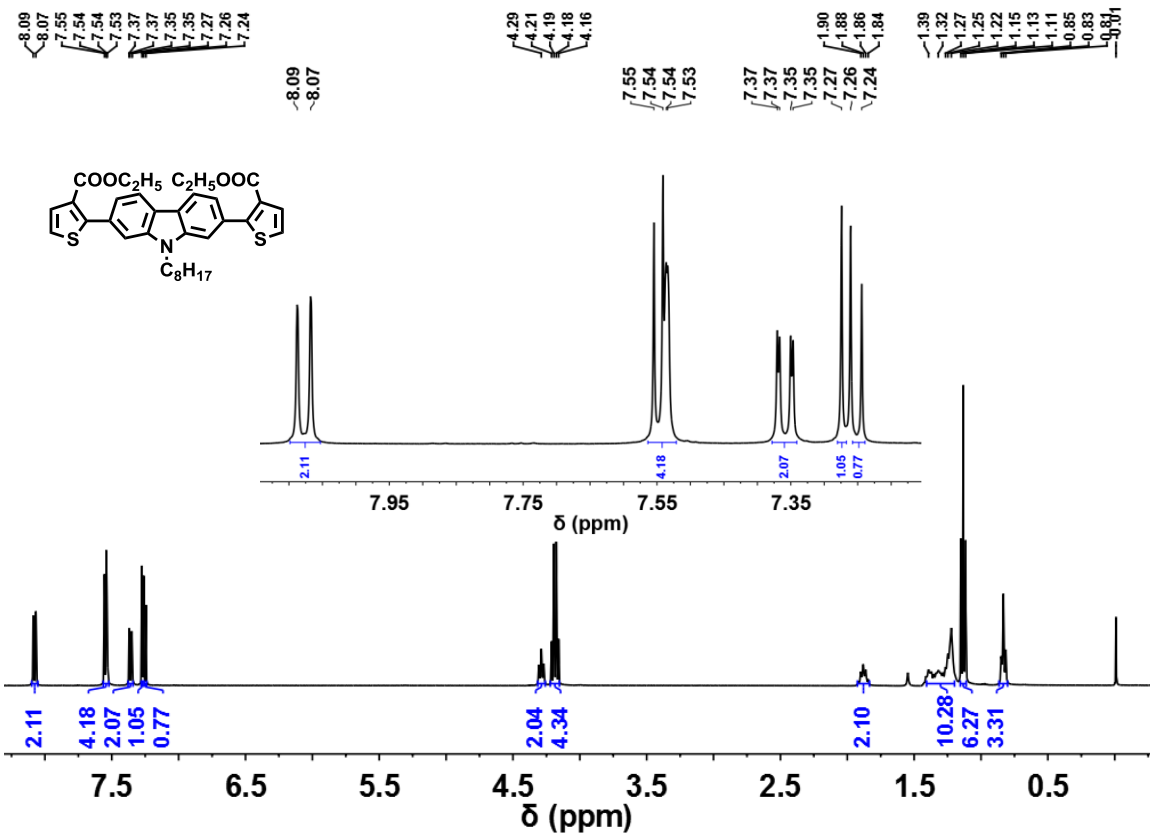

Figure S4. ^{1}H NMR spectrum of compound 3 in $CDCl_3$

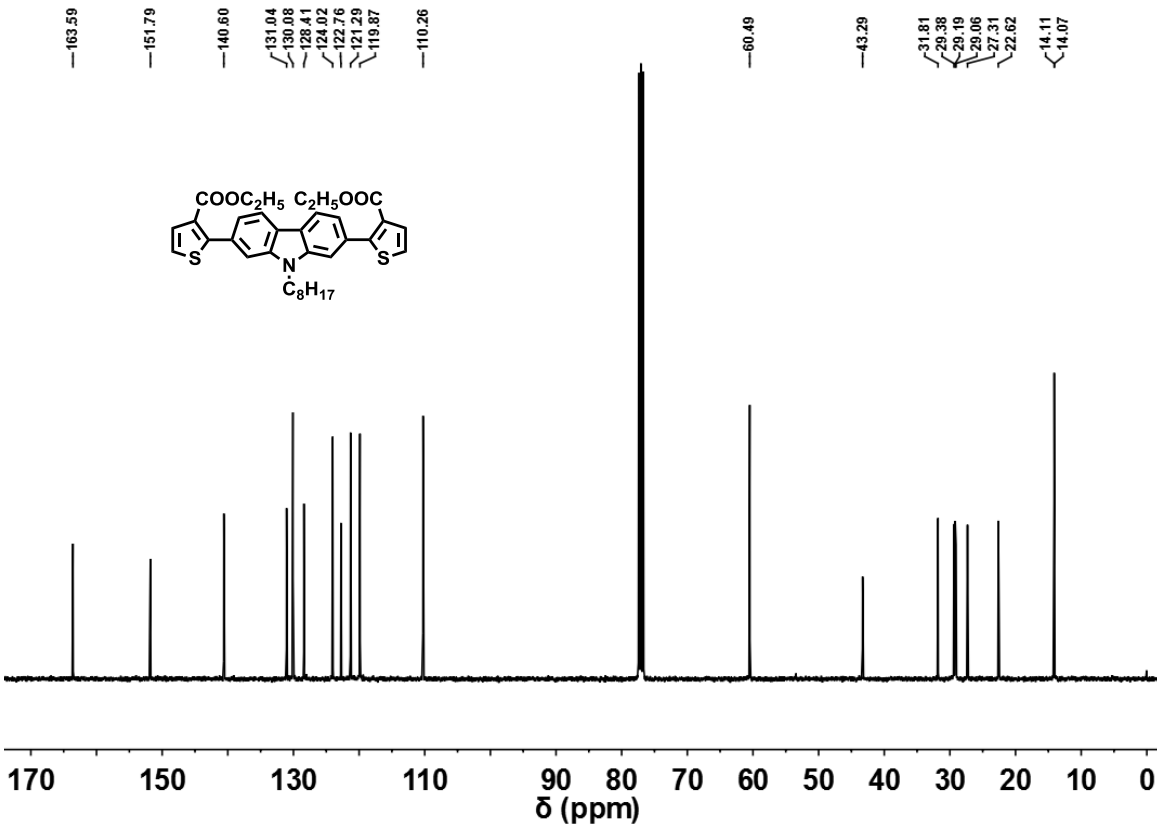

Figure S5. ^{13}C NMR spectrum of compound 3 in $CDCl_3$

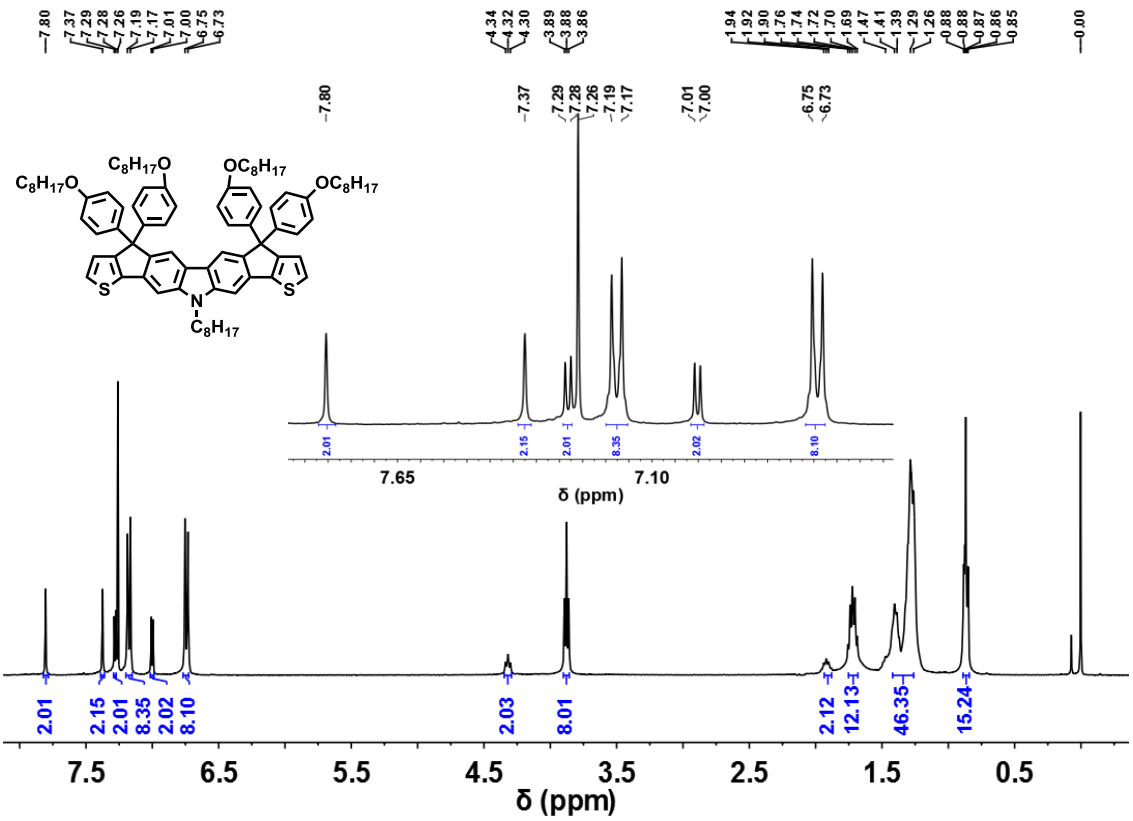

Figure S6. ^{1}H NMR spectrum of compound 4 in $CDCl_3$

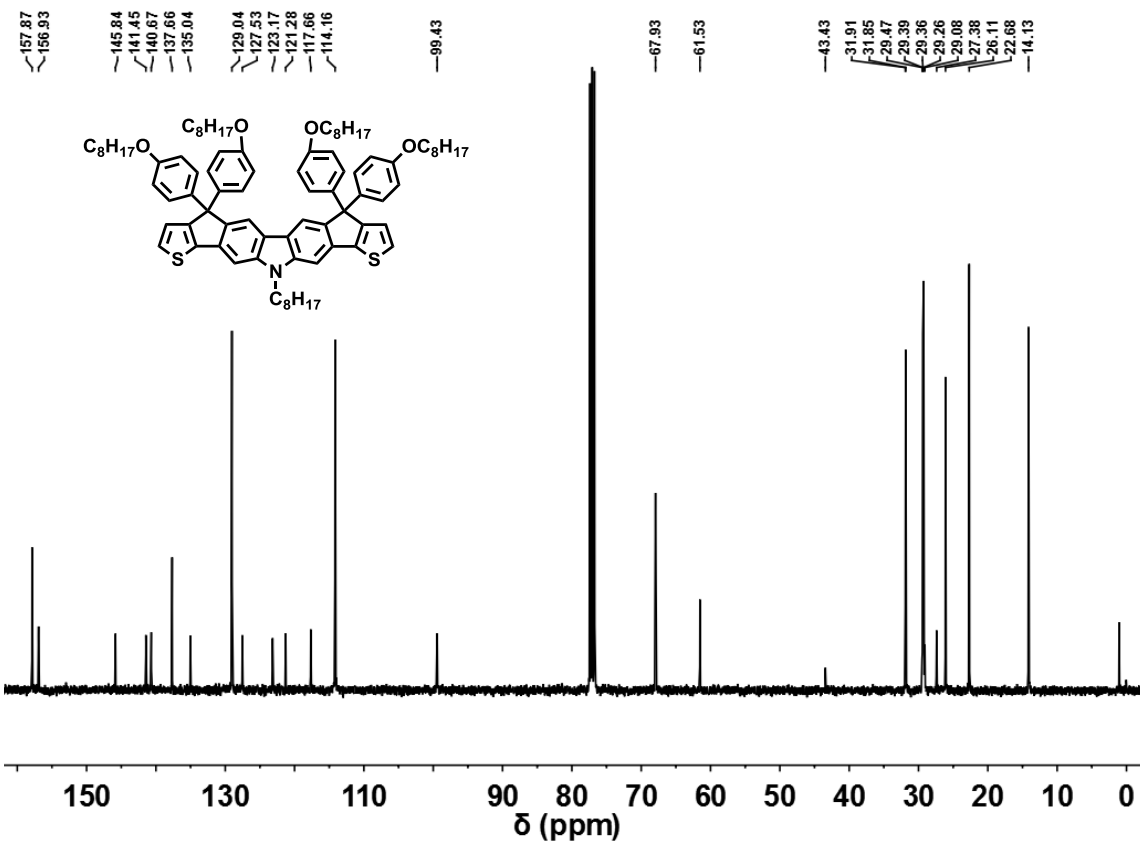

Figure S7. ^{13}C NMR spectrum of compound 4 in $CDCl_3$

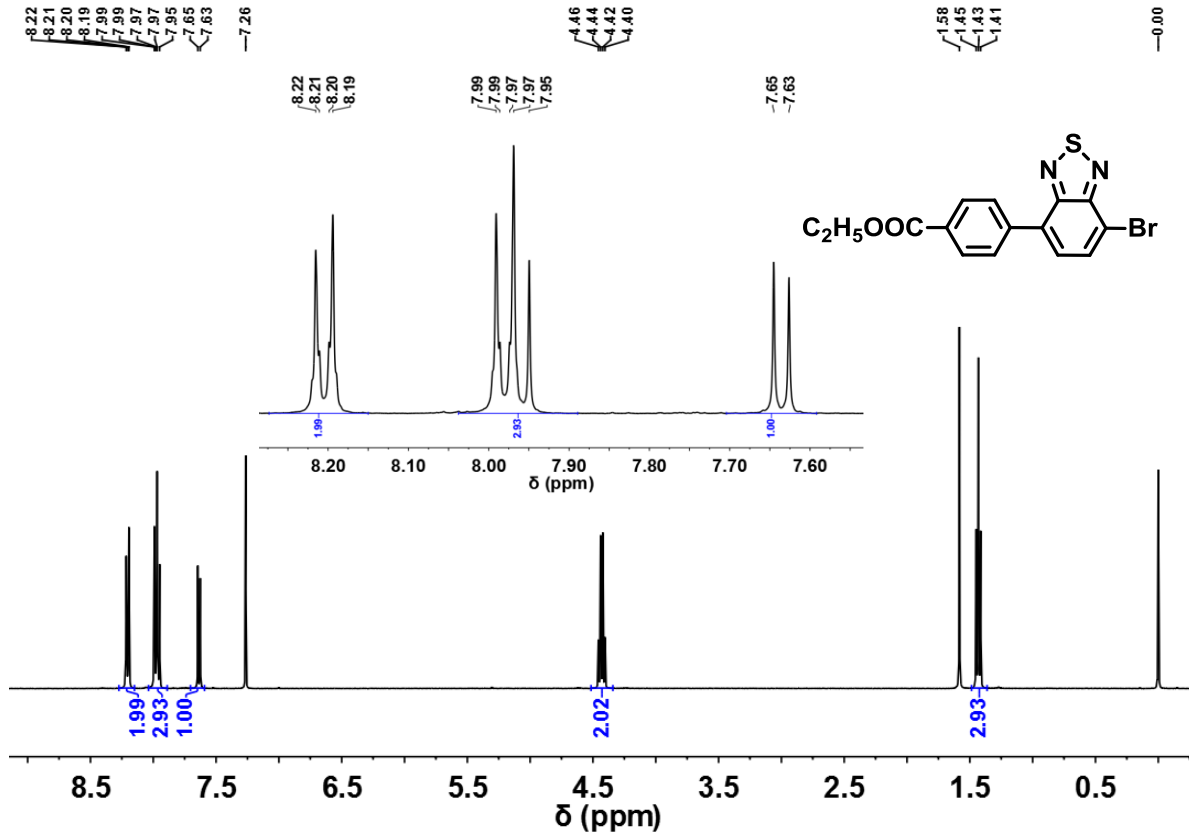

Figure S8. ^{1}H NMR spectrum of compound 9 in $CDCl_3$

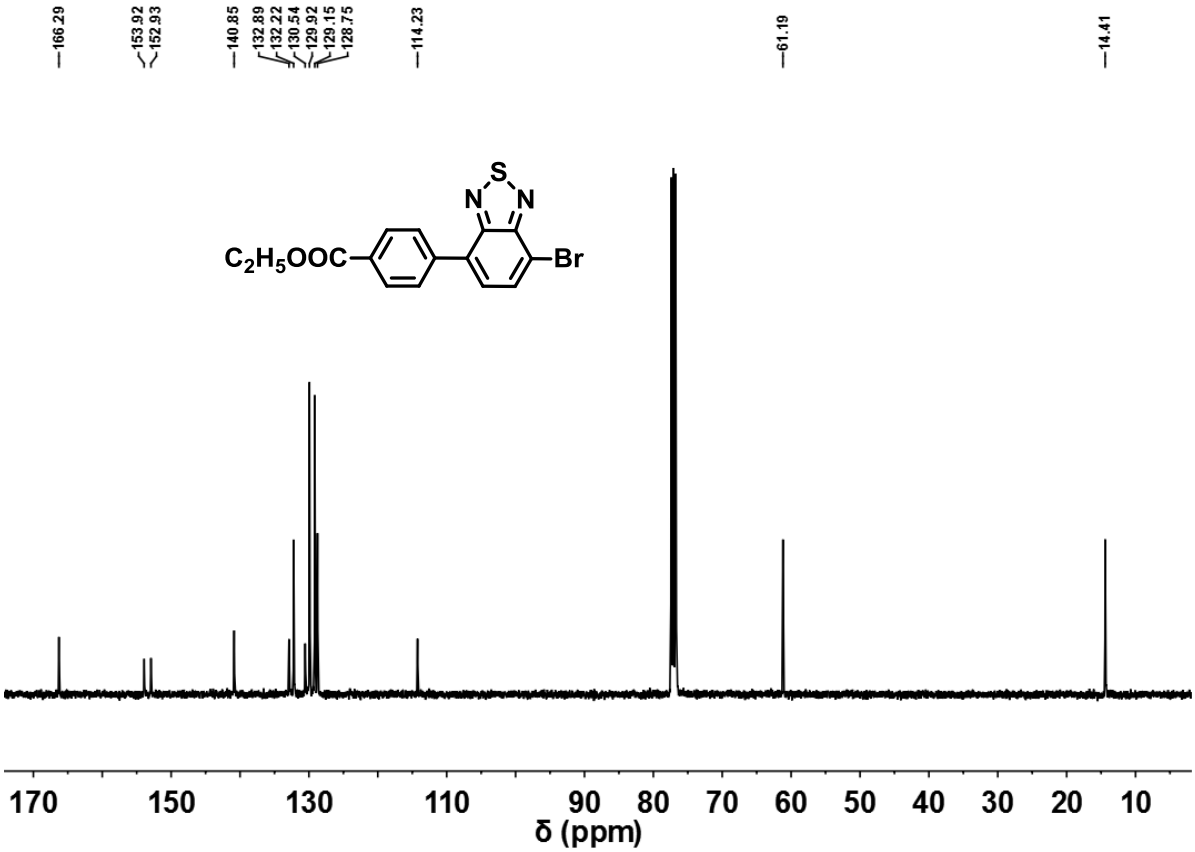

Figure S9. ^{13}C NMR spectrum of compound 9 in $CDCl_3$

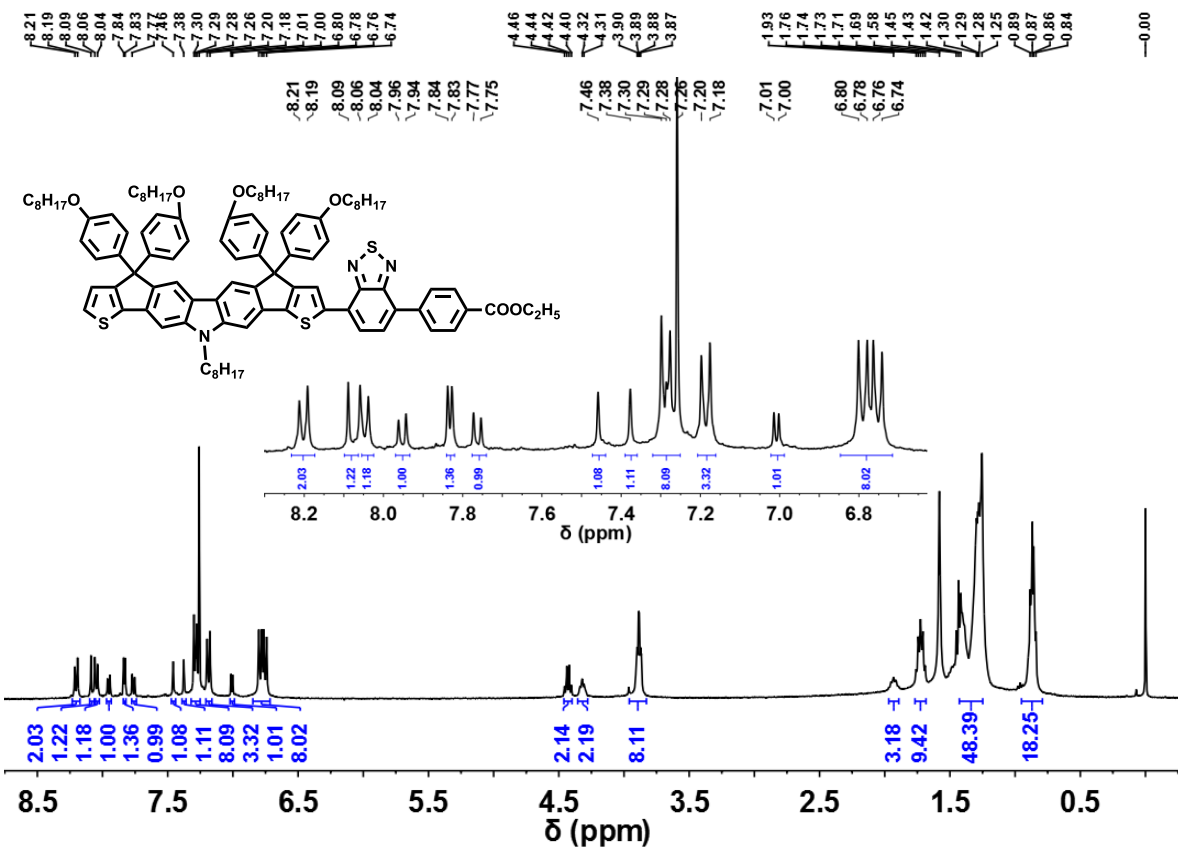

Figure S10. ^{1}H NMR spectrum of compound 12 in $CDCl_3$

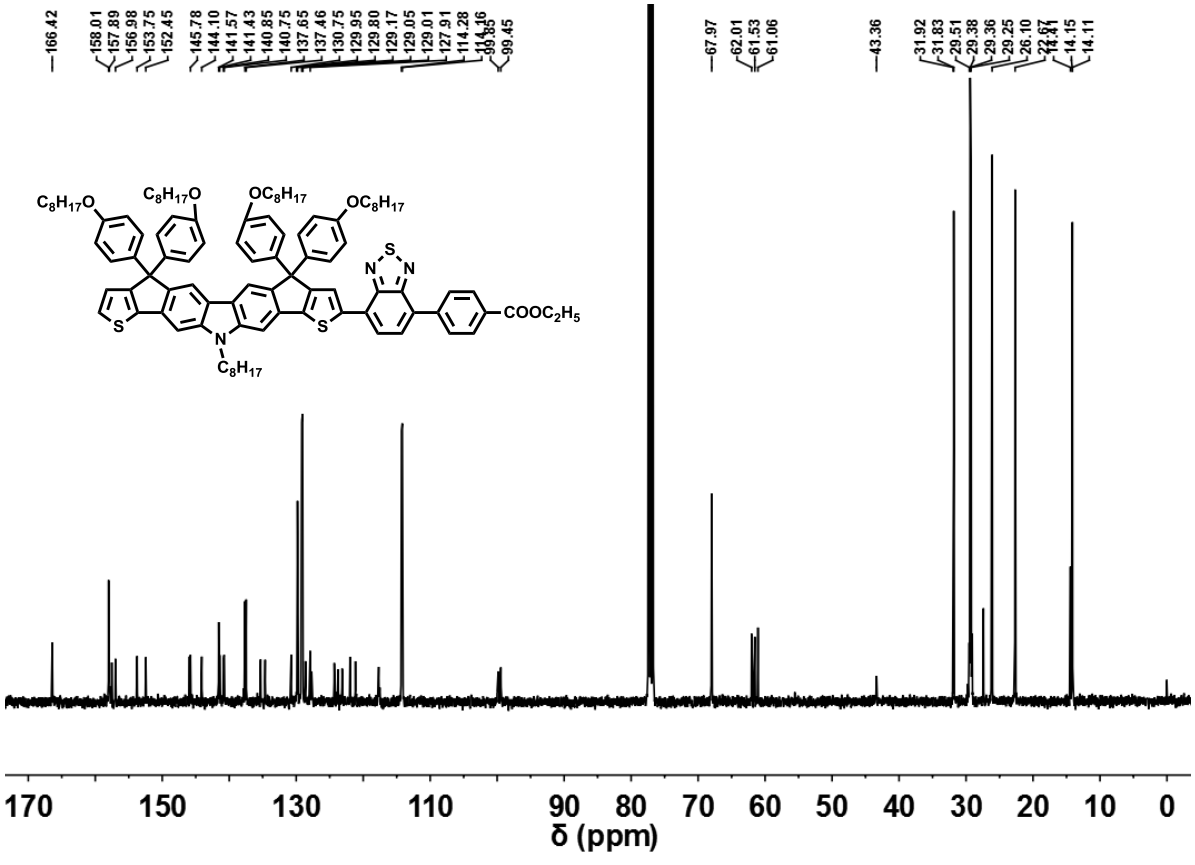

Figure S11. ^{13}C NMR spectrum of compound 12 in $CDCl_3$

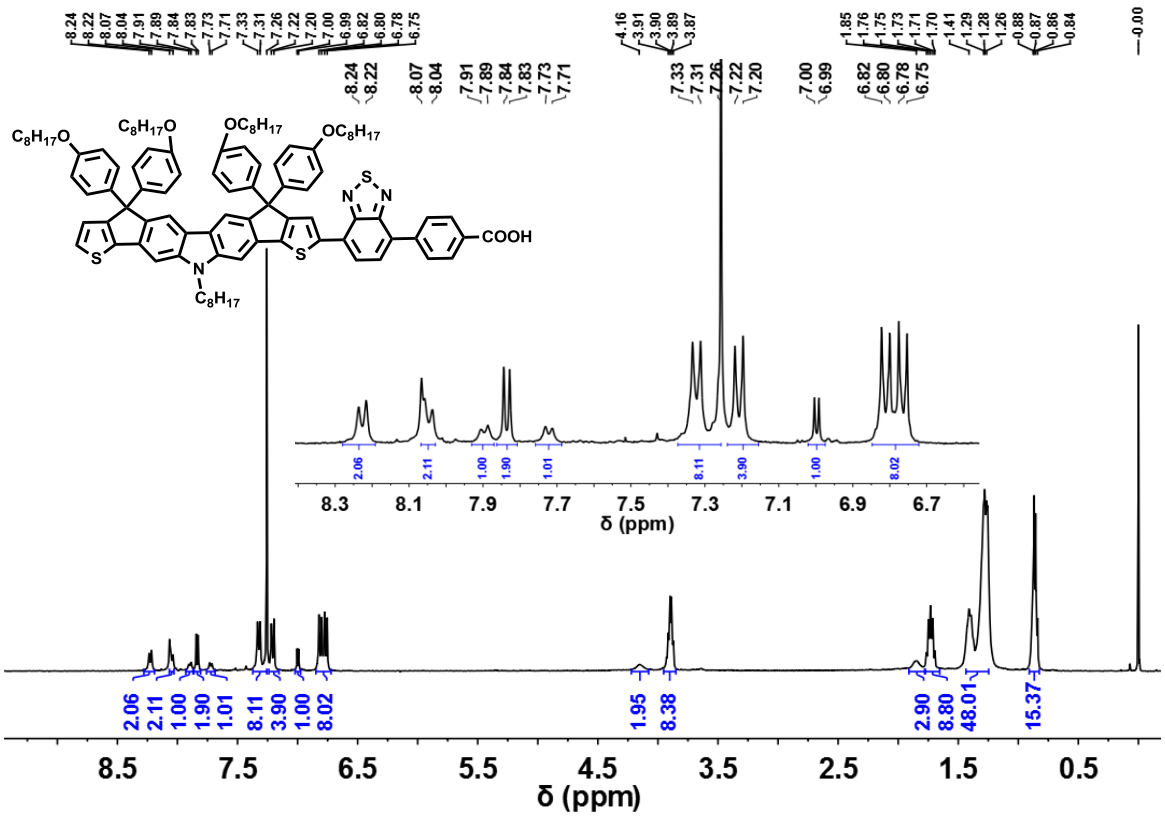

Figure S12. ^{1}H NMR spectrum of dye C1 in $CDCl_3$

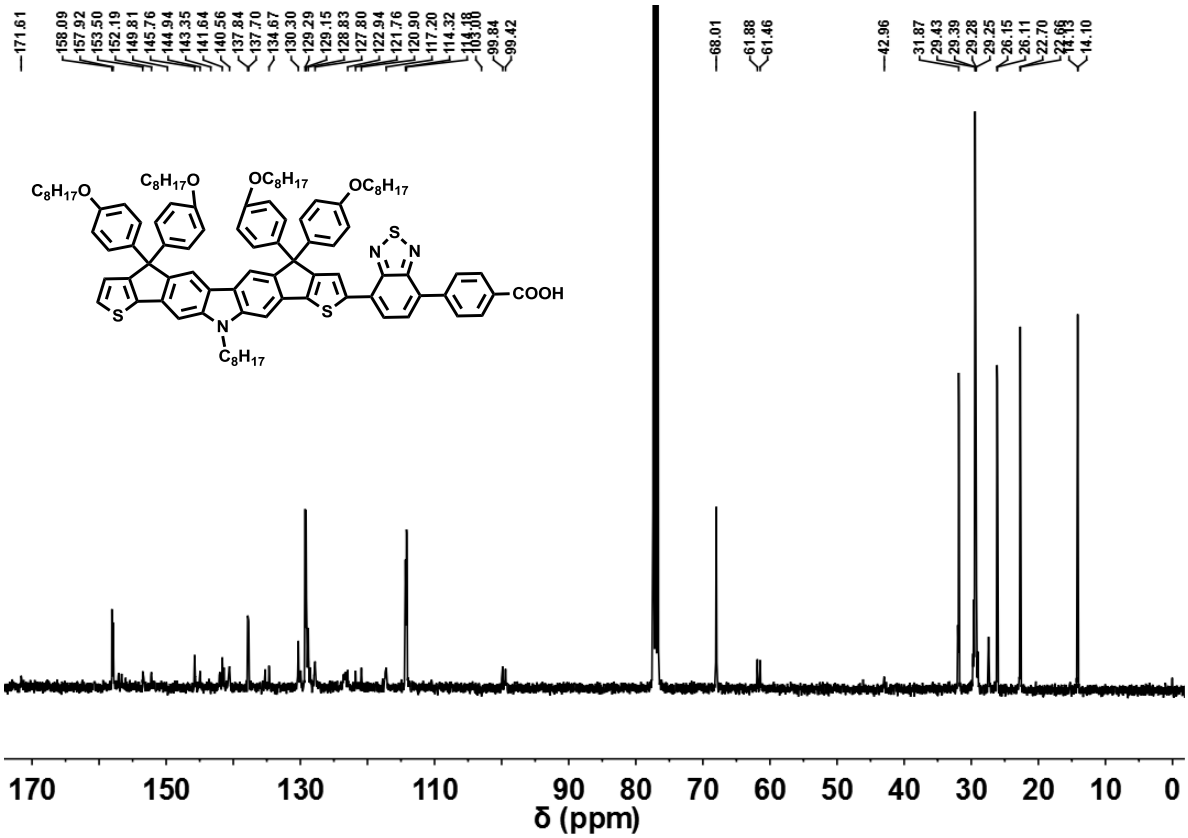

Figure S13. ^{13}C NMR spectrum of dye C1 in $CDCl_3$

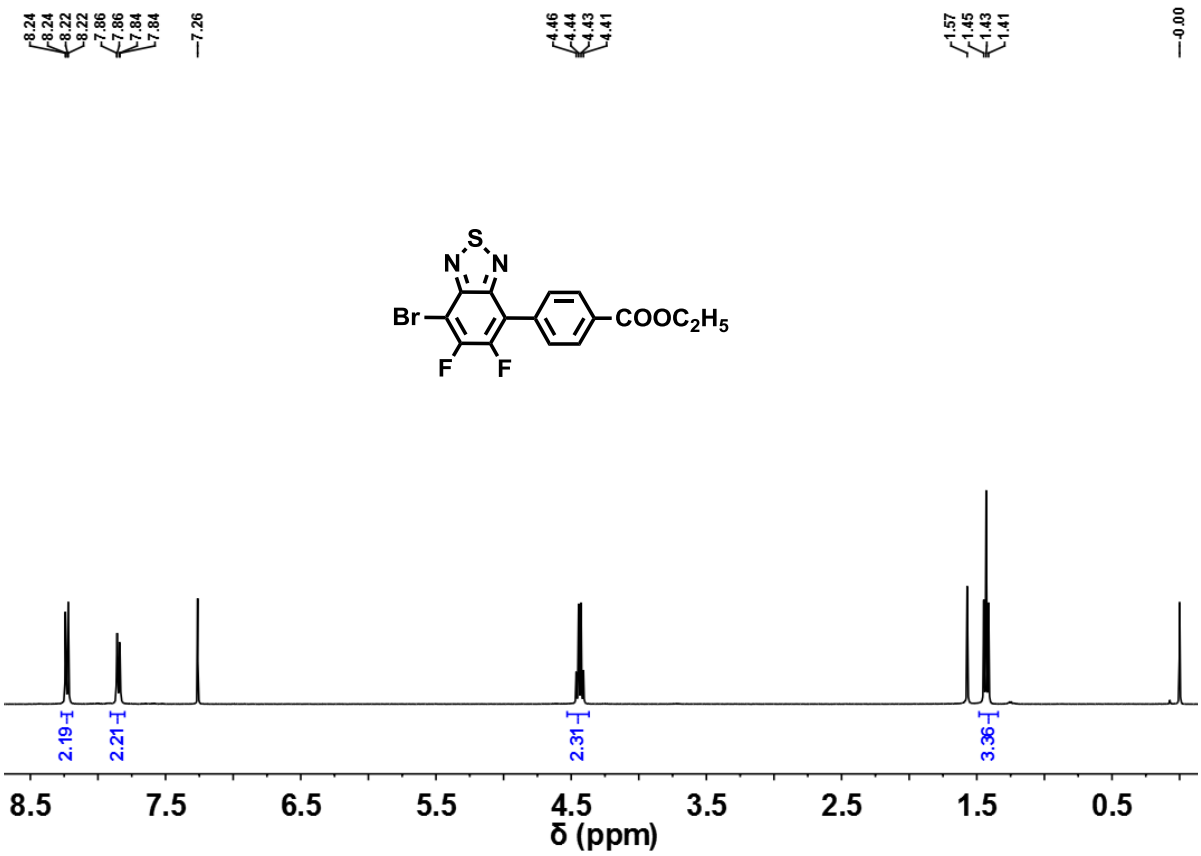

Figure S14. ^{1}H NMR spectrum of compound 10 in $CDCl_3$

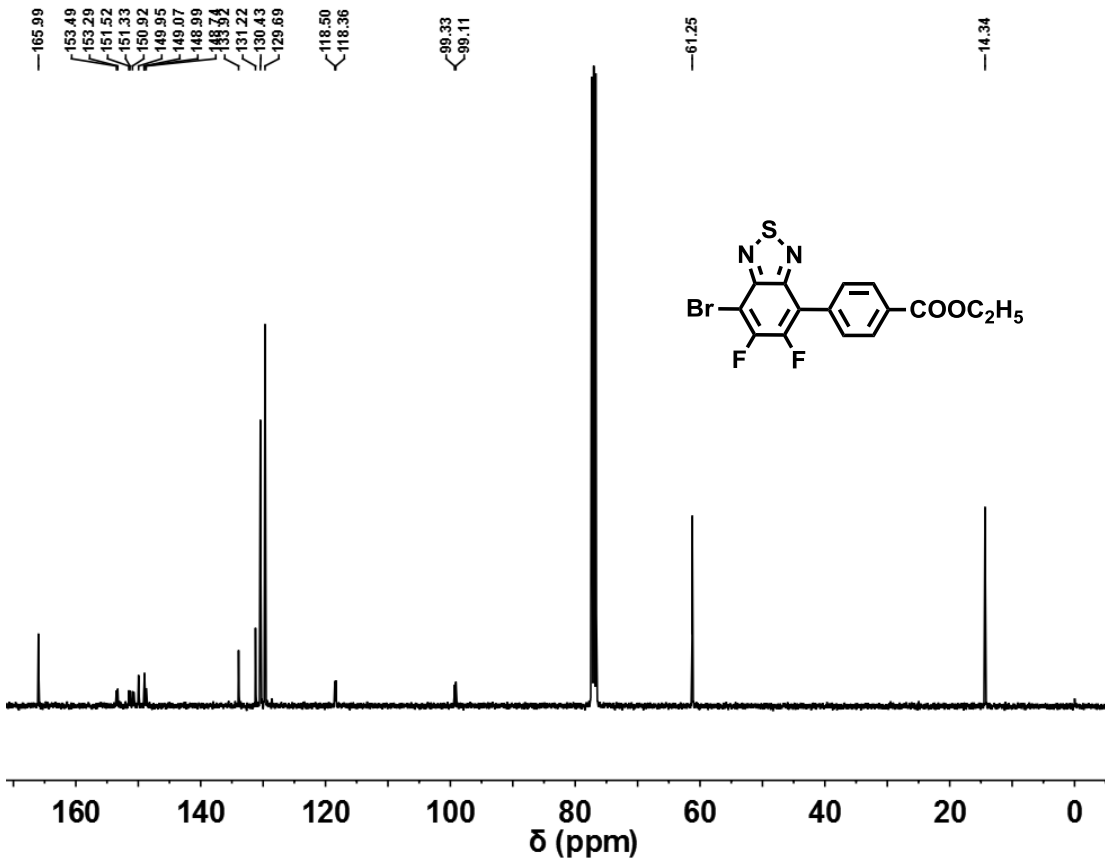

Figure S15. ^{13}C NMR spectrum of compound 10 in $CDCl_3$

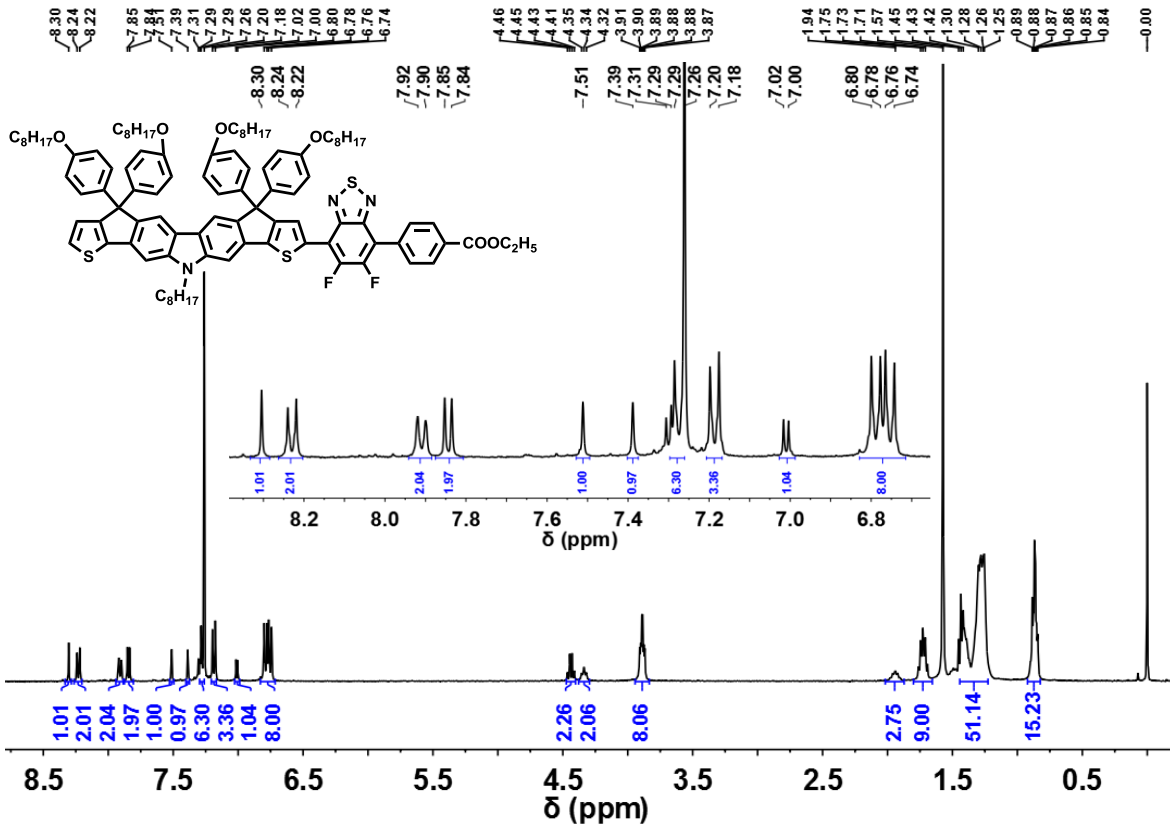

Figure S16. ^{1}H NMR spectrum of compound 13 in $CDCl_3$

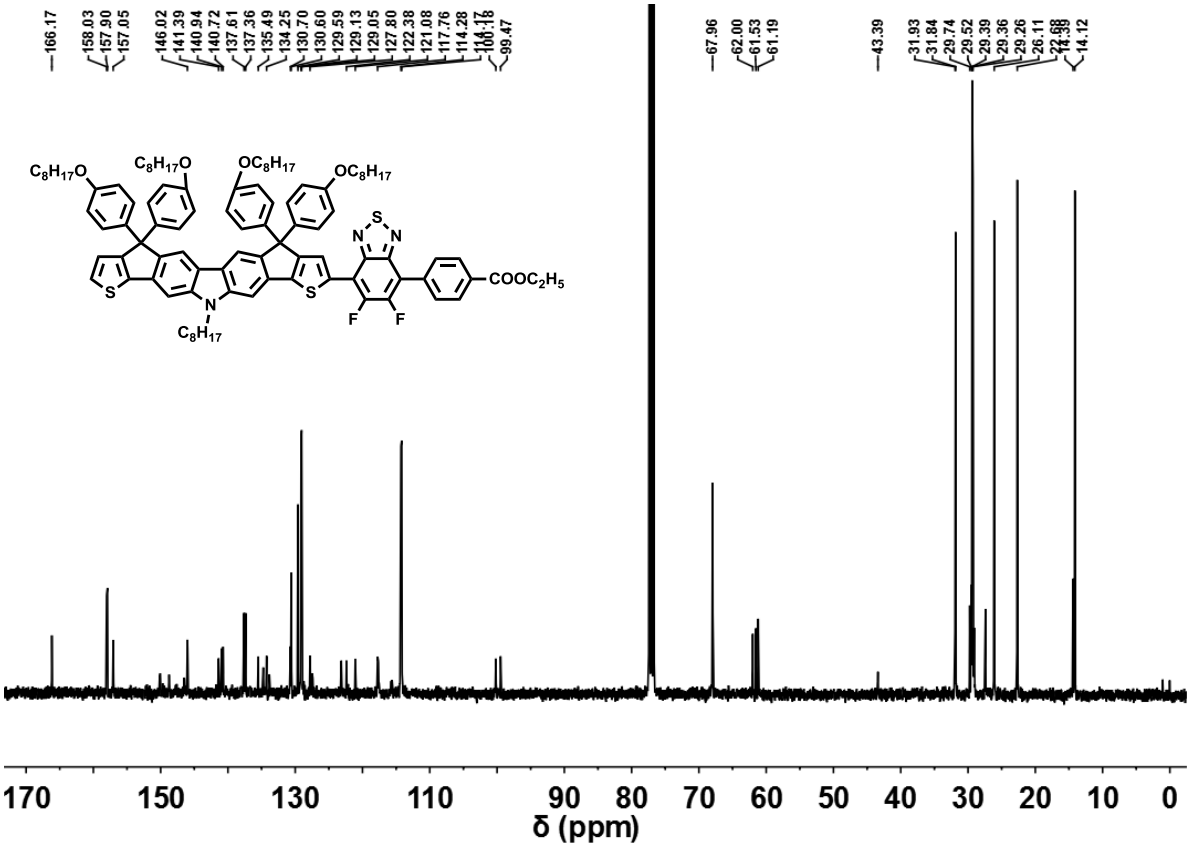

Figure S17. ^{13}C NMR spectrum of compound 13 in $CDCl_3$

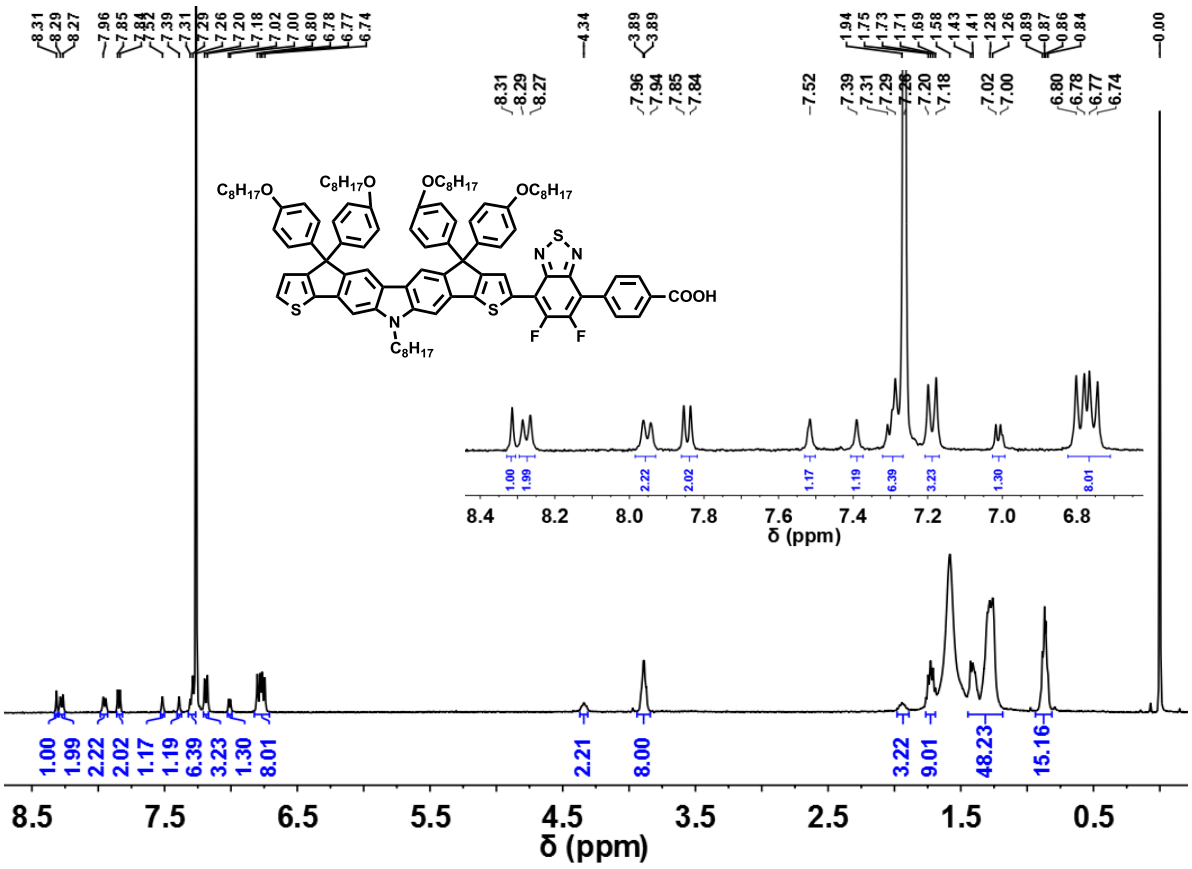

Figure S18. ^{1}H NMR spectrum of dye C2 in $CDCl_3$

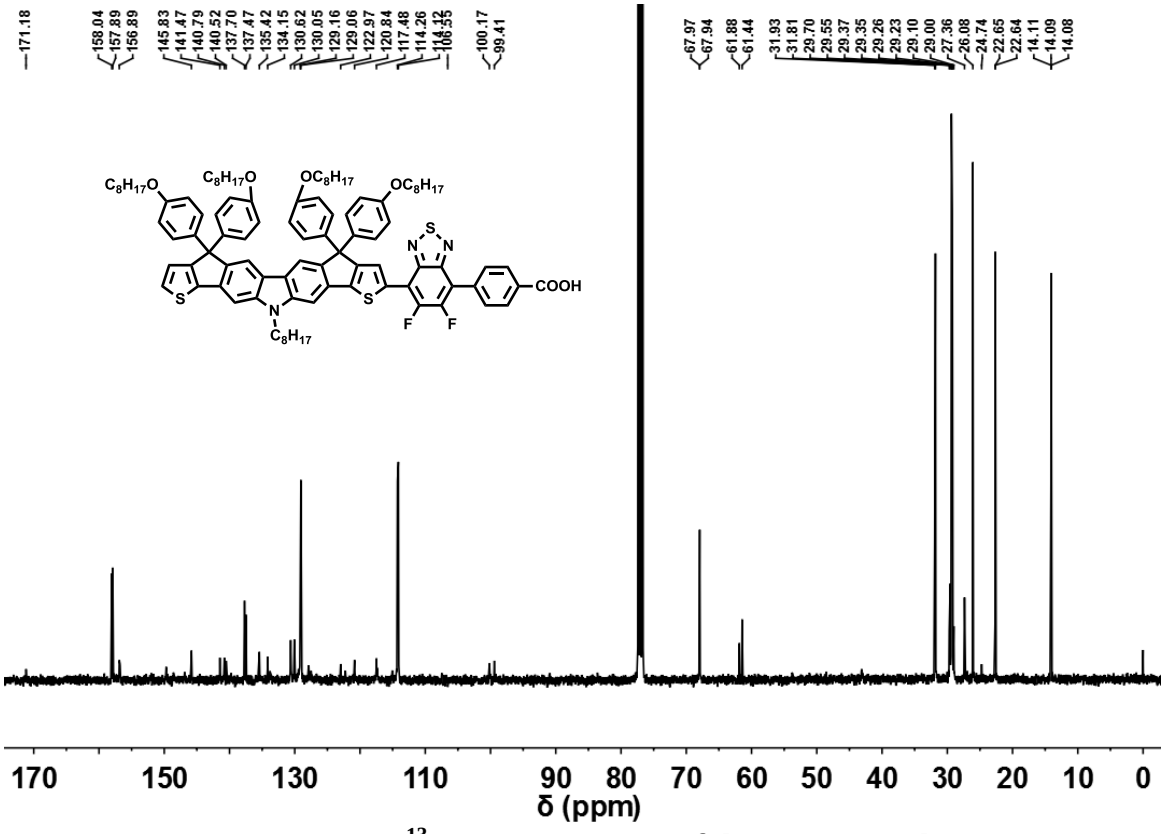

Figure S19. ^{13}C NMR spectrum of dye C2 in $CDCl_3$

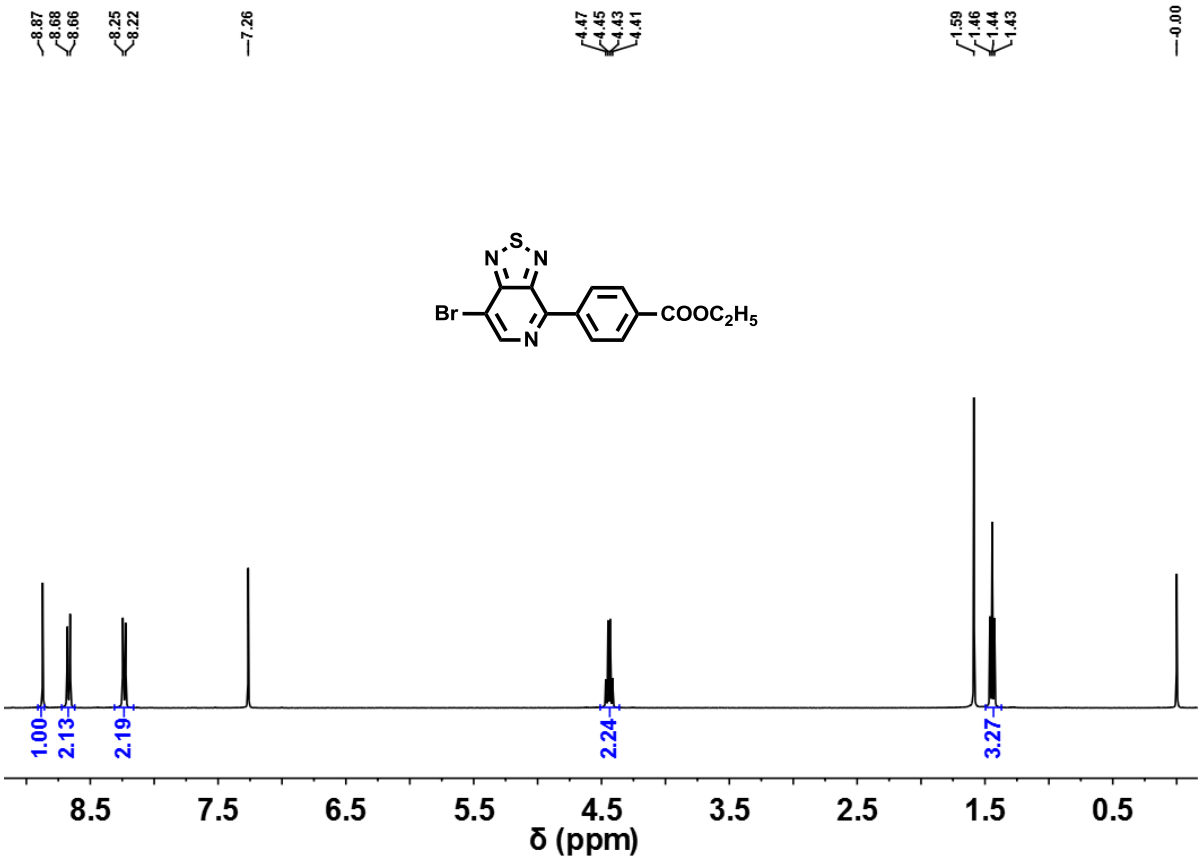

Figure S20. ^{1}H NMR spectrum of compound 11 in $CDCl_3$

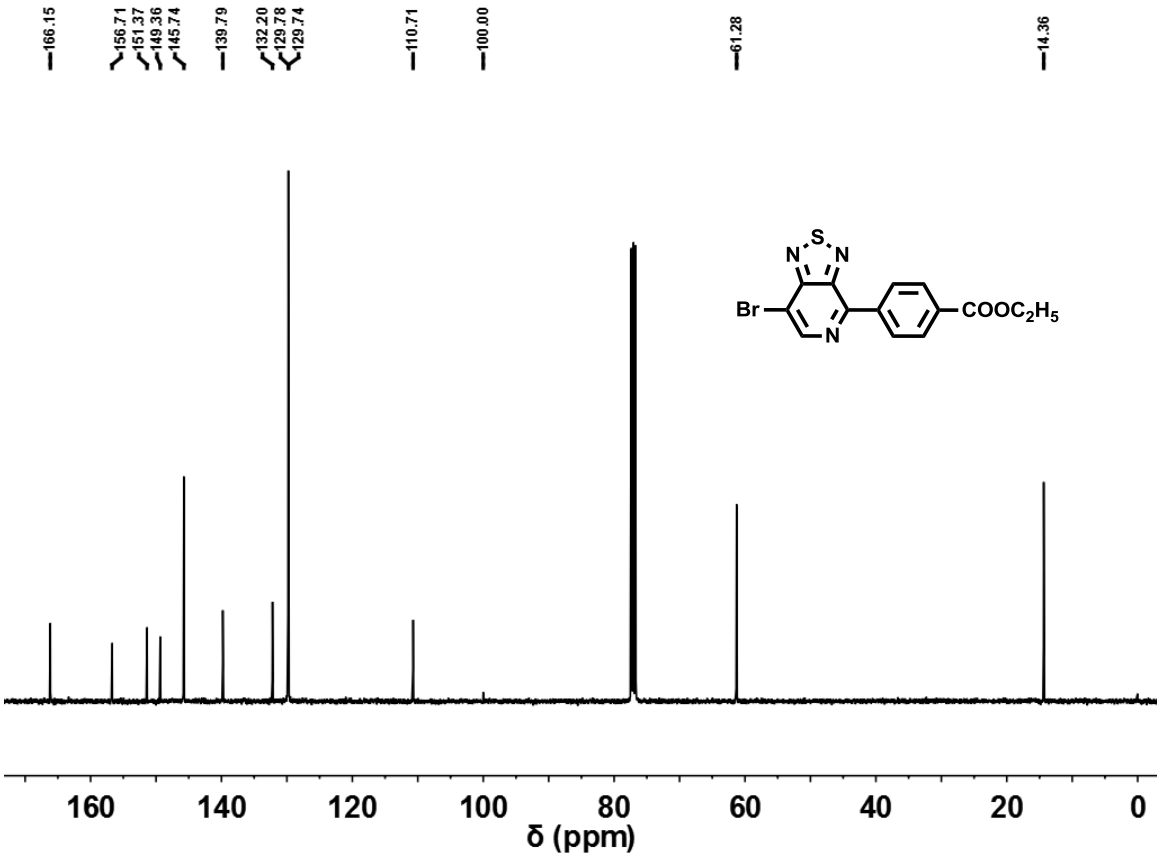

Figure S21. ^{13}C NMR spectrum of compound 11 in $CDCl_3$

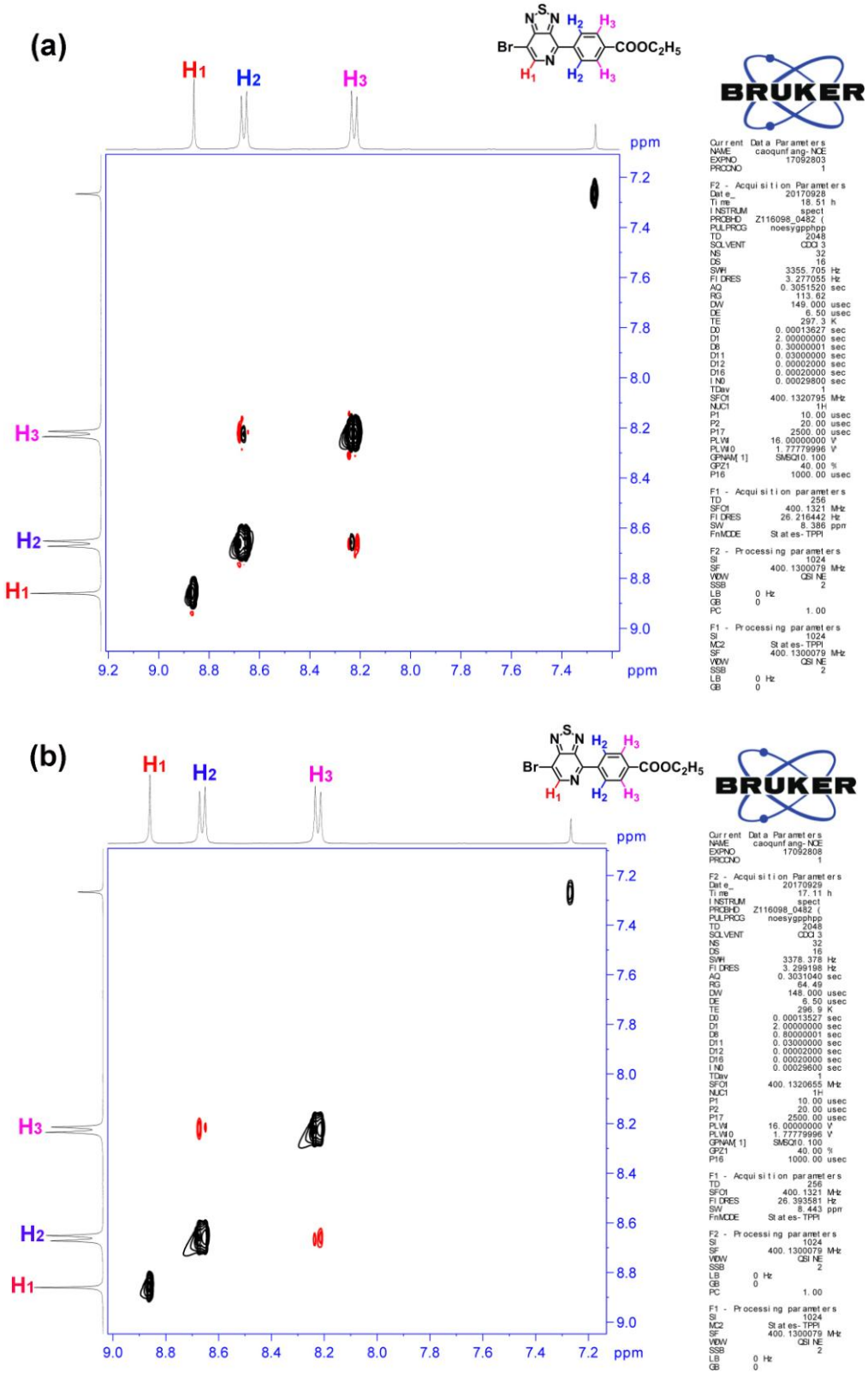

Figure S22. ^{1}H–^{1}H Nuclear Overhauser Effect spectroscopy data for compound 11 with mixing times of 0.3 seconds (a) and 0.8 seconds (b), no cross correlation peaks can be observed between the PT (H_1) and phenyl group (H_2 and H_3) protons, indicating that the proposed regioregular structure of compound 11 is right.

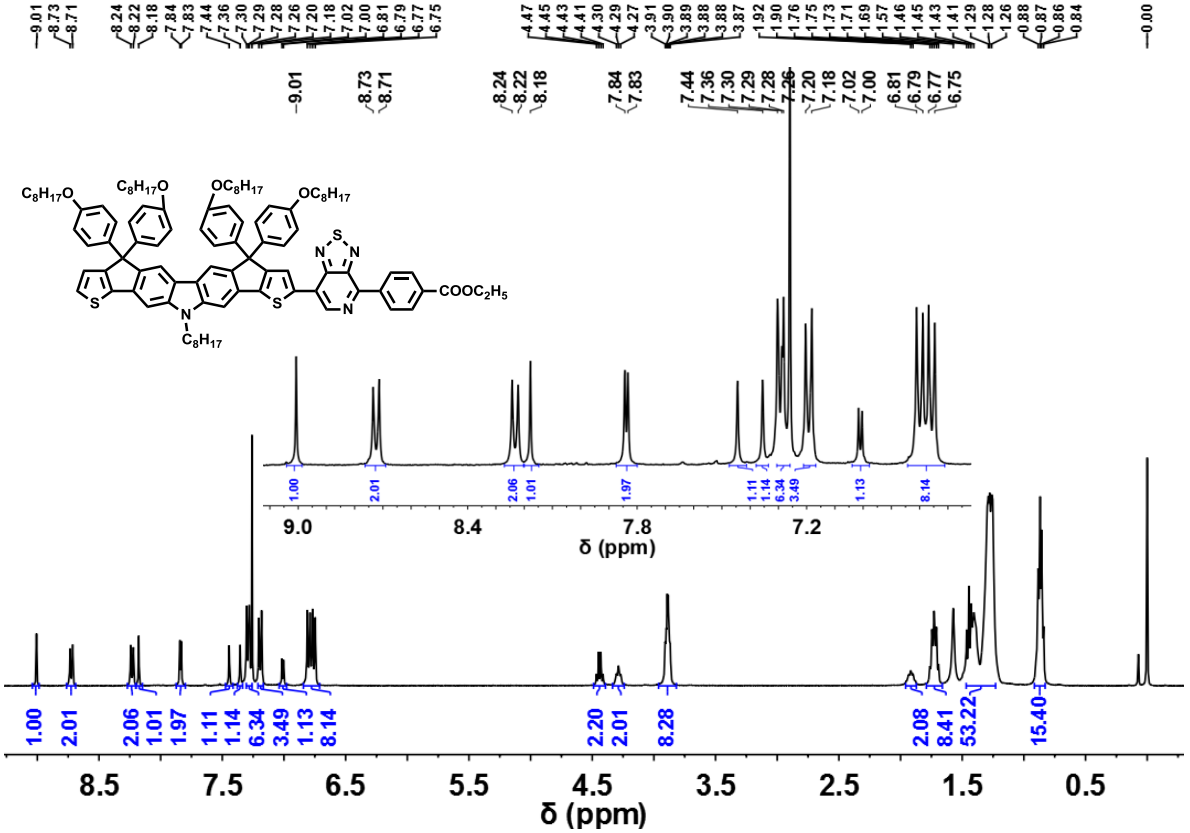

Figure S23. ^{1}H NMR spectrum of compound 14 in $CDCl_3$

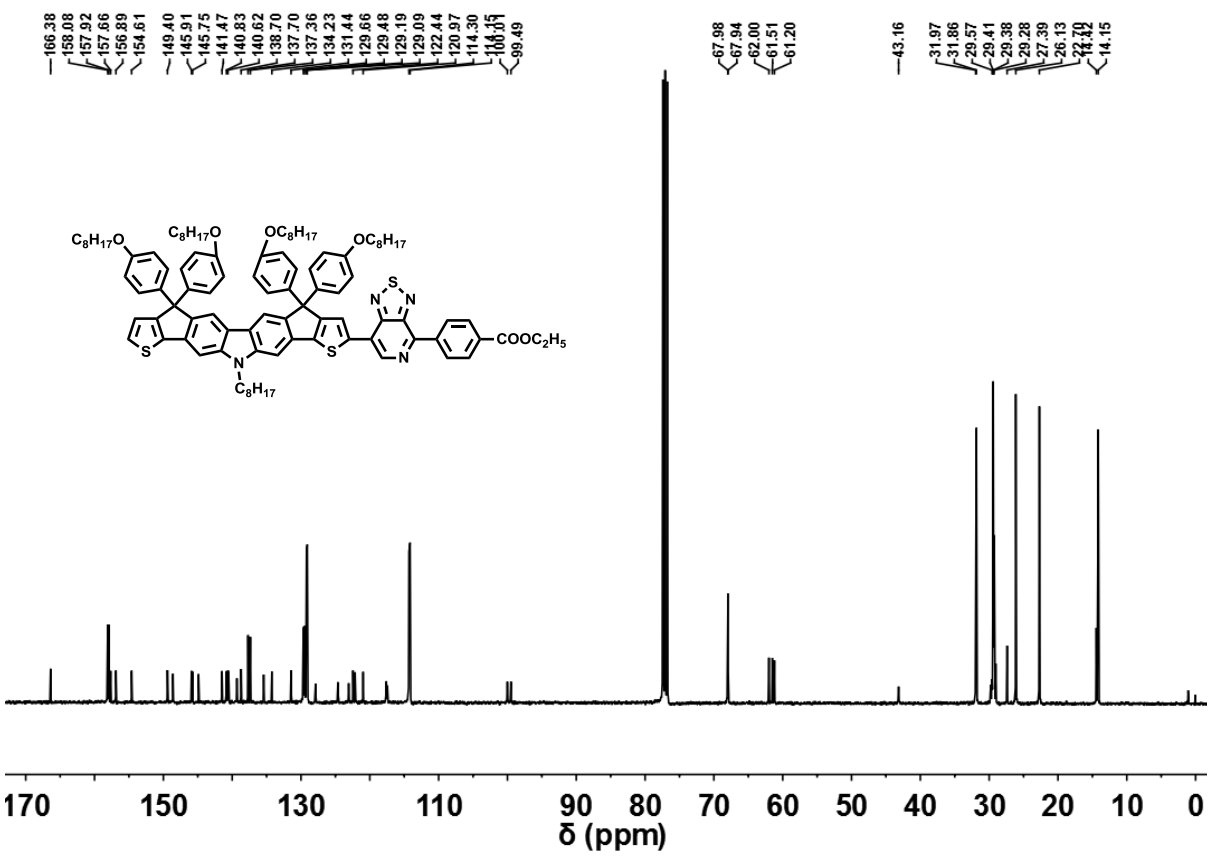

Figure S24. ^{13}C NMR spectrum of compound 14 in $CDCl_3$

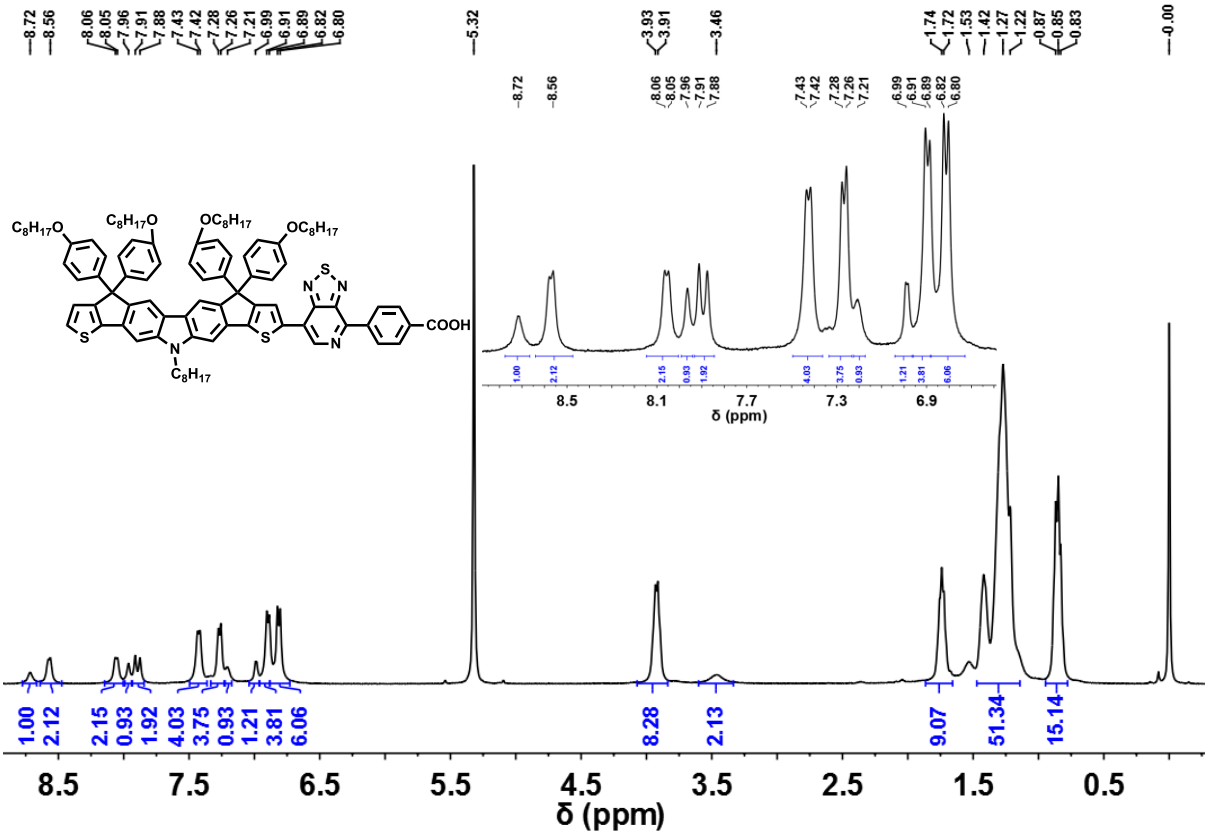

Figure S25. ^{1}H NMR spectrum of dye C3 in CD_2Cl_2

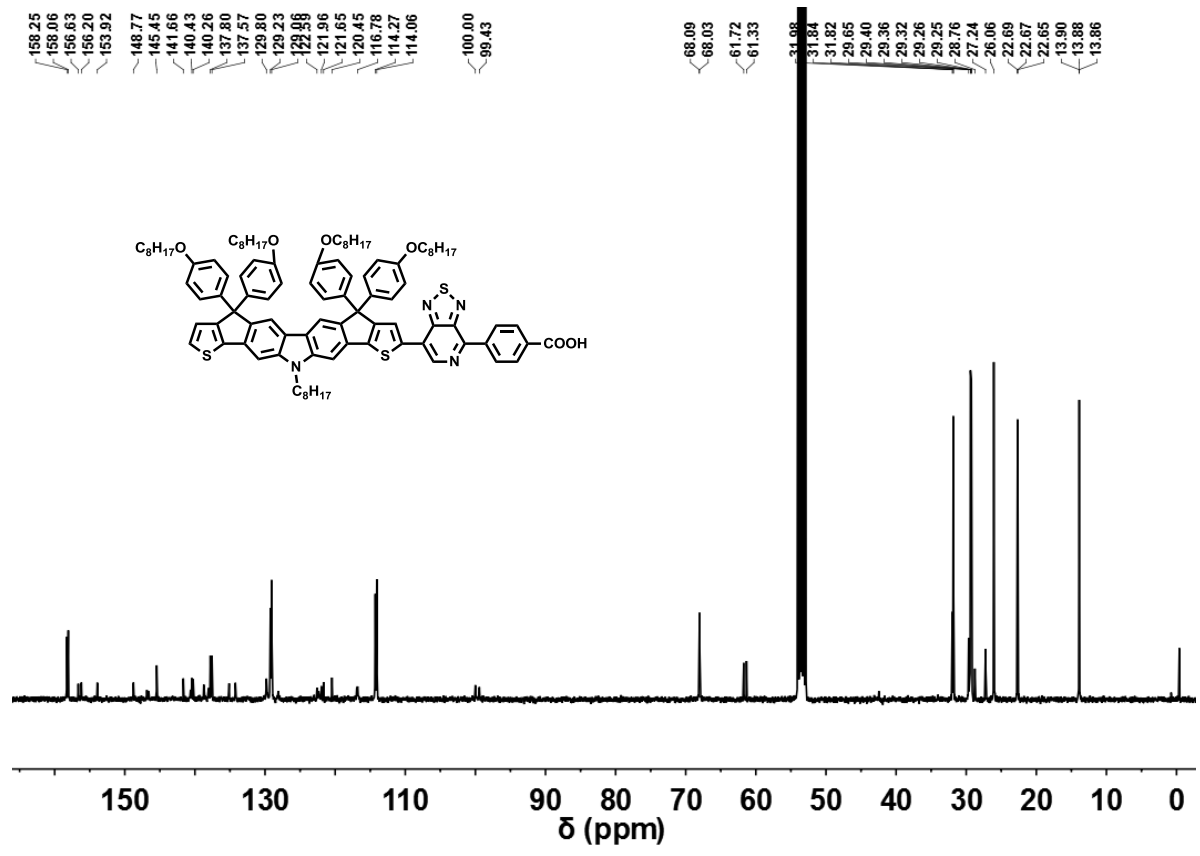

Figure S26. ^{13}C NMR spectrum of dye C3 in CD_2Cl_2

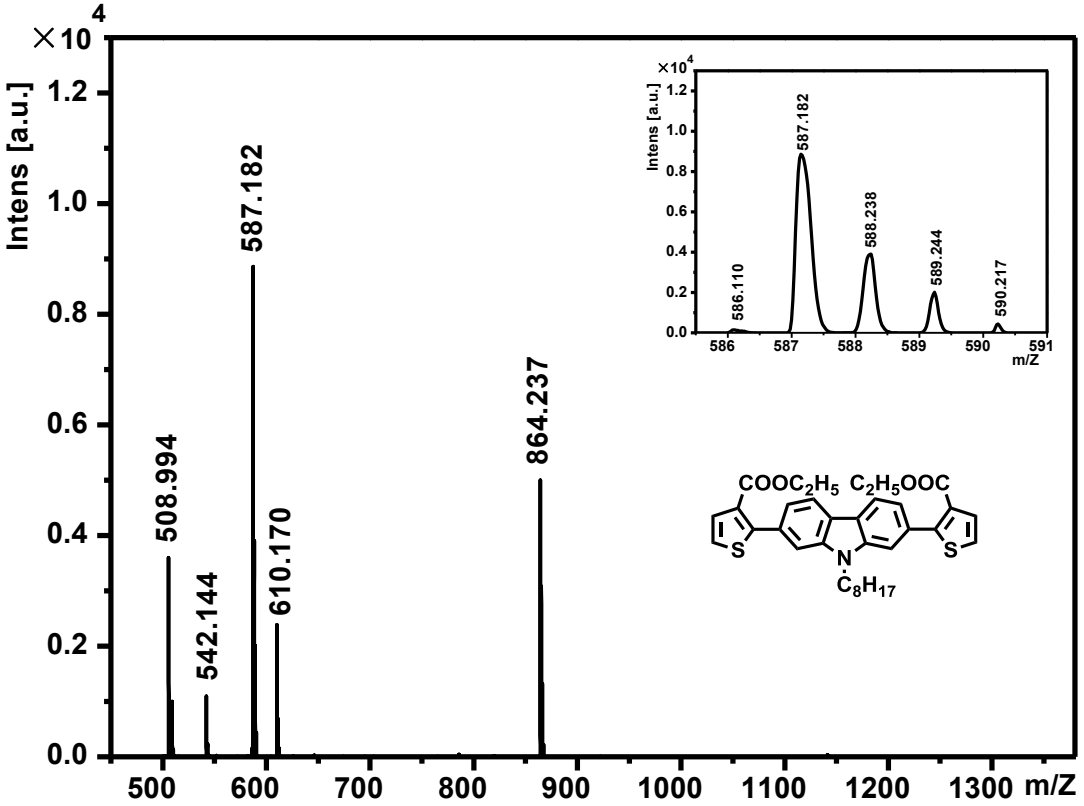

Figure S27. MS (MADI-TOF) spectrum of compound 3

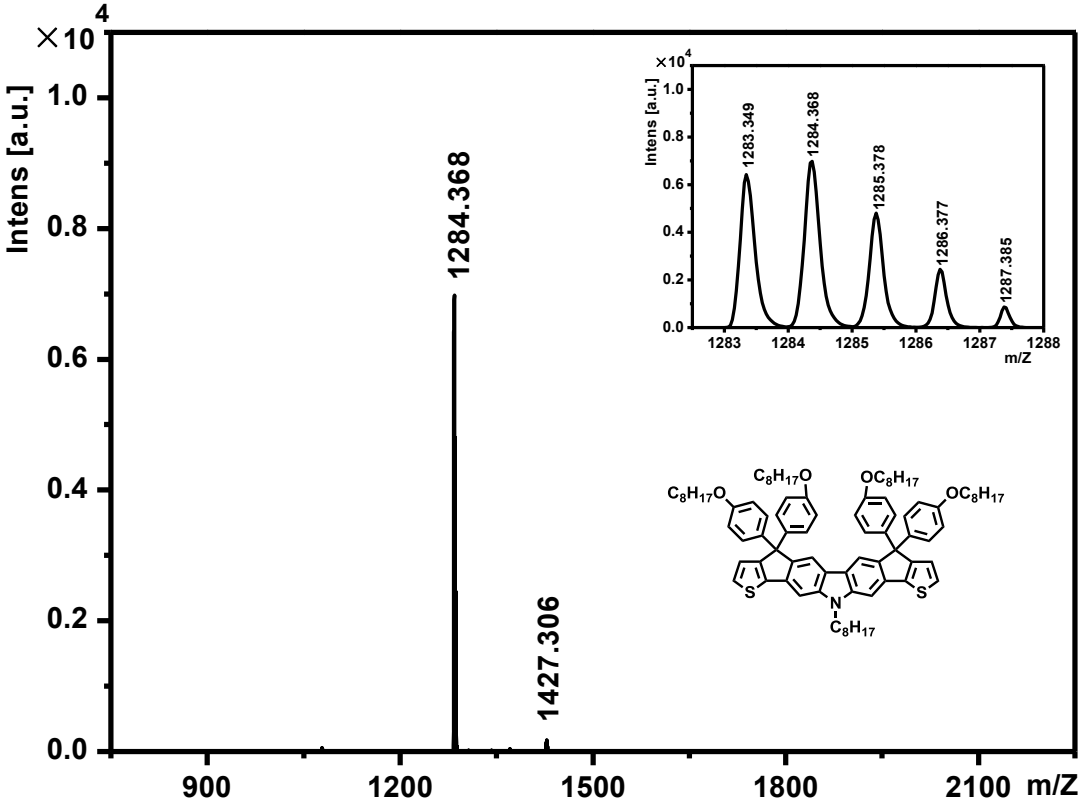

Figure S28. MS (MADI-TOF) spectrum of compound 4

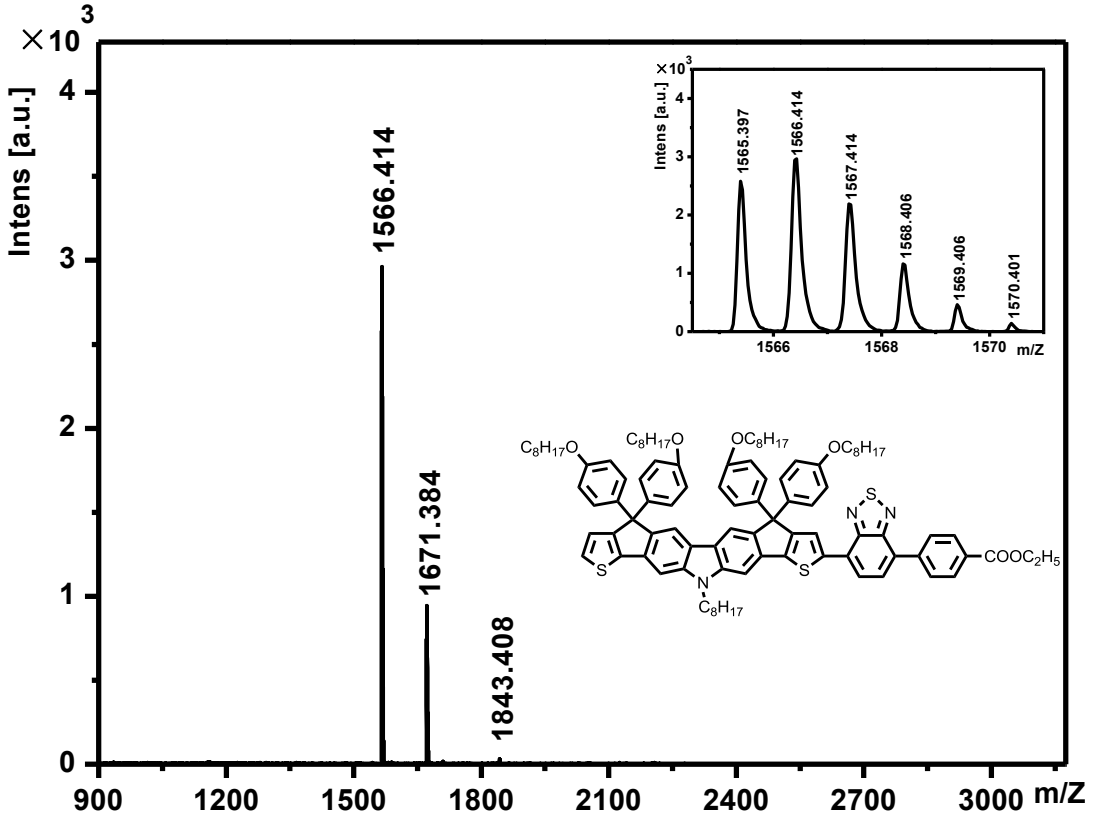

Figure S29. MS (MADI-TOF) spectrum of compound 12

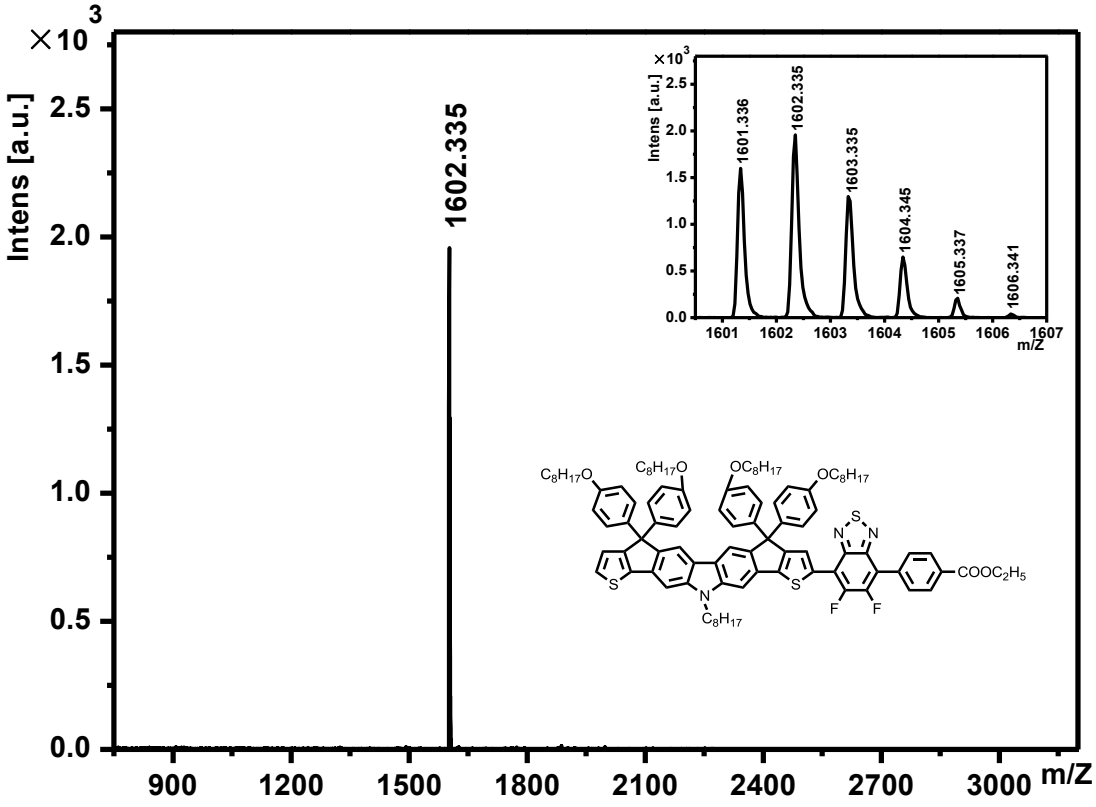

Figure S30. MS (MADI-TOF) spectrum of compound 13

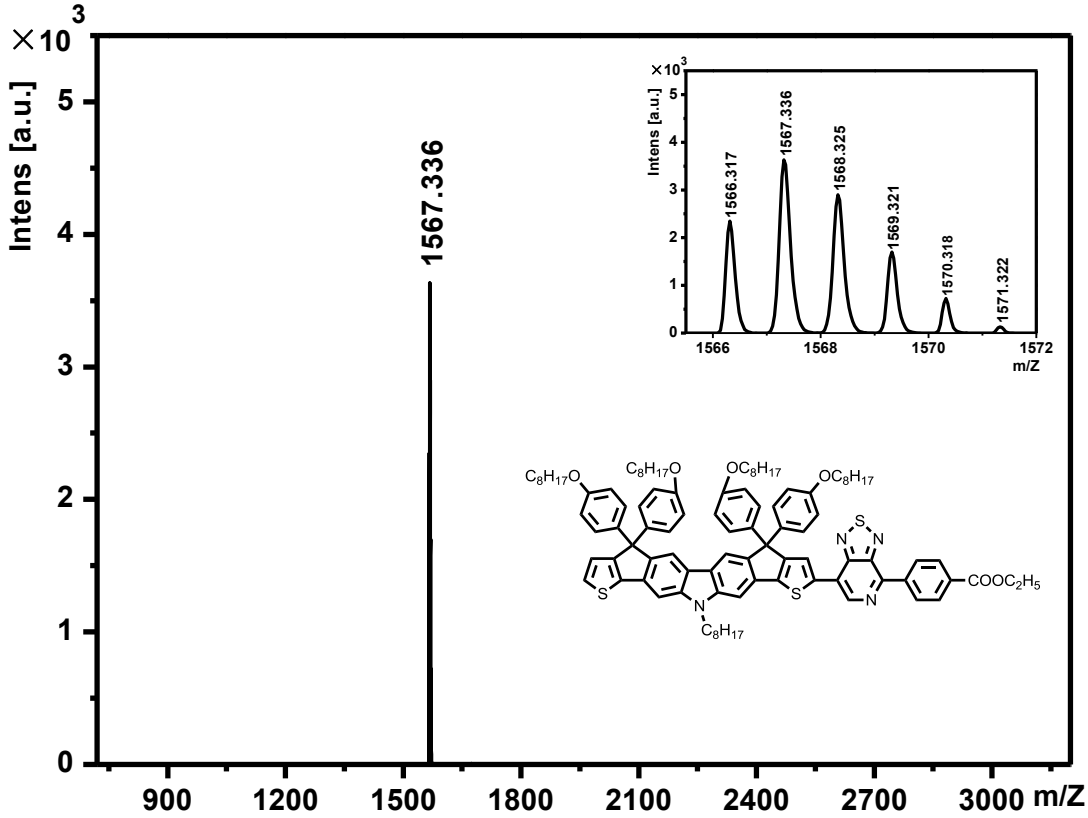

Figure S31. MS (MADI-TOF) spectrum of compound 14

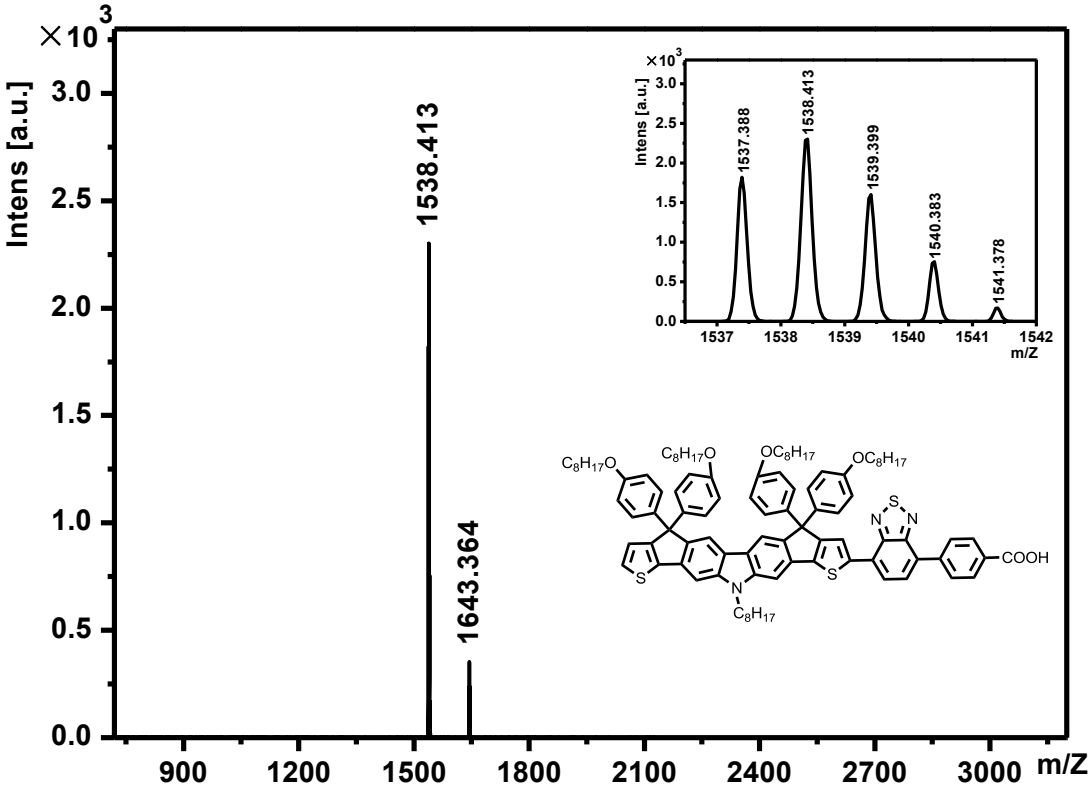

Figure S32. MS (MADI-TOF) spectrum of dye C1

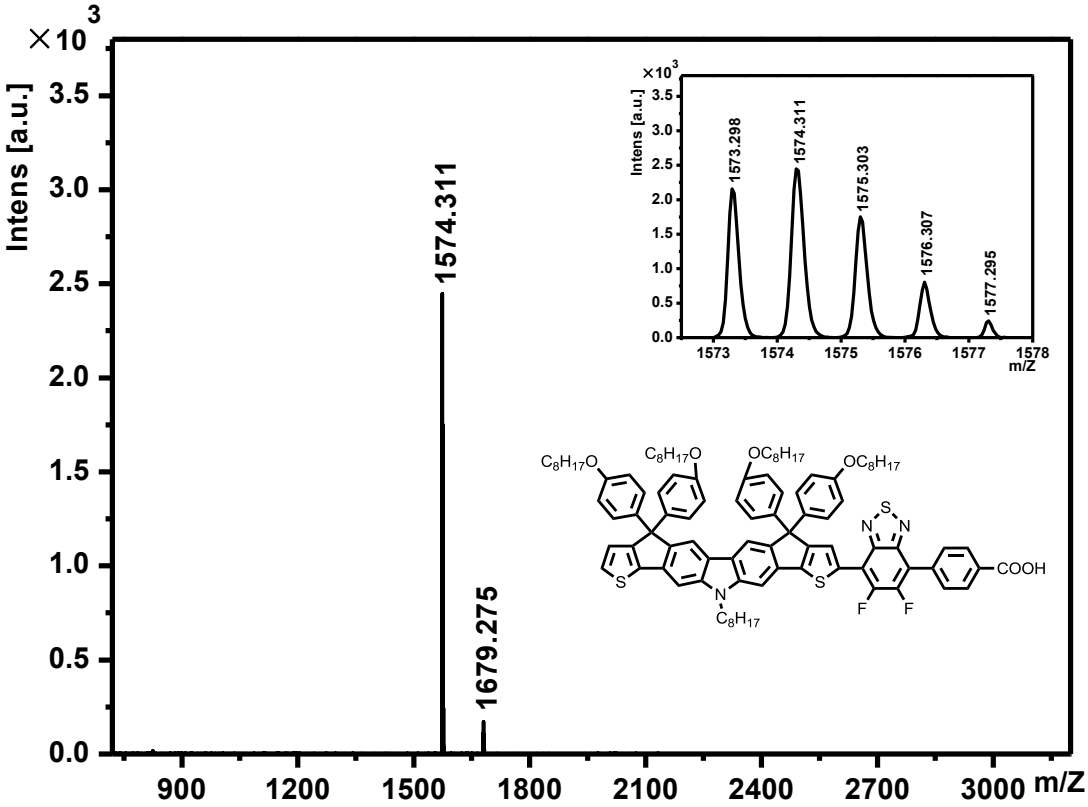

Figure S33. MS (MADI-TOF) spectrum of dye C2

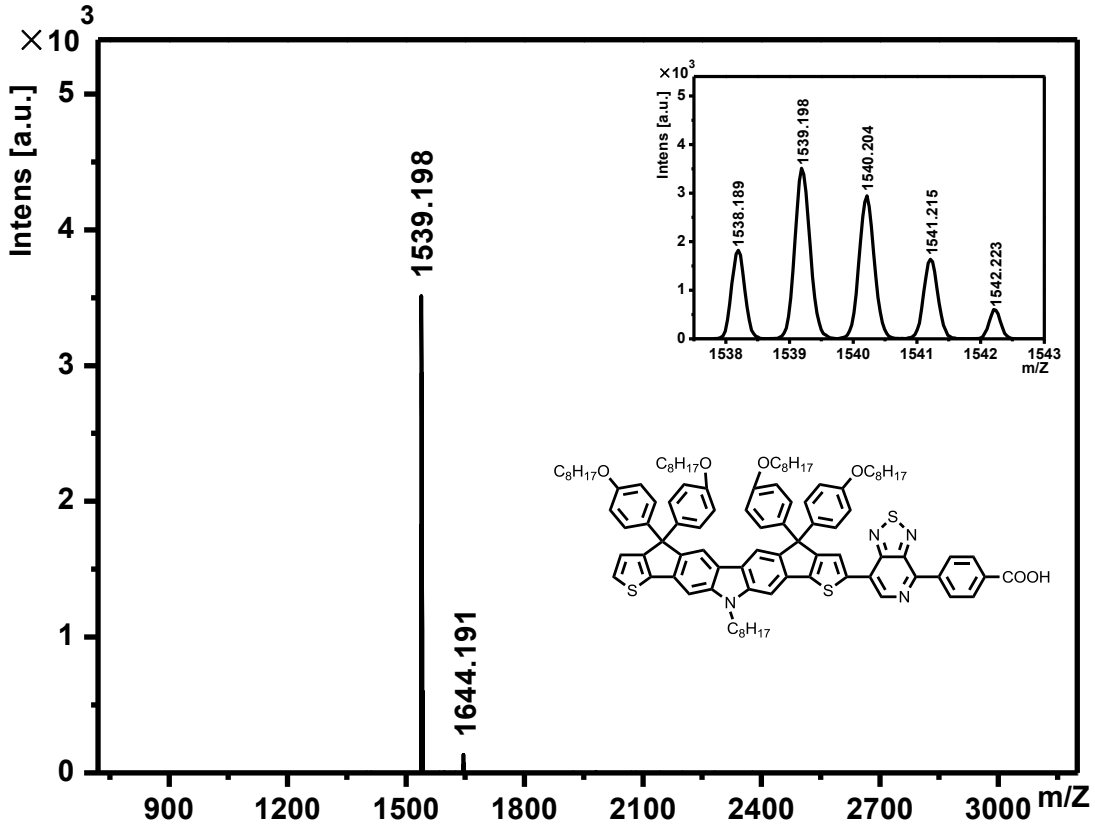

Figure S34. MS (MADI-TOF) spectrum of dye C3