Supporting information

Effect of π-bridge groups based on indeno[1,2-b]thiophene D-A-π-A sensitizers on performance of dye-sensitized solar cells and photocatalytic hydrogen evolution

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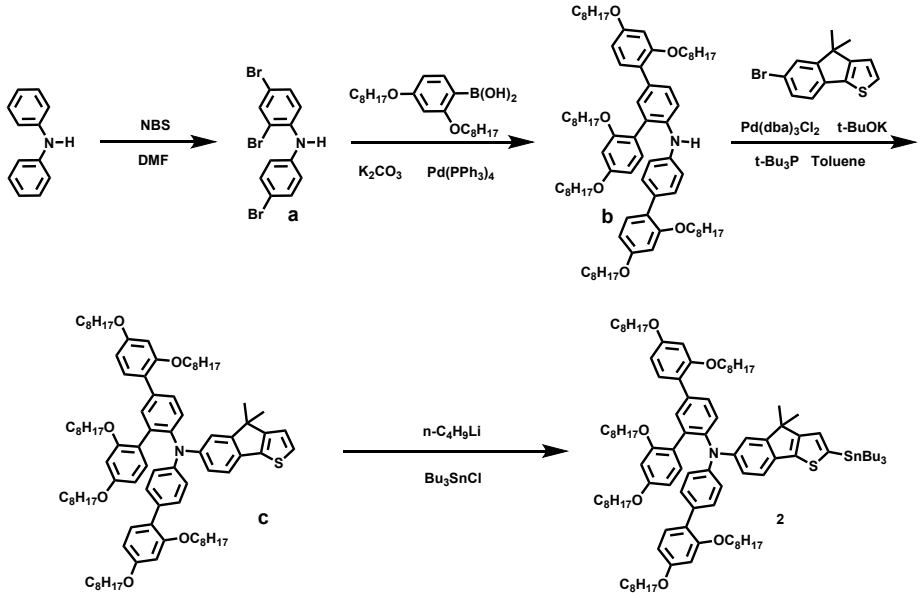
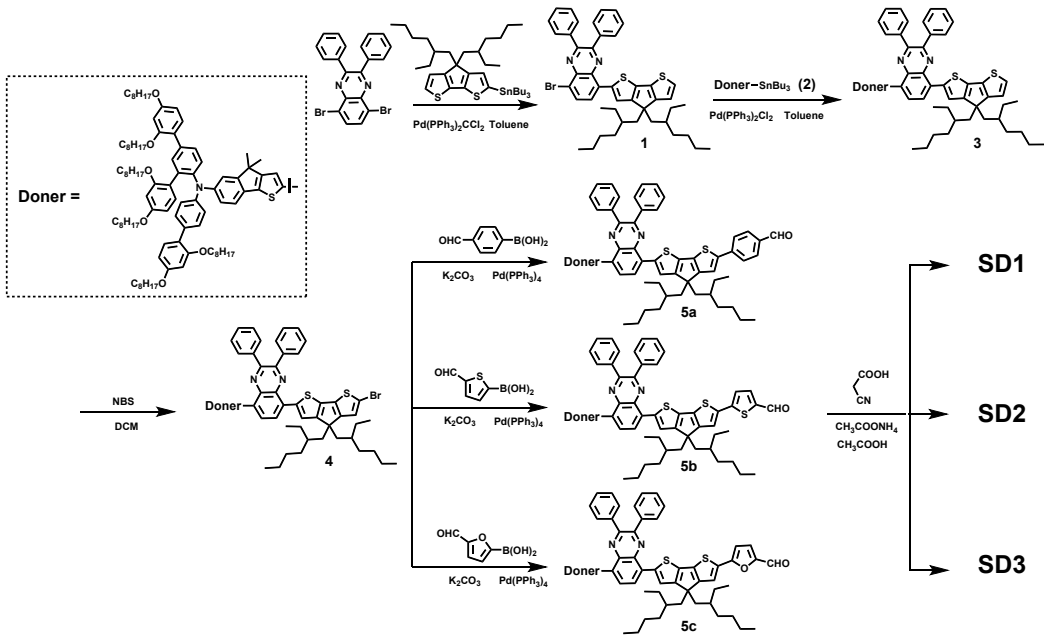
1. Materials and reagents

Fluorine-doped SnO2 conducting glass (FTO glass, transparency > 90%, sheet resistance 15 Ω/square) was obtained from the Geao Science and Educational Co. Ltd. of China. All chemicals and reagents were purchased from suppliers and used without further purification. Tetrahydrofuran (THF) was dried with sodium under argon before use. The starting materials (4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b'] dithiophen-2-yl)tributylstannane and N-(2',4'-bis((2-ethylhexyl)oxy)-[1,1'-biphenyl]-4-yl)-4,4-dimethyl-N-(2,2",4,4"-tetrakis((2-ethylhexyl)oxy)-[1,1':3',1"-terphenyl]-4'-yl)-2-(tributylstannyl)-4H-indeno[1,2-b]thiophen-6-amine (**2**) were synthesized according to literature.[1, 2]

2. Synthesis





2.1 *2,4-dibromo-N-(4-bromophenyl)aniline* (**a**)

Under an argon atmosphere, diphenylamine (5 g, 29.6 mmol) was dissolved in 100 mL DMF in a 250 mL flask. Under the ice bath, *N*-bromosuccinimide (13.33 g, 73.92 mmol) was added into the mixture and stirred at the room temperature overnight in the dark. The mixture was poured into saturated NaCl solution and stirred for 2 hours. The solid was collected by filtration and then the solid was purified by chromatography on a silica gel column with PE to give **a** as white solid (2.594 g, 27% yield). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (TMS, ppm): 7.83 (d, 2H, J = 12 Hz), 7.43 (d, 1H, J = 12 Hz), 7.39 (d, 2H, J = 8 Hz), 7.18 (d, 1H, J = 8 Hz), 6.97 (d, 2H, J = 8 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (TMS, ppm): 142.37, 140.58, 134.93, 131.78, 131.27, 121.56, 119.76, 115.57, 112.98, 111.88. HRMS (ESI, m/z): $[M-H]^+$ Calcd. for $C_{12}H_7Br_3N$: 401.8129; found: 401.8128.

2.2 *N-(2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)-2,2'',4,4''-tetrakis(octyl-oxy)-[1,1':3',1''-terphenyl]-4'-amine* (**b**)

Under an argon atmosphere, a mixture of **a** (0.53 g, 1.62 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) in THF (25 mL) was heated to 50 °C. Then 5 mL 2 M K_2CO_3 aqueous solution was added, followed by injecting a solution of (2,4-bis((2-

ethylhexyl)oxy)phenyl) boronic acid (2.14 g, 5.67 mmol) in THF slowly. The mixture was heated to 80 °C and refluxed for 8 h before cooling down to the room temperature. The raw product was extracted with CH_2Cl_2. The organic layers were combined and dried by anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was purified by chromatography on a silica gel column with CH_2Cl_2/PE (1:2 by volume) to give **b** as colorless liquid (0.945 g, 69.95% yield). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (TMS, ppm): 7.50 (d, 3H, *J* = 12 Hz), 7.45 (d, 2H, *J* = 8 Hz), 7.36 (d, 1H, *J* = 8 Hz), 7.32-7.27 (m, 2H), 7.08 (d, 2H, *J* = 8 Hz), 6.72 (s, 1H), 6.69 (d, 1H, *J*= 8Hz), 6.65-6.60 (m, 4H), 4.00-3.93 (m, 12H), 1.85-1.73 (m, 6H), 1.58-1.49 (m, 12H), 1.45-1.29 (m, 36H), 1.06-0.90 (m, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (TMS, ppm): 160.34, 130.66, 130.32, 130.19, 128.80, 128.76, 123.66, 123.59, 121.85, 116.86, 106.20, 105.13, 100.98, 100.33, 100.24, 70.56, 39.48, 39.46, 30.66, 29.21, 29.08, 24.04, 24.00, 23.16, 23.12, 23.06, 22.98, 14.17, 14.14, 14.09, 11.22, 11.16, 11.09. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{78}H_{120}NO_6$: 1166.9116; found: 1166.9125.

2.3 *N-(2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)-4,4-dimethyl-N-(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)-4H-indeno[1,2-b]thiophen-6-amine* (**c**)

Under an argon atmosphere, a mixture of **b** (4.15 g, 3.56 mmol), 6-bromo-4,4-dimethyl-4H-indeno[1,2-b]thiophene (1 g, 4.27 mmol), t-BuOK (1.35 g, 12.1 mmol) and $Pd_2(dba)_3$ (46 mg, 0.05 mmol) in toluene (50 mL) was heated to 50 °C. Then 1 mL P(t-Bu)$_3$ toluene solution was added, the mixture was heated to 80 °C and refluxed for 10 h. After cooling, the raw product was extracted using EA and water. The organic layers were combined and dried by anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was purified by chromatography on a silica gel column with CH_2Cl_2/PE (1:4 by volume) to give **c** as yellow liquid (2.5 g, 68.1% yield). ^{1}H NMR ($CO(CD_3)_2$, 400 MHz), δ (TMS, ppm): 7.35 (d, 1H, *J* = 8 Hz), 7.22 (d, 2H, *J* = 4 Hz), 7.18 (m, 2H), 7.13 (d, 1H, *J* = 8 Hz), 7.09 (d, 1H, *J* = 8 Hz), 7.04-6.96 (m, 4H), 6.84 (d, 2H, *J* = 8 Hz), 6.77 (s, 1H), 6.55 (s, 1H), 6.53 (s, 1H), 6.50-6.47 (m, 2H), 6.18 (d, 1H, *J* = 8 Hz), 6.10 (s, 1H), 3.83-3.79 (m, 8H), 3.61 (d, 2H, *J* =

4 Hz), 3.38 (s, 2H), 1.34-1.30 (m, 12H), 1.26-1.22 (m, 12H), 1.18- 1.14 (m, 36H), 0.81 -0.72 (m, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (TMS, ppm): 160.25, 159.77, 159.54, 159.50, 159.47, 157.45, 157.33, 157.26, 157.18, 143.98, 142.14, 139.86, 139.42, 136.23, 134.69, 134.35, 132.75, 132.26, 130.87, 130.72, 130.61, 130.27, 130.12, 129.61, 128.69, 123.48, 121.74, 120.73, 116.83, 106.11, 105.02, 103.97, 100.89, 100.21, 100.14, 99.23, 70.50, 39.49, 39.44, 39.36, 30.58, 29.15, 29.09, 29.00, 23.95, 23.92, 23.83, 23.11, 23.08, 23.06, 23.04, 23.00, 22.96, 22.92, 14.16, 14.14, 14.11, 14.05, 11.23, 11.17, 11.10, 11.04. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{91}H_{130}NO_6S$: 1364.9619; found: 1364.9623.

2.4 *N-(2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)-4,4-dimethyl-N-(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)-2-(tributylstannyl)-4H-indeno[1,2-b]thiophen-6-amine* (**2**)

Under an argon atmosphere, **c** (0.8 g, 0.775 mmol) was dissolved in 10 mL dry THF and injected into a 100 mL Schlenk Tube. Then put it into the refrigerator and stirred for 30 min at -78 °C. n-Bu_3Li (0.48 mL, 1.16 mmol) was injected into the mixture and stirred for 90 min. Trimethylchlorotin (0.25 g, 0.93 mmol) was added into the reaction solution and stirred for 60 min. Then take the tube out of the refrigerator and stirred at the room temperature overnight. The mixture was poured into saturated NaCl solution, the THF layer was collected by extracted and was removed under reduced pressure. Then the raw product was extracted using CH_2Cl_2 and water. The organic layers were combined and dried by anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The product was without further purification.

2.5 *5-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-8-bromo-2,3-diphenylquinoxaline* (**1**)

Under an argon atmosphere, 5, 8-dibromo-2, 3-diphenylquinoxaline (484 mg, 1 mmol) and $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol) were dissolved in anhydrous toluene (20 mL) and heated to 50 °C. Then a solution of (4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b'] dithiophen-2-yl)tributylstannane (762 mg, 1.1 mmol) was injected in toluene

slowly. The mixture was heated to 120 °C and refluxed for 3 h. After cooling, the mixture was extracted with EA and H_2O for multiple extractions. The organic layers were collected and dried by anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography with CH_2Cl_2/PE (1:8 by volume) to give **1** as orange solid (660 mg, 53% yield). 1H NMR (400 MHz, Chloroform-d) δ 8.06 (t, J = 5.9 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.67 (m, 1H), 7.22 (d, J = 4.9 Hz, 1H), 6.97 (dt, J = 4.6, 2.2 Hz, 1H), 1.96 (m, 4H), 0.96 (m, , 18H), 0.75 (t, J = 6.8 Hz, 3H), 0.67–0.57 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (TMS, ppm): 158.72, 155.92, 152.75, 152.36, 147.21, 143.27, 140.95, 138.73, 136.97, 136.75, 136.01, 133.79, 132.80, 129.23, 129.18, 128.94, 128.51, 127.95, 127.39, 127.36, 126.23, 125.40, 121.36, 114.38, 52.51, 42.26, 34.18, 33.21, 33.07, 30.91, 30.41, 29.17, 28.69, 28.65, 28.36, 27.50, 27.46, 27.14, 26.39, 26.32, 25.77, 21.73, 21.68, 16.30, 13.11, 13.04, 12.94, 12.58, 9.64, 9.58. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{45}H_{50}BrN_2S_2$: 761.2599; found: 761.2607.

2.6 *2-(8-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)-N-(2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)-4,4-dimethyl-N-(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)-4H-indeno[1,2-b]thiophen-6-amine* (**3**)

Under an argon atmosphere, compound **1** (1.06 mg, 1.39 mmol) and $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol) were dissolved in anhydrous toluene (30 mL) and heated to 50 °C. Then a solution of compound **2** (2.2 g, 1.4 mmol) was injected in toluene slowly. The mixture was heated to 120 °C and refluxed for 5 h. After cooling, the mixture was extracted with EA and H_2O for multiple extractions. The organic layers were collected and dried by anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography with CH_2Cl_2/PE (1:3 by volume) to give **3** as blue-purple solid (2.1 g, 74% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.81–7.65 (m, 6H), 7.41–7.35 (m, 4H), 7.34–7.27 (m, 4H), 7.25–7.20 (m, 2H), 7.18–7.10 (m, 2H), 7.06 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.98–6.77 (m, 4H), 6.50–6.42 (m, 4H), 6.17 (d, *J* = 9.1 Hz, 1H), 6.03(s, 1H), 3.84–3.74 (m, 8H), 3.58 (t, *J* = 4.6 Hz,

2H), 3.36 (s, 2H), 1.86 (m, 4H), 1.44–1.33 (m, 13H), 1.31–1.23 (m, 24H), 1.21 (s, 6H), 1.18 (s, 18H), 0.86 (m, 24H), 0.82–0.74 (m, 21H), 0.74–0.63 (m, 13H), 0.62–0.51 (m, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 203.40, 192.60, 190.05, 159.83, 157.25, 138.73, 130.52, 130.50, 128.33, 128.16, 125.30, 100.27, 99.19, 99.09, 96.13, 71.68, 70.54, 70.52, 55.11, 54.25, 48.60, 43.24, 39.60, 39.50, 39.49, 39.38, 35.11, 34.16, 34.14, 30.57, 29.71, 29.15, 28.58, 27.48, 27.46, 26.21, 24.06, 23.07, 22.85, 14.34, 14.14, 11.17, 10.69. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{136}H_{178}N_3O_6S_3$: 2045.2878; found: 2045.2877.

2.7 *N-(2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)-2-(8-(6-bromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)-4,4-dimethyl-N-(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)-4H-indeno[1,2-b]thiophen-6-amine* (**4**)

Under an argon atmosphere, compound **3** (1.05 g, 0.5 mmol) was dissolved in 20 mL CH_2Cl_2 in a 100 mL flask. Under the ice bath, N-bromosuccinimide (NBS) (137 mg, 0.7 mmol) was added into the mixture and stirred at the room temperature over night in the dark. The mixture was extracted with DCM and H_2O for multiple extractions. The organic layers were collected and dried by anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography with CH_2Cl_2/PE (1:4 by volume) to give **4** as purplish black solid (880 mg, 83% yield). It used for the next borate reaction without characterization.

2.8 *4-(6-(8-(6-((2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)amino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)benzaldehyde* (**5a**)

Under an argon atmosphere, compound **4** (200 mg, 0.09 mmol) and $Pd(PPh_3)_4$ (20 mg, 0.016 mmol) in THF (20 mL) was heated to 50 °C. Then 5 mL 2 M K_2CO_3 aqueous solution was added, followed by injecting a solution of (4-formylphenyl)boronic acid (28 g, 0.18 mmol) in THF slowly. The mixture was heated to 80 °C and refluxed for 8

h before cooling down to the room temperature. After cooling, the mixture was extracted with EA and H_2O for multiple extractions. The organic layers were collected and dried by anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography with CH_2Cl_2/PE (1:1 by volume) to give **5a** as fuchsia solid (110 mg, 55% yield). ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.88 (s, 1H), 8.27 (d, J = 8.3 Hz, 1H), 8.19 (dt, J = 8.2, 4.2 Hz, 1H), 8.10 (s, 1H), 7.97–7.92 (m, 1H), 7.80 (d, J = 3.6 Hz, 3H), 7.75 (t, J = 2.7 Hz, 1H), 7.69 (dd, J = 5.2, 2.1 Hz, 4H), 7.38–7.29 (m, 8H), 7.24–7.18 (m, 4H), 7.12–7.06 (m, 2H), 6.91 (dd, J = 17.5, 8.7 Hz, 3H), 6.80 (s, 1H), 6.64 (d, J = 7.5 Hz, 1H), 6.55 (dd, J = 6.8, 2.1 Hz, 2H), 6.51–6.44 (m, 2H), 6.19 (d, J = 8.6 Hz, 1H), 6.11 (s, 1H), 3.82 (t, J = 5.4 Hz, 8H), 3.63–3.57 (m, 2H), 3.44–3.37 (m, 2H), 2.04–1.98 (m, 4H), 1.65–1.51 (m, 6H), 1.28–1.20 (m, 25H), 1.18-1.14 (m, 27H), 0.83 (d, J = 7.4 Hz, 12H), 0.82–0.76 (m, 16H), 0.76–0.69 (m, 21H), 0.69–0.59 (m, 9H), 0.56–0.50 (m, 13H).^{13}C NMR (101 MHz, Acetone) δ 191.91, 161.00, 160.66, 158.24, 158.10, 152.90, 152.64, 139.67, 135.49, 131.39, 131.26, 129.01, 125.80, 123.89, 106.61, 101.03, 71.14, 71.02, 70.74, 54.89, 43.86, 40.50, 40.34, 40.24, 36.15, 31.54, 31.34, 28.33, 27.78, 26.65, 24.91, 24.83, 24.62, 24.56, 23.81, 23.75, 23.72, 23.64, 23.49, 14.54, 14.51, 14.39, 14.35, 11.79, 11.71, 11.66, 11.48, 11.18, 11.14, 11.12. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{143}H_{182}N_3O_7S_3$: 2149.3140; found: 2149.3130.

2.9 *5-(6-(8-(6-((2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)amino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)thiophene-2-carbaldehyde* (**5b**)

Compound **5b** was synthesized as fuchsia solid (120 mg, 51% yield) in a similar way to **5a** by compound **4** with (5-formylthiophen-2-yl)boronic acid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.78 (s, 1H), 8.30 (d, J = 10.2 Hz, 1H), 8.22 (t, J = 3.2 Hz, 1H), 8.11 (d, J = 2.3 Hz, 1H), 7.97 (d, J = 1.7 Hz, 1H), 7.78 (d, J = 4.0 Hz, 1H), 7.72 – 7.68 (m, 4H), 7.57 (t, J = 1.7 Hz, 1H), 7.42 (dd, J = 8.3, 2.2 Hz, 1H), 7.37 (s, 4H), 7.33 (d, J = 4.0 Hz, 4H), 7.24 – 7.18 (m, 4H), 7.10 (dd, J = 8.2, 4.8 Hz, 2H), 6.91 (dd, J = 17.3, 8.8 Hz,

3H), 6.80 (s, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.55 (dd, *J* = 7.2, 2.2 Hz, 2H), 6.48 (t, *J* = 10.4 Hz, 2H), 6.19 (d, *J* = 8.2 Hz, 1H), 6.11 (s, 1H), 3.82 (t, *J* = 5.3 Hz, 8H), 3.60 (d, *J* = 5.3 Hz, 2H), 3.41 (d, *J* = 4.7 Hz, 2H), 1.68–1.50 (m, 6H), 1.29–1.21 (m, 25H), 1.18–1.12 (m, 27H), 0.83 (d, *J* = 7.3 Hz, 12H), 0.82–0.76 (m, 15H), 0.76-0.68 (m, 21H), 0.64-0.60 (m, 12H), 0.56-0.50 (m, 9H).^{13}C NMR (101 MHz, Acetone) δ161.02, 160.77, 160.67, 159.47, 158.24, 139.67, 131.42, 131.39, 130.60, 130.56, 129.98, 129.96, 129.93, 129.14, 129.01, 124.29, 123.89, 106.64, 106.60, 101.02, 101.00, 71.20, 71.03, 71.02, 64.32, 54.92, 46.25, 43.73, 40.51, 40.46, 40.35, 40.24, 36.19, 36.16, 36.14, 35.04, 32.64, 31.35, 27.78, 26.66, 26.32, 24.91, 24.83, 24.63, 24.56, 23.82, 23.76, 23.64, 23.53, 23.49, 23.34, 14.54, 14.39, 11.71, 11.66, 11.48, 11.45, 11.19, 11.10. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{141}H_{180}N_3O_7S_4$: 2155.2704; found: 2155.2722.

2.10 *5-(6-(8-(6-((2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)amino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)furan-2-carbaldehyde* (**5c**)

Compound **5c** was synthesized as fuchsia solid (120 mg, 60% yield) in a similar way to **5a** by compound **4** with (5-formylfuran-2-yl)boronic acid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.61 (s, 1H), 8.43 (dd, *J* = 8.4, 2.0 Hz, 1H), 8.34 (dd, *J* = 8.3, 3.8 Hz, 1H), 8.25 (s, 1H), 8.10 (d, *J* = 1.4 Hz, 1H), 7.87 – 7.80 (m, 4H), 7.77 (t, *J* = 4.0 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.53 – 7.49 (m, 4H), 7.47 (d, *J* = 6.0 Hz, 3H), 7.39 – 7.31 (m, 4H), 7.23 (dd, *J* = 8.2, 4.6 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 3.7 Hz, 1H), 6.94 (s, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.68 (dd, *J* = 7.2, 2.1 Hz, 2H), 6.65–6.58 (m, 2H), 6.33 (d, *J* = 8.3 Hz, 1H), 6.25 (s, 1H), 3.95 (t, *J* = 5.3 Hz, 8H), 3.78–3.71 (m, 2H), 3.60–3.49 (m, 2H), 2.18–2.11 (m, 4H), 1.80–1.63 (m, 6H), 1.40-1.36 (m, 25H), 1.32–1.25 (m, 27H), 0.97 (d, *J* = 7.4 Hz, 12H), 0.95–0.90 (m, 15H), 0.88-0.84 (m, 21H), 0.82–0.72 (m, 9H), 0.70–0.62 (m, 12H).^{13}C NMR (101 MHz, Acetone) δ 160.06, 159.82, 157.29, 157.20, 157.15, 151.73, 151.47, 147.03, 147.01, 143.89, 140.42, 139.99, 139.28, 138.72, 136.72, 134.54, 130.48, 130.45, 129.59, 129.08, 128.21, 128.07, 126.83, 126.29, 123.11, 122.93, 120.80, 120.06, 118.89,

110.87, 109.03, 106.81, 105.64, 101.72, 100.07, 100.04, 70.26, 70.25, 70.19, 70.16, 70.06, 70.05, 69.78, 61.51, 60.25, 55.28, 53.87, 52.66, 45.29, 42.85, 39.56, 39.50, 39.47, 39.40, 39.29, 35.21, 35.18, 34.02, 33.97, 33.93, 30.74, 30.58, 30.56, 30.52, 30.40, 30.34, 27.31, 26.84, 25.70, 25.49, 25.30, 23.96, 23.89, 23.87, 23.67, 23.61, 23.50, 22.87, 22.81, 22.78, 22.70, 22.53, 13.59, 13.56, 13.53, 13.44, 13.35, 10.84, 10.75, 10.70, 10.53, 10.50, 10.19, 10.16. HRMS (MALDI, m/z): $[M+H]^+$ Calcd. for $C_{141}H_{180}N_3O_8S_3$: 2139.2933; found: 2139.3761.

2.11 *3-(4-(6-(8-(6-((2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)amino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)phenyl)-2-cyanoacrylic acid* (**SD1**)

Under an argon atmosphere, a mixture of compound **5a** (110 mg, 0.051 mmol), 2-cyanoacetic acid (85 mg, 1 mmol) and ammonium acetate (115 mg, 1.5 mmol) in 50 mL acetic acid was heated to 120 °C for 10 h before cooling down. The mixture was poured into 200 mL water and stirred for 30 min. Precipitated solid was extracted with CH_2Cl_2 and H_2O for multiple extractions. The organic layers were collected and dried by anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography with CH_2Cl_2/MeOH (20:1 by volume) to give **S6** as blue-purple solid (69 mg, 60% yield). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.41 (d, J = 7.1 Hz, 1H), 8.32 (d, J = 10.5 Hz, 2H), 8.25 (s, 1H), 8.16 (d, J = 8.4 Hz, 2H), 8.08 (s, 1H), 7.93 (d, J = 7.9 Hz, 3H), 7.83 (d, J = 6.7 Hz, 4H), 7.54 (dd, J = 8.2, 2.0 Hz, 1H), 7.50 (s, 4H), 7.46 (d, J = 6.9 Hz, 3H), 7.35 (dd, J = 8.3, 5.3 Hz, 4H), 7.23 (t, J = 8.3 Hz, 2H), 7.07 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.6 Hz, 2H), 6.93 (s, 1H), 6.79–6.75 (m, 1H), 6.68 (dd, J = 6.6, 2.0 Hz, 2H), 6.65–6.58 (m, 2H), 6.32 (d, J = 8.9 Hz, 1H), 6.24 (s, 1H), 3.95 (t, J = 5.5 Hz, 8H), 3.73 (d, J = 4.3 Hz, 2H), 3.54 (d, J = 3.9 Hz, 2H), 2.19–2.12 (m, 4H), 1.81–1.60 (m, 6H), 1.42–1.33 (m, 24H), 1.32–1.24 (m, 27H), 0.97 (d, J = 7.4 Hz, 12H), 0.96–0.89 (m, 15H), 0.87-0.83 (m, 21H), 0.82–0.70 (m, 9H), 0.70–0.63 (m, 12H).^{13}C NMR (101 MHz, Acetone-d_6) δ 160.07, 159.71, 157.29, 157.18, 156.95, 156.69, 138.73, 134.53, 131.89, 130.48, 130.44, 129.61, 128.18,

128.05, 124.88, 105.64, 100.04, 70.18, 70.06, 69.70, 53.93, 45.28, 42.91, 39.55, 39.40, 39.29, 35.20, 30.59, 30.40, 27.44, 25.72, 23.97, 23.67, 22.81, 22.56, 13.57, 13.42, 10.85, 10.71, 10.53, 10.51, 10.23, 10.20. HRMS (MALDI, m/z): $[M]^+$ Calcd. for $C_{146}H_{182}N_4O_8S_3$: 2215.3120; found: 2215.4082.

2.12 *3-(5-(6-(8-(6-((2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)amino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid* (**SD2**)

SD2 was synthesized as blue-purple solid (82 mg, 62% yield) with the same procedure for **SD1**. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.27 (s, 2H), 8.22–8.17 (m, 1H), 8.12 (d, J = 2.7 Hz, 1H), 7.95 (s, 1H), 7.77 (d, J = 4.0 Hz, 1H), 7.71–7.68 (m, 4H), 7.63 (s, 1H), 7.37–7.35 (m, 5H), 7.34–7.31 (m, 4H), 7.21 (dd, J = 8.3, 5.3 Hz, 4H), 7.10 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 6.82–6.74 (m, 2H), 6.66–6.62 (m, 1H), 6.55 (dd, J = 6.7, 2.0 Hz, 2H), 6.51–6.44 (m, 2H), 6.22–6.17 (m, 1H), 6.11 (s, 1H), 3.95 (dd, J = 7.0, 3.7 Hz, 2H), 3.91–3.85 (m, 2H), 3.82 (t, J = 5.5 Hz, 8H), 2.04–2.01 (m, 4H), 1.63–1.55 (m, 6H), 1.33–1.28 (m, 24H), 1.17-1.13 (m, 27H), 0.85–0.82 (m, 12H), 0.81–0.78 (m, 15H), 0.77-0.73 (m, 21H), 0.63–0.57 (m, 9H), 0.55–0.50 (m, 12H). ^{13}C NMR (101 MHz, Acetone) δ 206.44, 165.37, 165.21, 165.17, 160.76, 158.24, 158.19, 158.09, 137.69, 131.42, 131.38, 131.33, 130.57, 130.55, 130.54, 129.19, 129.16, 129.06, 129.02, 128.97, 127.17, 125.46, 124.91, 119.86, 117.25, 106.62, 104.04, 102.82, 101.87, 101.07, 101.02, 74.52, 71.04, 70.19, 57.69, 54.98, 43.70, 43.69, 43.66, 40.50, 40.45, 40.40, 40.34, 40.32, 40.26, 40.23, 37.03, 36.19, 35.55, 34.99, 34.95, 34.28, 34.26, 33.88, 33.87, 33.46, 32.64, 31.69, 31.67, 31.53, 31.51, 31.48, 31.46, 31.34, 30.60, 30.55, 29.08, 28.37, 28.33, 28.31, 27.78, 26.67, 25.68, 24.84, 24.70, 24.62, 24.56, 23.81, 23.72, 23.64, 23.55, 23.50, 23.33, 18.86, 14.52, 14.40, 11.71, 11.66, 11.48, 11.19, 11.14, 8.93. HRMS (MALDI, m/z): $[M]^+$ Calcd. for $C_{144}H_{180}N_4O_8S_4$: 2221.2684; found: 2221.4580.

2.13 *(Z)-3-(5-(6-(8-(6-((2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)(2,2'',4,4''-tetrakis(oct*

yloxy)-[1,1':3',1''-terphenyl]-4'-yl)amino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)furan-2-yl)-2-cyanoacrylic acid (**SD3**)

SD3 was synthesized as blue-purple solid (70 mg, 57% yield) with the same procedure for **SD1**. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.45–8.42 (m, 1H), 8.37–8.33 (m, 1H), 8.26 (t, J = 1.8 Hz, 1H), 8.12–8.09 (m, 1H), 8.02 (s, 1H), 7.85–7.82 (m, 4H), 7.57–7.53 (m, 2H), 7.52–7.44 (m, 8H), 7.37–7.32 (m, 4H), 7.24 (dd, J = 8.3, 3.5 Hz, 2H), 7.10 (d, J = 3.8 Hz, 1H), 7.02 (d, J = 8.6 Hz, 2H), 6.96–6.93 (m, 1H), 6.77 (dd, J = 8.2, 1.8 Hz, 1H), 6.68 (dd, J = 7.2, 2.2 Hz, 2H), 6.62 (ddd, J = 10.5, 8.6, 2.3 Hz, 2H), 6.35–6.31 (m, 1H), 6.25 (d, J = 2.3 Hz, 1H), 3.96 (t, J = 5.3 Hz, 8H), 3.74 (d, J = 6.4 Hz, 2H), 3.57–3.52 (m, 2H), 2.17–2.10 (m, 4H), 1.81–1.64 (m, 6H), 1.40-1.36 (m, 24H), 1.32-1.26 (m, 27H), 1.08-0.96 (m, 12H), 0.95–0.90 (m, 15H), 0.89–0.84 (m, 21H), 0.81–0.68 (m, 12H), 0.70-0.63 (m, 9H).^{13}C NMR (101 MHz, Acetone) δ 161.00, 158.26, 158.25, 158.16, 157.92, 148.30, 139.67, 131.49, 131.46, 131.42, 131.38, 131.36, 131.26, 130.54, 130.54, 129.94, 129.15, 129.01, 106.61, 101.04, 101.00, 71.24, 71.23, 71.21, 71.14, 71.13, 71.03, 71.02, 54.73, 46.24, 43.82, 40.50, 40.48, 40.45, 40.34, 40.32, 40.27, 40.24, 36.22, 36.17, 34.96, 34.91, 34.25, 32.63, 31.53, 31.51, 31.47, 31.34, 31.32, 31.28, 28.34, 27.78, 26.66, 25.69, 24.91, 24.63, 24.56, 23.81, 23.75, 23.72, 23.64, 23.49, 23.48, 23.33, 14.54, 14.51, 14.48, 14.39, 14.31, 11.79, 11.71, 11.66, 11.48, 11.45, 11.16. HRMS (MALDI, m/z): $[M]^+$ Calcd. for $C_{144}H_{180}N_4O_9S_3$: 2205.2912; found: 2205.3804.

3. Preparation of TiO_2 film (4 + 1)

Firstly, a paste consists of 20 nm anatase TiO_2 particles was screen printed onto clean FTO glass, dried at 130 °C, and then screen printed for the second layer. This procedure was repeated for four times, getting a film with a thickness of about 8 μm. Next, a paste of the scattering layer containing 400-nm sized anatase particles was deposited onto the transparent layer. The scattering layer is about 4 μm. These TiO_2 films were treated with 40 mm $TiCl_4$ aqueous solution at 70 °C for 30 min, then calcined at 450 °C for 30 min.

4. Characterization

Photophysical measurements: The UV-visible absorption spectra of the dyes and sensitized TiO_2 films were measured by a Shimdtzu UV-260 UV-Vis spectrometer. Diffuse reflectance absorption (DRS) spectra were obtained on a Varian Cary 500 spectrophotometer. The Fourier transform infrared (FTIR) spectra were recorded on NICOLET 380 spectrometer using a standard KBr pellet technique in the frequency range of 4000–400 cm^{-1}. Photoluminescence (PL) spectrum were carried out on a Hitachi F-4500 fluorescence spectrophotometer at RT. Monochromatic incident photon-to-current conversion efficiency (IPCE) of DSCs devices was obtained via the setup using a SR830 lock-in amplifier, a 300 W xenon lamp (ILC Technology) and a Gemini-180 double monochromator (Jobin-Yvon Ltd.).

Electrochemical analysis: Cyclic voltammetry (CV) curves were measured in a normal three electrode system, where Ag/AgCl electrode, Pt wire and glassy carbon were used as the reference electrode, counter electrode and working electrode, respectively.[3] 2 mg dye was dissolved in 5 mL of 0.1 M tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) in THF solution, which was used as the supporting electrolyte. Then the CV spectra were measured by a CHI650E electrochemical workstation with a scan rate of 100 mV s^{-1}. Ferrocenium/ferrocene (Fc/Fc^+) redox couple was treated as an external standard ($E^0_{Fc^+/Fc}$= 0.63 V vs. NHE). The photocurrent-voltage (*J-V*) photovoltaic characterization was performed by a Keithley 2400 source meter under standard AM 1.5 solar simulator (450 W xenon lamp). The

electrochemical impedance spectra (EIS) of DSCs devices with cobalt electrolyte was performed by a Zahner IM6e Impedance Analyzer. The frequency range was 0.1 Hz-100 KHz and applied bias was from -0.35 V to -0.85 V with the alternating signal of 5 mV.

Photoelectrochemical measurements: The EIS and transient photocurrents (I-t) of dye-sensitized TiO_2 photocatalytic hydrogen evolution system were measured in a three electrode system, which was quite similar to the above CV test system, except that dye-sensitized TiO_2 membrane electrode was used as a working electrode. And in order to further simulate the real conditions of photocatalytic hydrogen evolution, photoelectrochemical measurements were performed with 0.1 M phosphate buffered solution (PBS) as the supporting electrolyte and 300 W Xe lamp (light intensity 100 mW cm^{-2}). The photocurrent intensity of dye-sensitized TiO2 membrane electrodes were surveyed at 0.1 V vs Ag/AgCl with the light on and off. EIS was measured over the frequency range of 10^2 Hz to 10^6 Hz with a modulation amplitude of 0.01 V at the open circuit voltage in dark state.

5. LUMO levels for the dyes

LUMO levels for the dyes obtained by equation $E_{LUMO} = E_{HOMO} - E_{0-0}$, where band gap ($E_{0-0}$) was calculated by the equation $E_{0-0} = \frac{1240}{\lambda_{int}}$ λ_{int} is the wavelength at cross point of the normalized emission and absorption spectrum, see Figure S15.

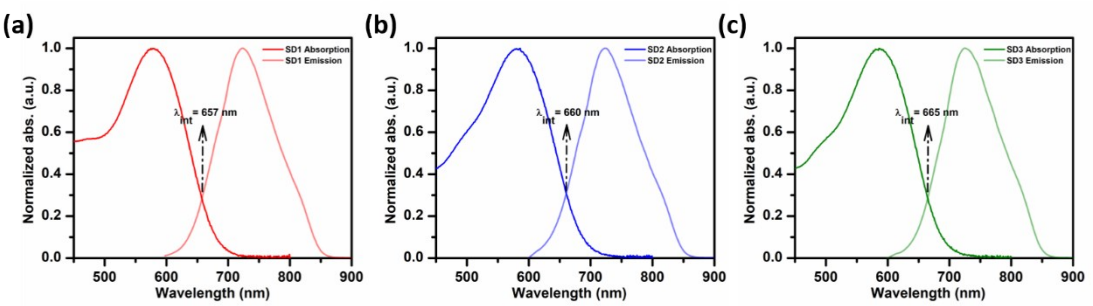


Fig. S1 Normalized absorption and emission spectra of **SD1**, **SD2** and **SD3** in THF solution.

6. DFT calculation

Methodology: Geometry optimizations were carried out on the molecules in the gas phase, using the software Avogadro[4] to enter the starting geometry. The molecules were distorted to form a variety of conformers which were then allowed to optimize, in order to find the global minimum on the potential energy surface. Frequency calculations were performed on all the optimized geometries to distinguish whether they were minima or transition states on the potential energy surfaces. Where transition state geometries were found, the bond lengths and angles were distorted in the direction of the vibration and the structure was reoptimised until only positive frequencies were obtained. All calculations were carried out using the Gaussian 09 program[5] with the B3LYP functional and UB3LYP[6] and the standard 6-31G(d) basis set. The MO transition assignment was (CI coefficient)^2/0.5*100%.

Table S1. TD-DFT calculated energies and compositions of selected transitions

Dye		E (nm)	*f* (oscillator strength)	Composition
SD1	S0-S1	787.02	**1.0720**	(48.08%) HOMO→LUMO (1.63%) HOMO→LUMO+1
	S0-S2	656.42	**0.3308**	(3.14%) HOMO-1→LUMO (43.69%) HOMO→LUMO+1
	S0-S3	590.77	**0.7326**	(44.70%) HOMO-1→LUMO (3.72%) HOMO→LUMO+1
	S0-S4	519.19	**0.0252**	(1.93%) HOMO-4→LUMO (1.54%) HOMO-2→LUMO (42.01%) HOMO-1→LUMO+1
SD2	S0-S1	818.99	**1.0603**	(48.91%) HOMO→LUMO
	S0-S2	664.14	**0.4981**	(6.75%) HOMO-1→LUMO (40.81%) HOMO→LUMO+1
	S0-S3	606.35	**0.6790**	(41.82%) HOMO-1→LUMO (7.12%) HOMO→LUMO+1
	S0-S4	528.35	**0.0088**	(3.85%) HOMO-4→LUMO (7.17%) HOMO-2→LUMO (35.28%) HOMO-1→LUMO+1
SD3	S0-S1	788.77	**1.0949**	(48.35%) HOMO→LUMO (1.37%) HOMO→LUMO+1

	S0-S2	651.97	**0.3007**	(4.92%) HOMO-1→LUMO (42.10%) HOMO→LUMO+1
	S0-S3	593.76	**0.6585**	(43.22%) HOMO-1→LUMO (5.49%) HOMO→LUMO+1
	S0-S4	521.20	**0.0234**	(2.37%) HOMO-4→LUMO (3.24%) HOMO-2→LUMO (39.88%) HOMO-1→LUMO+1

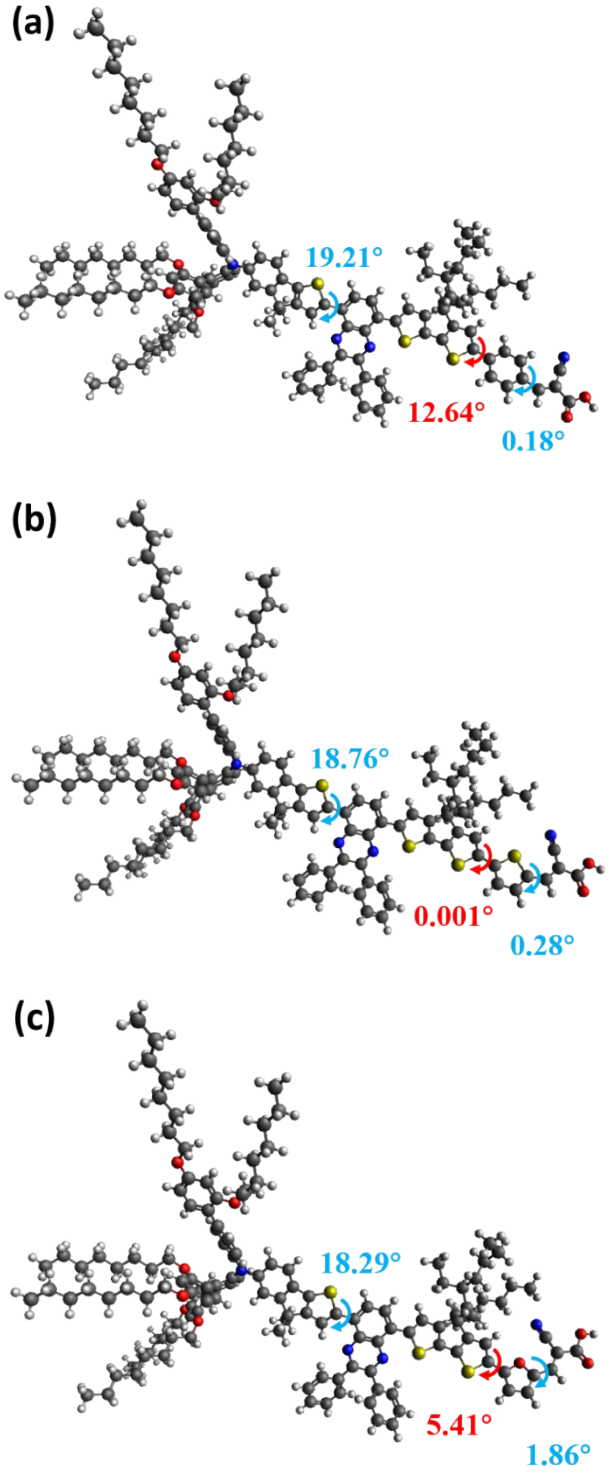


Fig. S2 Optimized molecular structures with dihedral angles of the dyes **SD1**, **SD2** and **SD3**.

7. Calculated apparent quantum yield (AQY) at different wavelengths

AQY for H_2 evolution at monochromatic light irradiation obtained by band-pass filters (λ = 435, 450, 500, 550, 630, 700 nm) was estimated as Equation (1)[7]

$$AQY = \frac{2 \times \text{Number of evolved } H_2 \text{ molecules}}{\text{Number of incidident photons}} \times 100\%$$

$$= \frac{2 \times C \times N_A}{S \times P \times t \times \frac{\lambda}{h \times c}} \times 100\%$$

Where, C is the H_2 production amount (μmol) per hour; N_A is the Avogadro constant (6.02×10^{23} mol^{-1}); S is the irradiation area (12.56 cm^2); P is the monochromatic light intensity (W cm^{-2}) (P is detected by optical power meter); t is the light irradiation time (1 h); λ is the wavelength of the monochromatic light (nm); h is the Plank constant (6.626×10^{-34} J s); c is the speed of light (3×10^8 m s^{-1}).

Table S2. Calculated AQY at different wavelengths

Wavelength (nm)	Light intensity (10^{-3} W cm^{-2})	[a]Amount of H_2 (μmol h^{-1})			AQY (%)		
		SD1	**SD2**	**SD3**	**SD1**	**SD2**	**SD3**
435	2.124	2.03	6.68	4.01	1.16	3.83	2.29
450	2.062	2.51	4.25	4.33	1.43	2.42	2.47
500	2.506	9.06	9.01	8.67	3.83	3.80	3.66
550	2.585	12.3	16.3	12.9	4.58	6.07	4.79
630	2.325	13.4	16.8	14.8	4.85	6.06	5.33
700	2.518	7.42	10.6	9.26	2.02	2.88	2.52

a. Reaction conditions: 20 mg photocatalyst, 5 g AA, 50 mL deionized water.

Calculate AQY at different wavelengths with **SD2** as an example:

λ = 435 nm

$$AQY\ (\%) = \frac{2 \times 6.68 \times 10^{-6} \times 6.02 \times 10^{23}}{12.56 \times 2.124 \times 10^{-3} \times 3600 \times \frac{435 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}}} \times 100\% = 3.83\%$$

λ = 450 nm

$$AQY\ (\%) = \frac{2 \times 4.25 \times 10^{-6} \times 6.02 \times 10^{23}}{12.56 \times 2.062 \times 10^{-3} \times 3600 \times \frac{450 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}}} \times 100\% = 2.42\%$$

λ = 500 nm

$$AQY\ (\%) = \frac{2 \times 9.01 \times 10^{-6} \times 6.02 \times 10^{23}}{12.56 \times 2.506 \times 10^{-3} \times 3600 \times \frac{500 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}}} \times 100\% = 3.80\%$$

λ=550 nm

$$AQY\ (\%) = \frac{2 \times 16.3 \times 10^{-6} \times 6.02 \times 10^{23}}{12.56 \times 2.585 \times 10^{-3} \times 3600 \times \frac{550 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}}} \times 100\% = 6.07\%$$

λ = 630 nm

$$AQY\ (\%) = \frac{2 \times 16.8 \times 10^{-6} \times 6.02 \times 10^{23}}{12.56 \times 2.325 \times 10^{-3} \times 3600 \times \frac{630 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}}} \times 100\% = 6.06\%$$

λ = 700 nm

$$AQY\ (\%) = \frac{2 \times 10.6 \times 10^{-6} \times 6.02 \times 10^{23}}{12.56 \times 2.518 \times 10^{-3} \times 3600 \times \frac{700 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}}} \times 100\% = 2.88\%$$

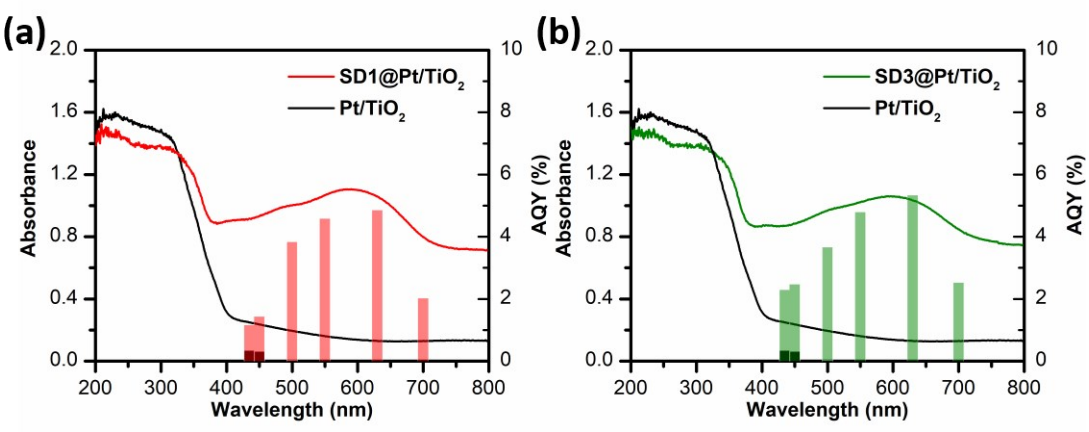


Fig. S3 Comparison of AQY values and DRS spectra of **SD1**@Pt/TiO_2, **SD3**@Pt/TiO_2 and Pt/TiO_2 under optimal photocatalytic conditions.

8. The fitted fluorescence lifetime for all samples

Table S3. The fitted fluorescence lifetimes and corresponding amplitudes of photoinduced charge carriers in **SD1**, **SD2**, **SD3**, **SD1**-Pt/TiO_2, **SD2**-Pt/TiO_2 and **SD3**-Pt/TiO_2

Sample	τ1 [ns] （Rel.%）	τ2 [ns] （Rel.%）	τ [ns]	χ2
SD1	1.514 (92.99)	4.705 (7.01)	1.74	2.115
SD2	1.205 (88.40)	3.211 (11.6)	1.44	1.542
SD3	1.358 (98.09)	12.191(1.91)	1.57	1.666
SD1-Pt/TiO_2	1.076 (75.65)	2.514 (24.35)	1.43	2.393
SD2-Pt/TiO_2	0.544 (81.35)	2.158(18.65)	0.85	3.129
SD3-Pt/TiO_2	0.613 (65.68)	1.803 (34.32)	1.02	3.776

9. Characterization of intermediate compounds and SD1-SD3

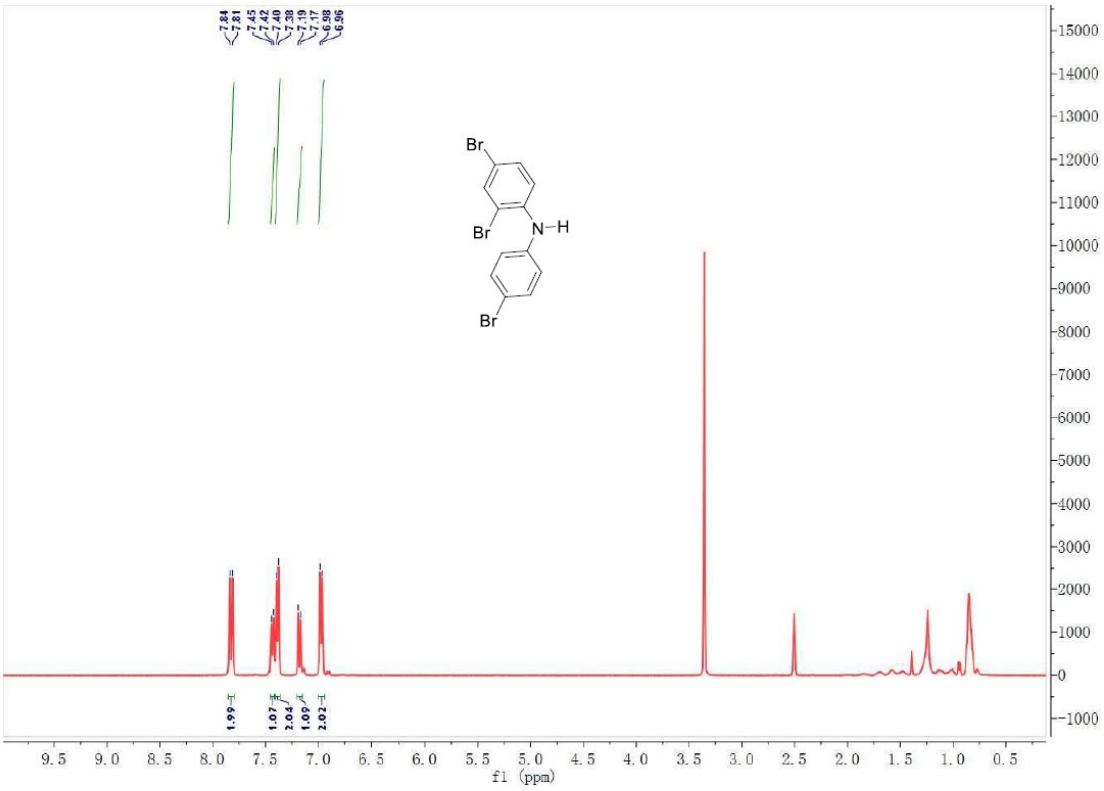


Fig. S4 ^{1}H NMR spectrum of compound a in DMSO-$d_{6.}$

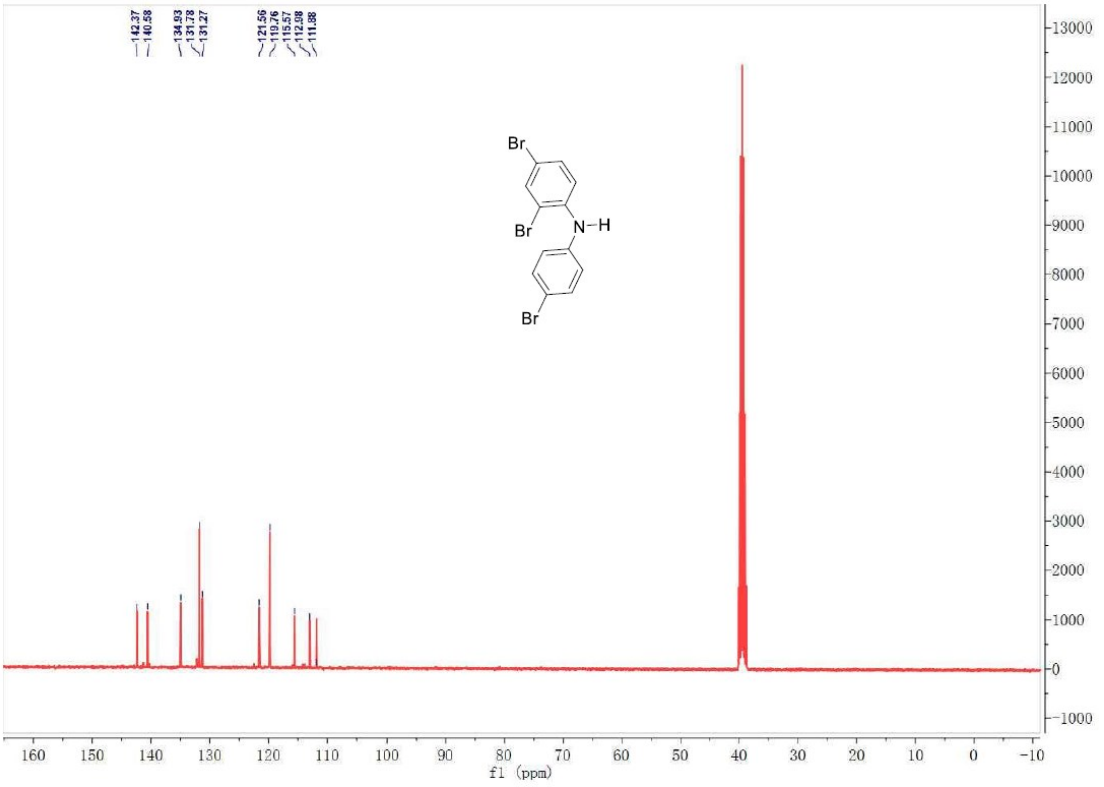


Fig. S5 ^{13}C NMR spectrum of compound **a** in DMSO-$d_{6.}$

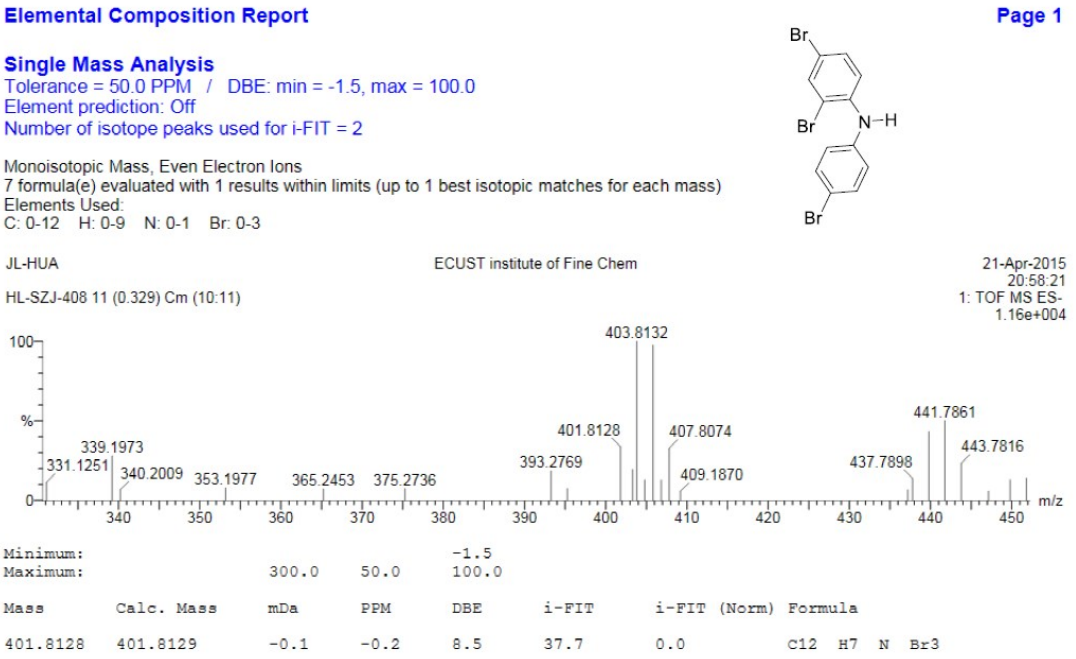


Fig. S6 HRMS of compound **a.**

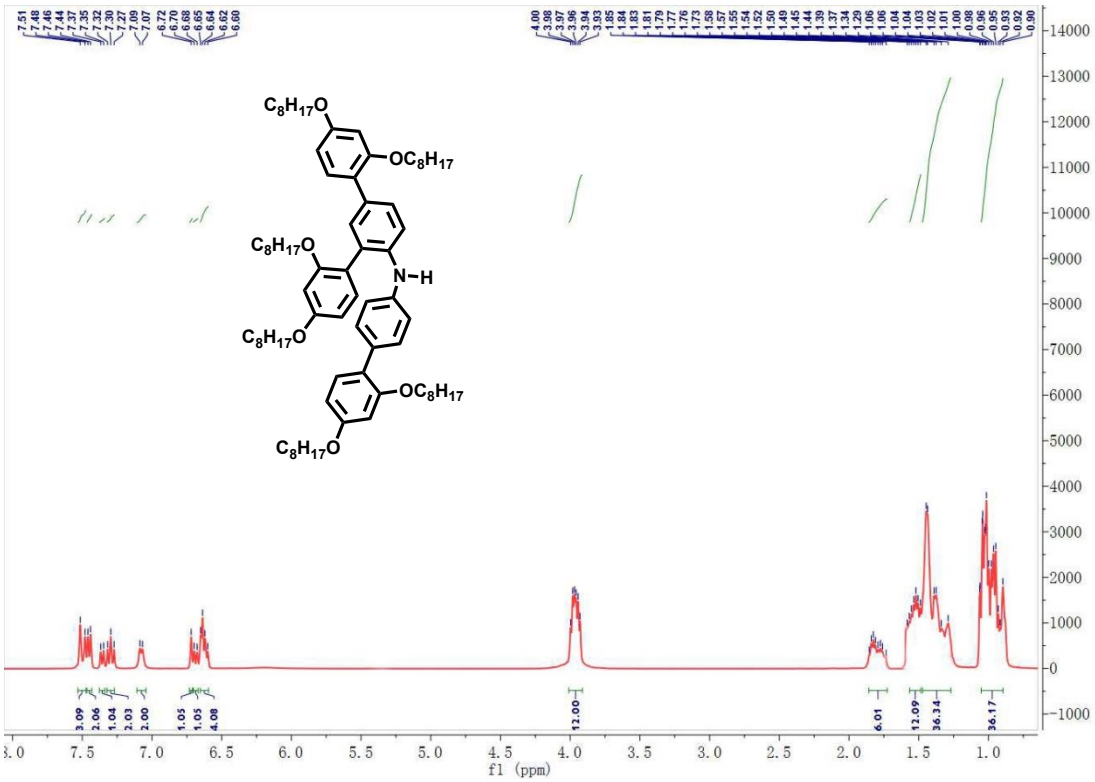


Fig. S7 ^{1}H NMR spectrum of compound **b** in $CDCl_3$.

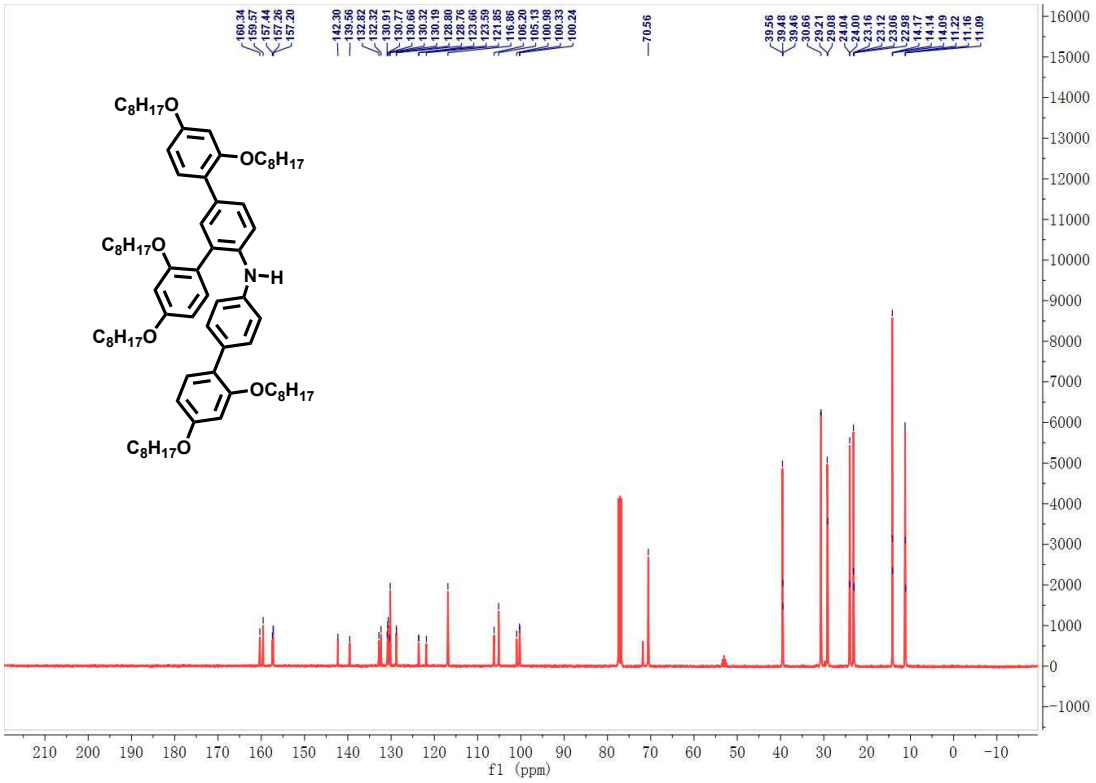


Fig. S8 ^{13}C NMR spectrum of compound **b** in $CDCl_3$.

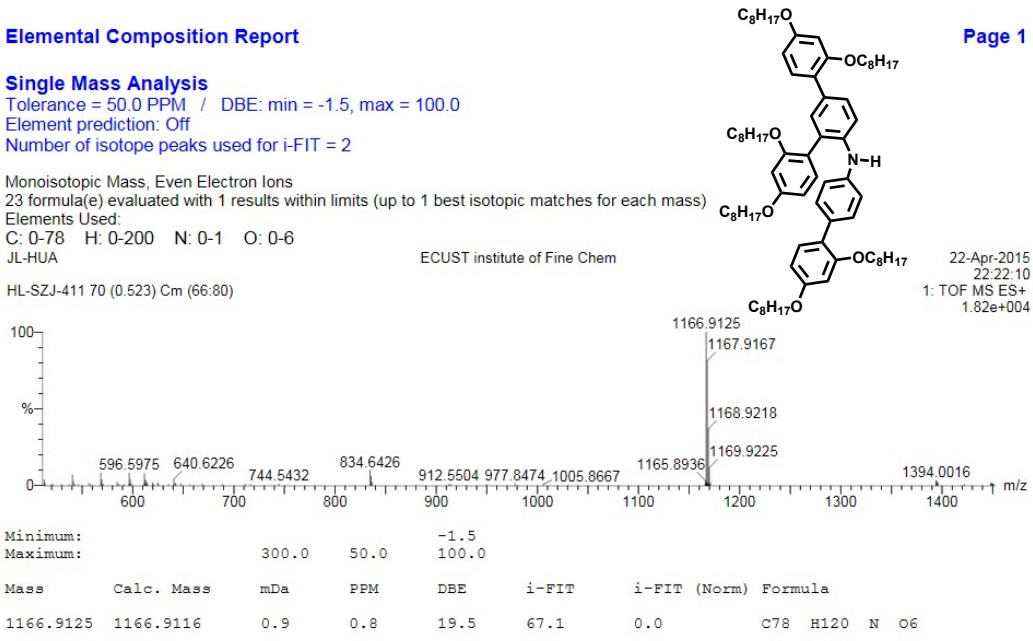


Fig. S9 HRMS of compound **b.**

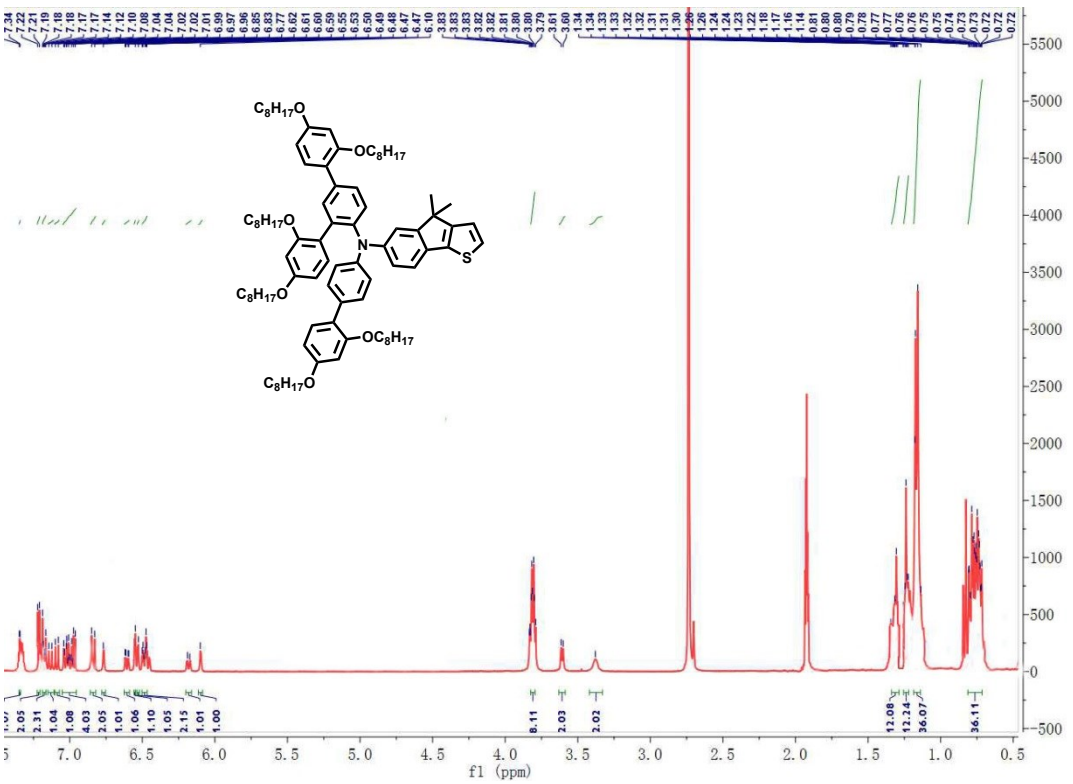


Fig. S10 ^{1}H NMR spectrum of compound **c** in acetone-d_6.

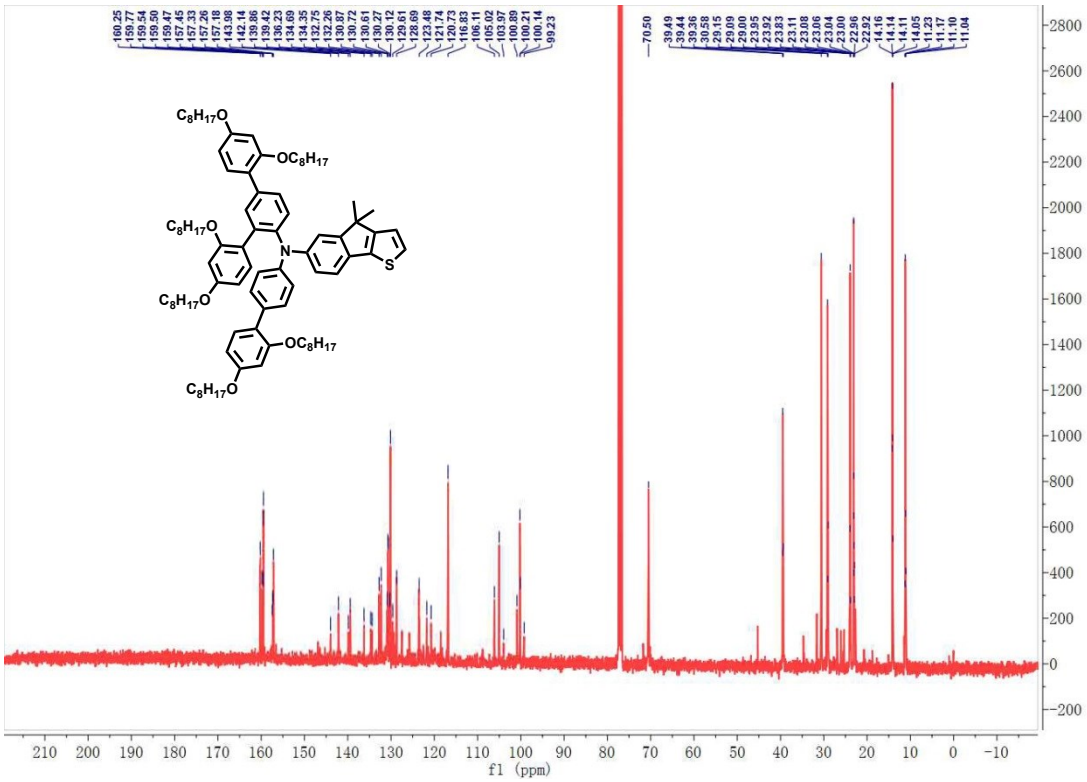


Fig. S11 ^{13}C NMR spectrum of compound **c** in acetone-d_6.

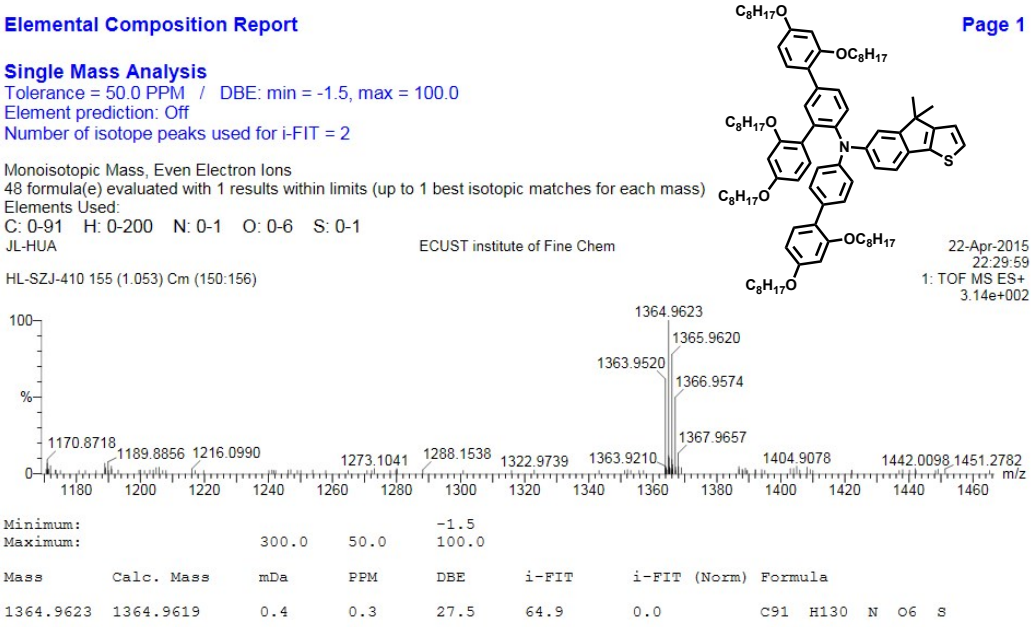


Fig. S12 HRMS of compound **c.**

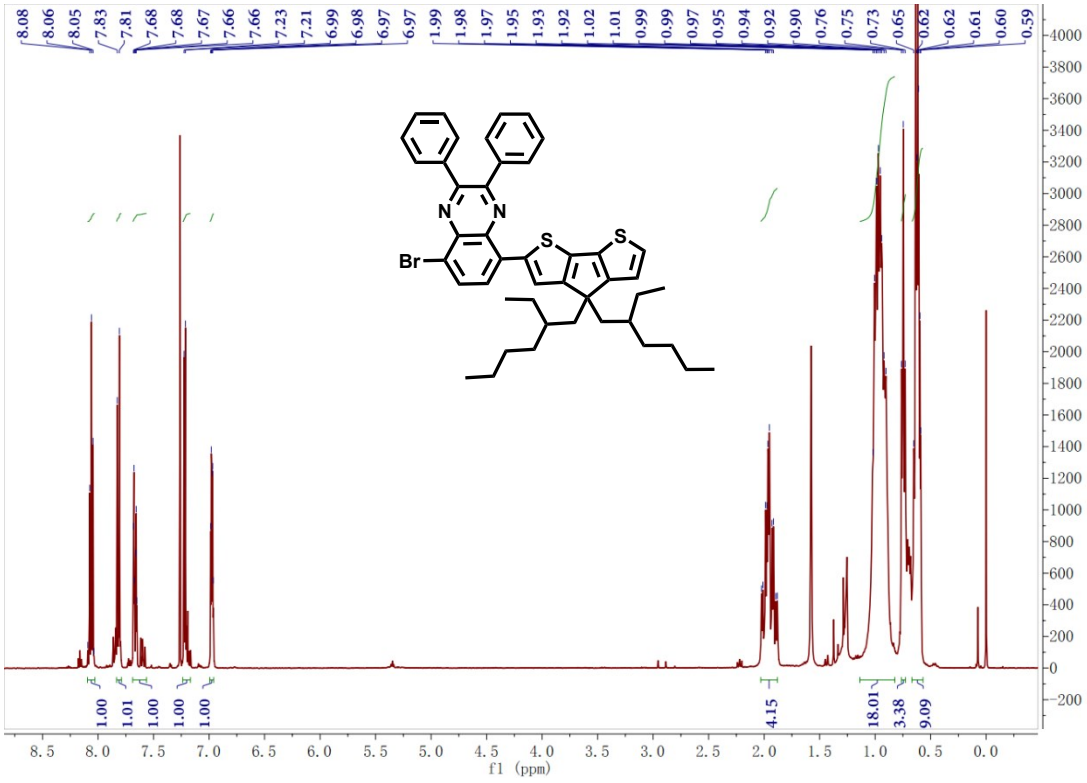


Fig. S13 ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

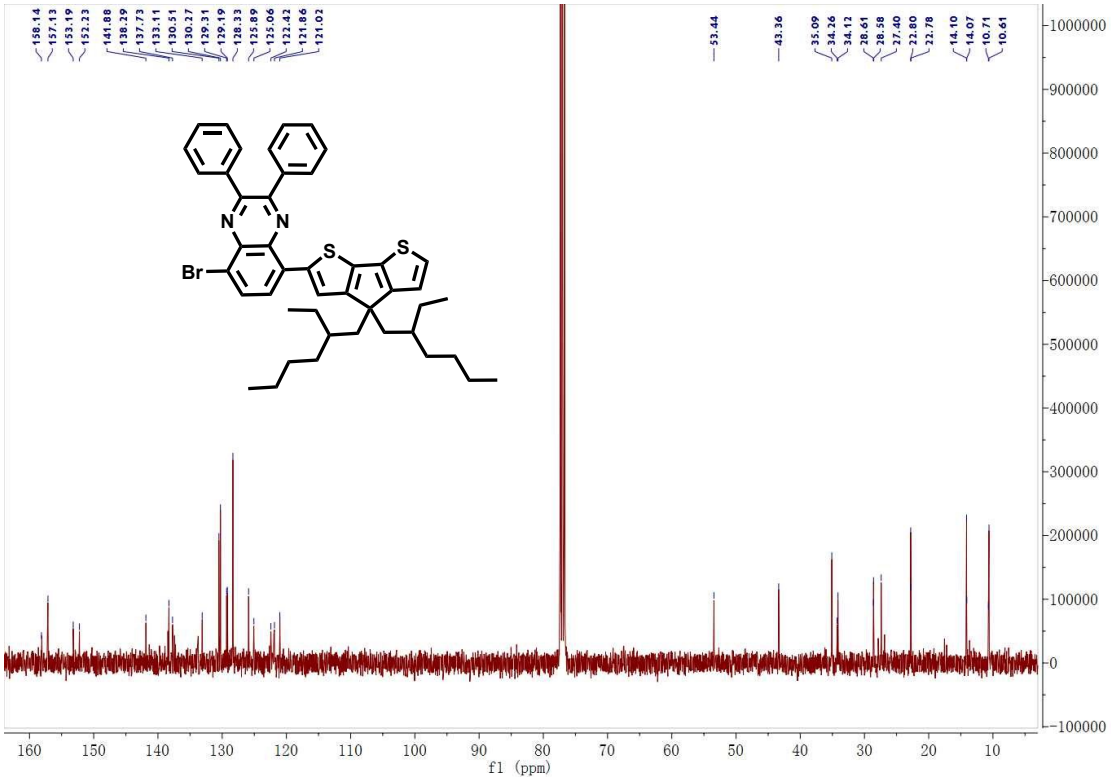


Fig. S14 ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

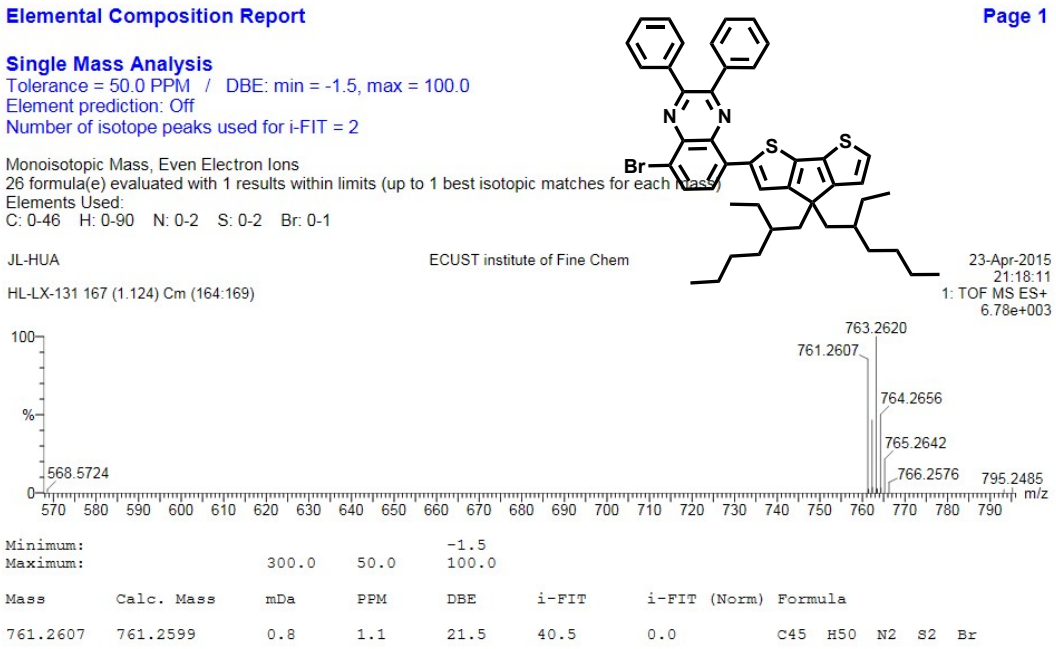


Fig. S15 HRMS of compound **1.**

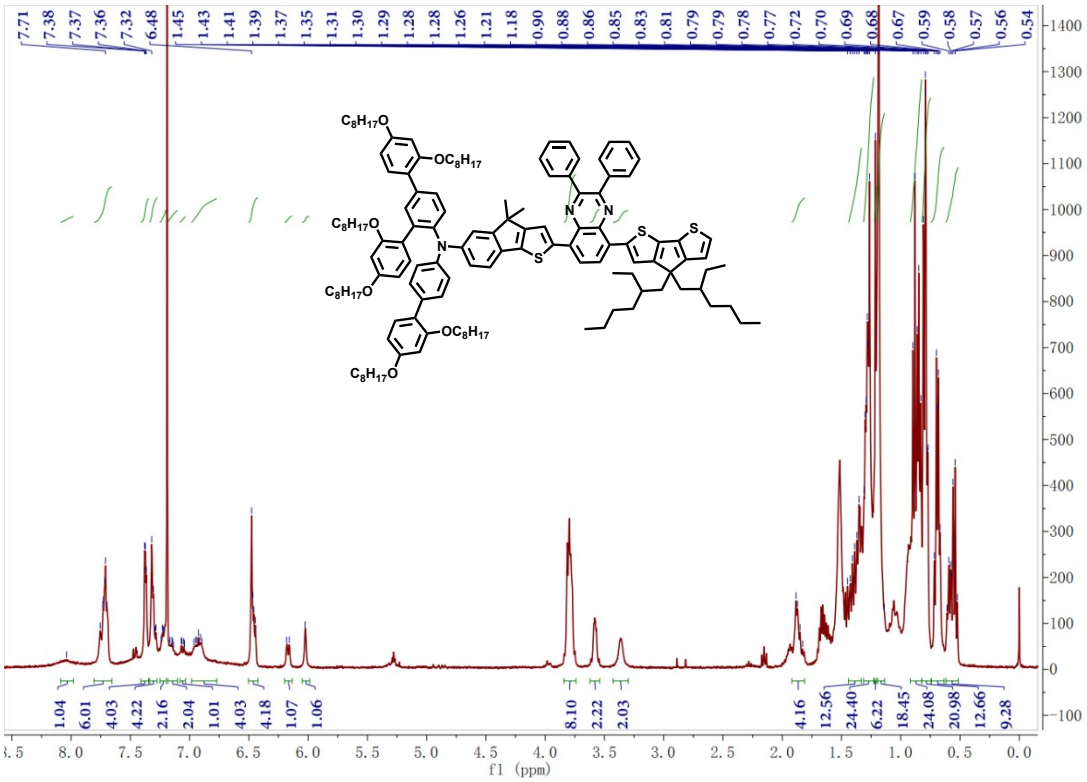


Fig. S16 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

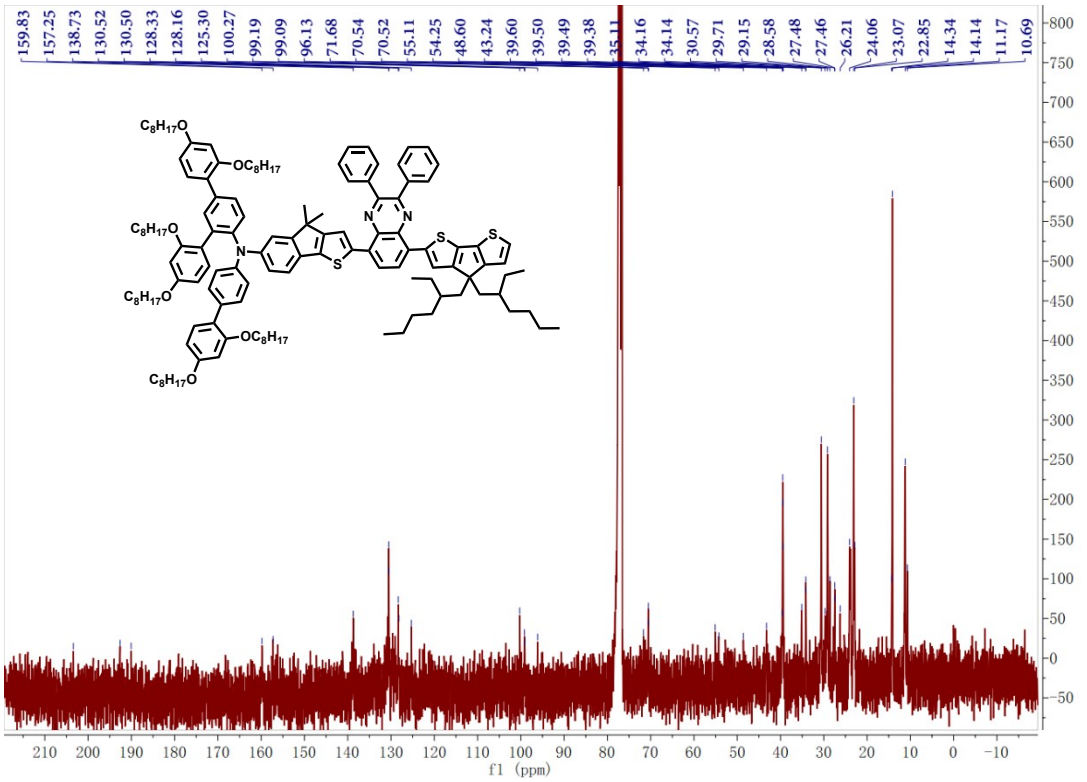
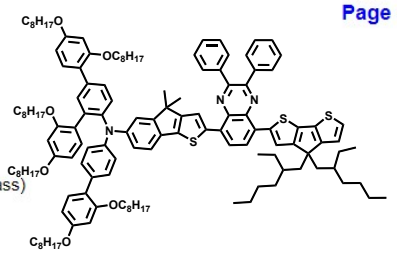


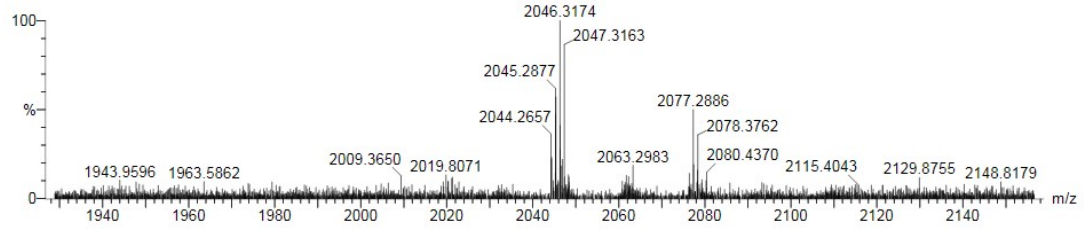
Fig. S17 ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
70 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-136 H: 0-200 N: 0-3 O: 0-6 S: 0-3
1 101 (1.143) Cm (97:103)
1: TOF MS ES+





Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
2045.2877	2045.2878	-0.1	0.0	49.5	130.4	0.0	C136 H178 N3 O6 S3

Fig. S18 HRMS of compound **3.**

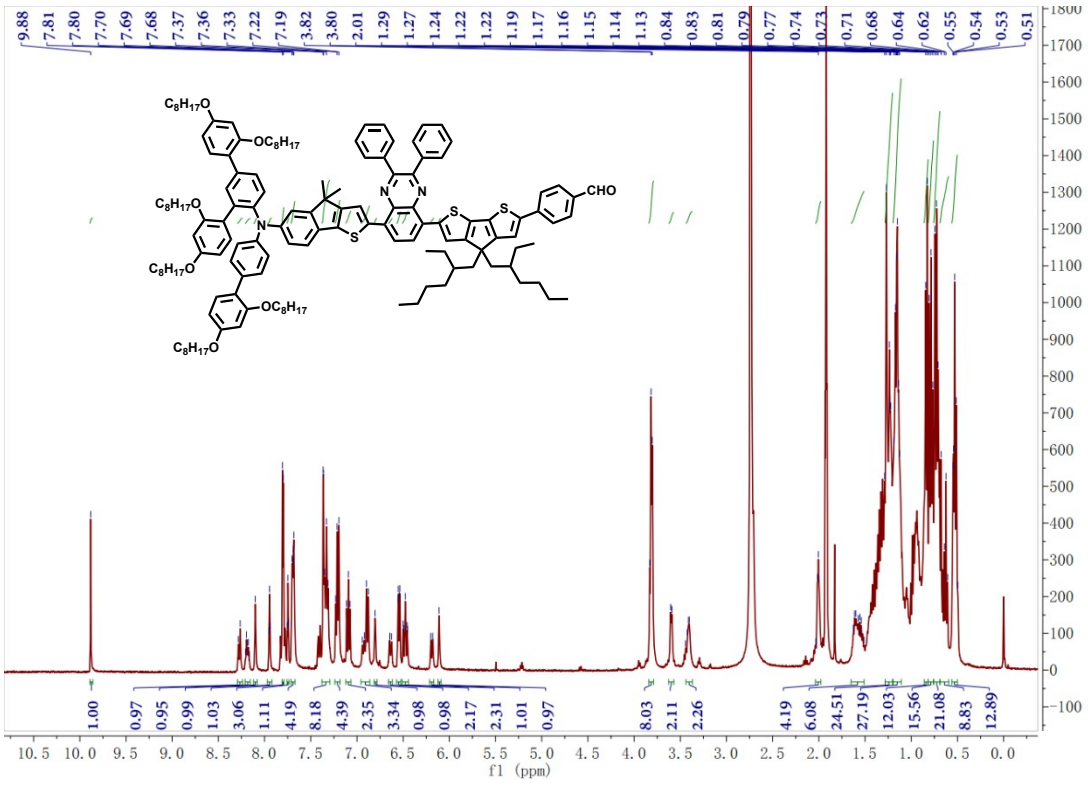


Fig. S19 ^{1}H NMR spectrum of compound **5a** in acetone-d_6.

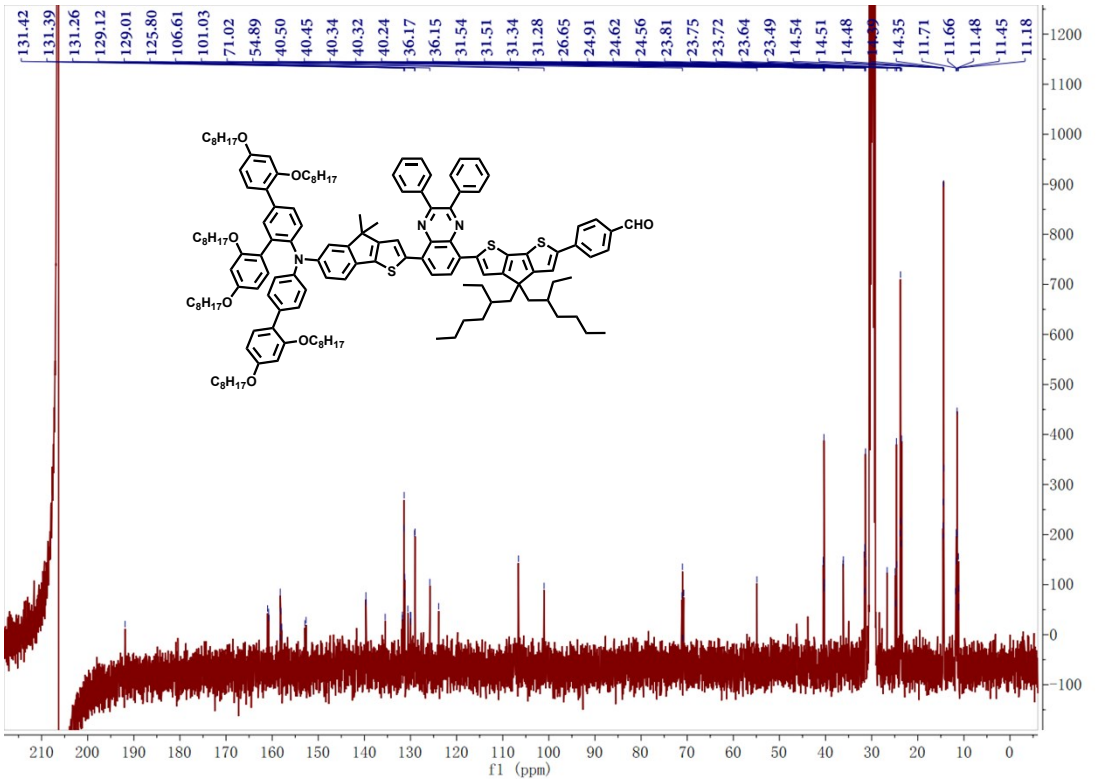


Fig. S20 ^{1}C NMR spectrum of compound **5a** in acetone-d_6.

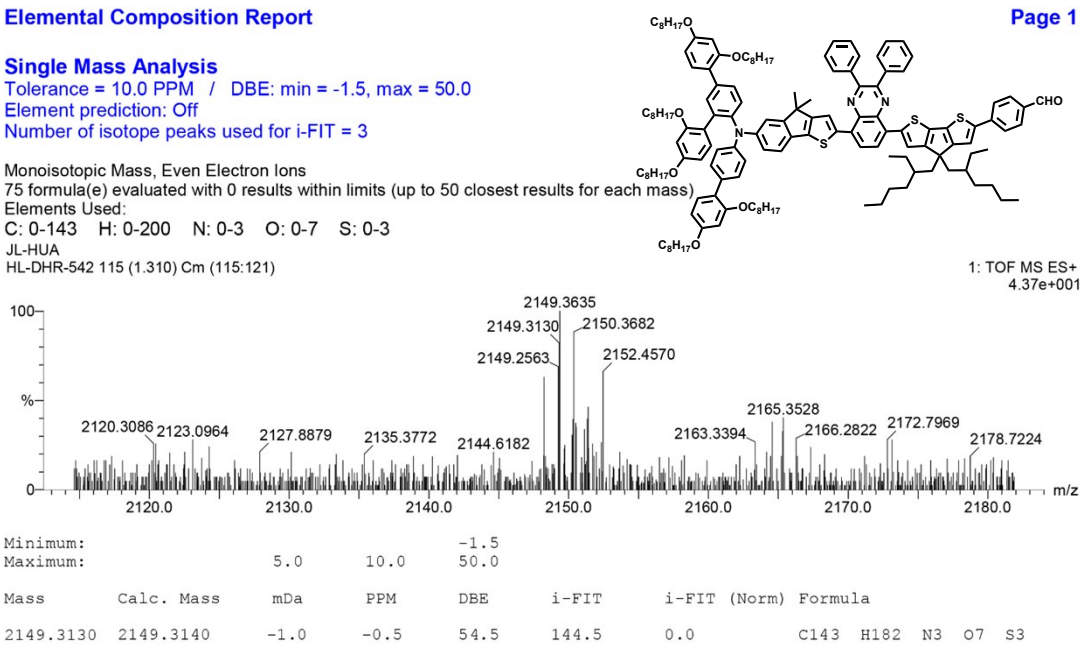


Fig. S21 HRMS of compound **5a.**

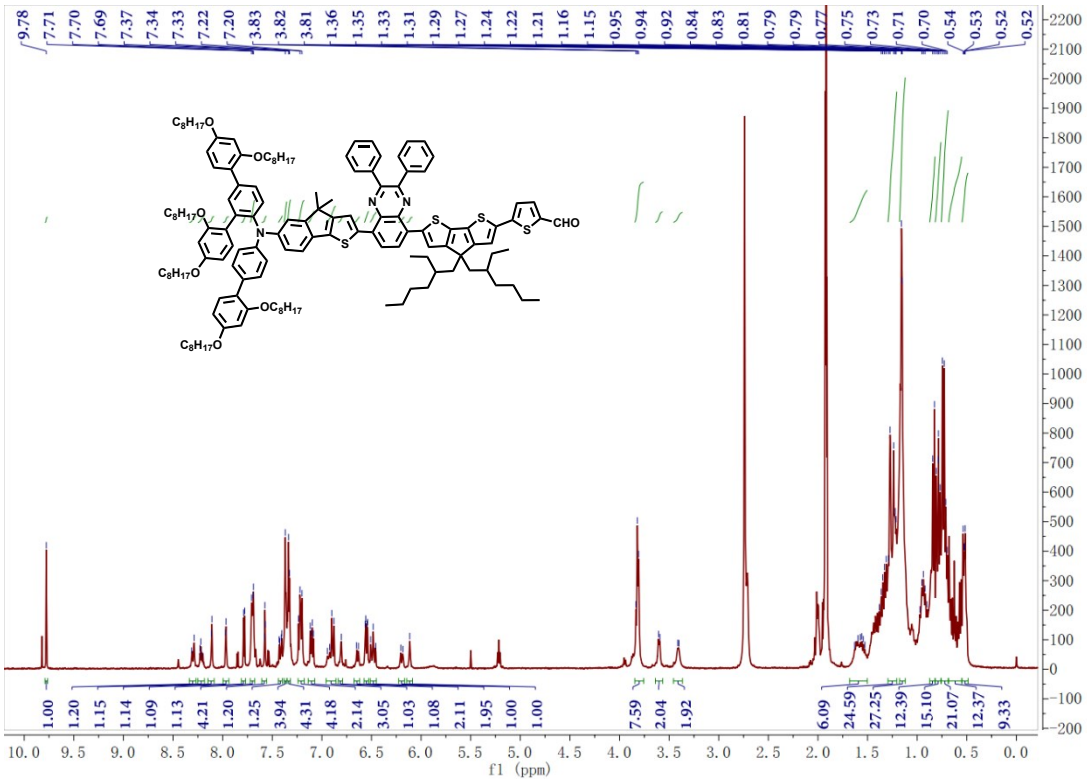


Fig. S22 [1]H NMR spectrum of compound **5b** in acetone-d_6.

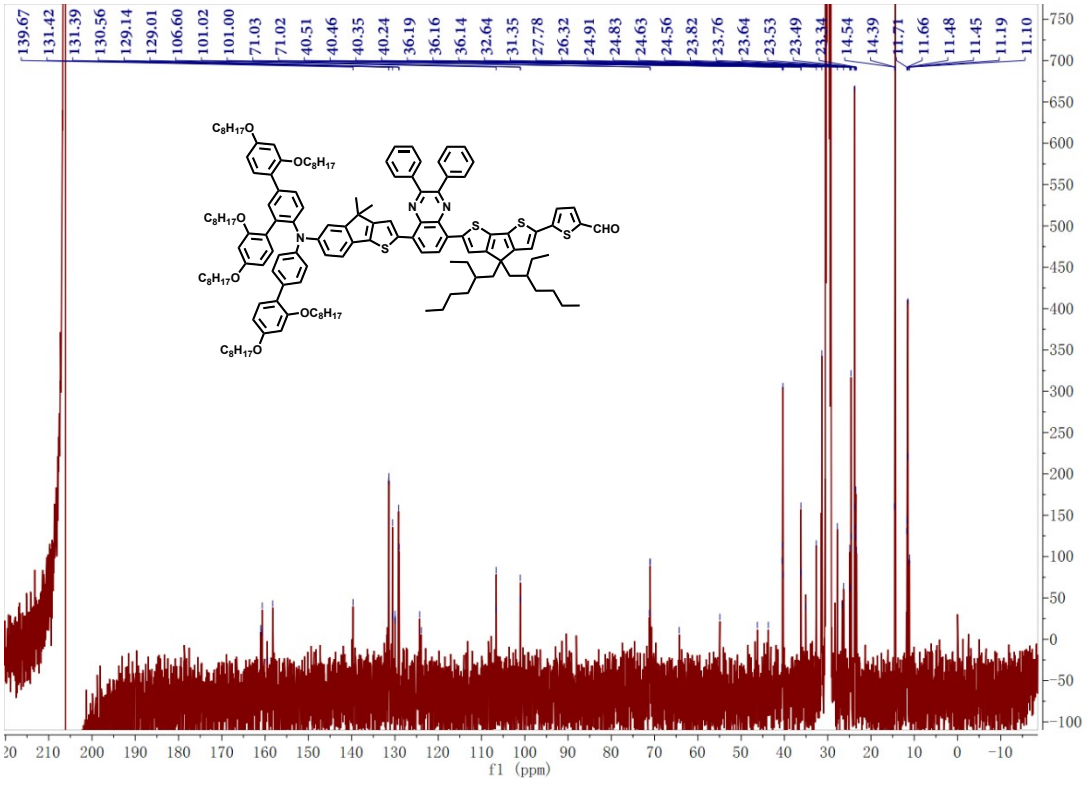


Fig. S23 [1]C NMR spectrum of compound **5b** in acetone-d_6.

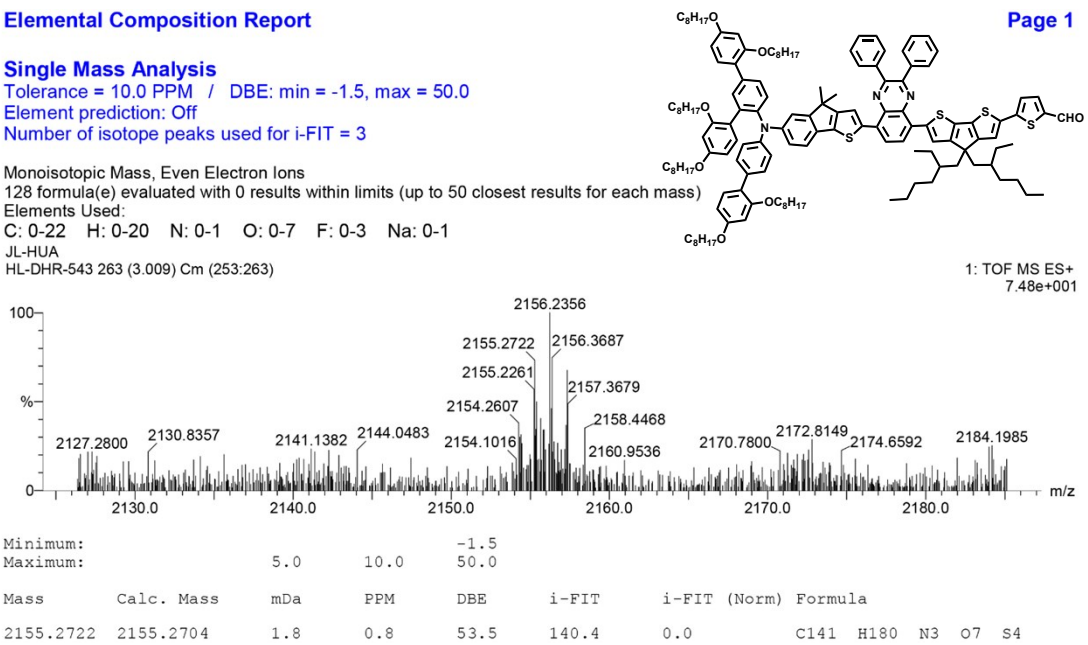


Fig. S24 HRMS of compound **5b.**

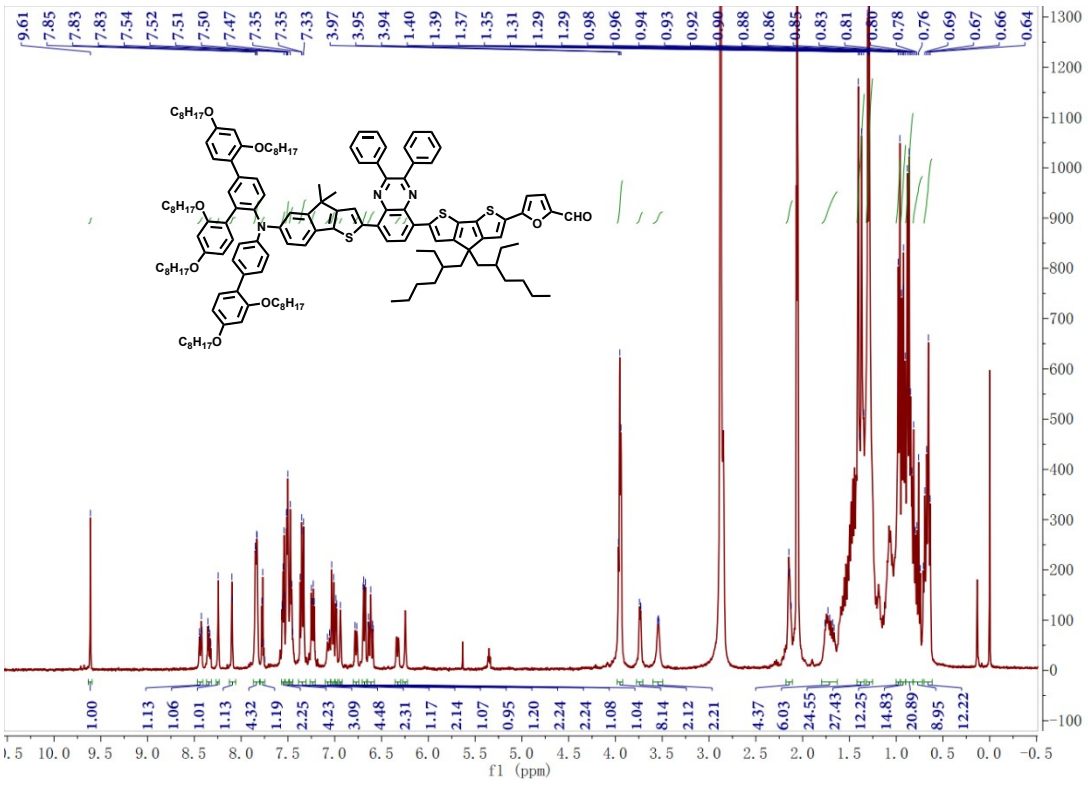


Fig. S25 ^{1}H NMR spectrum of compound **5c** in acetone-d_6.

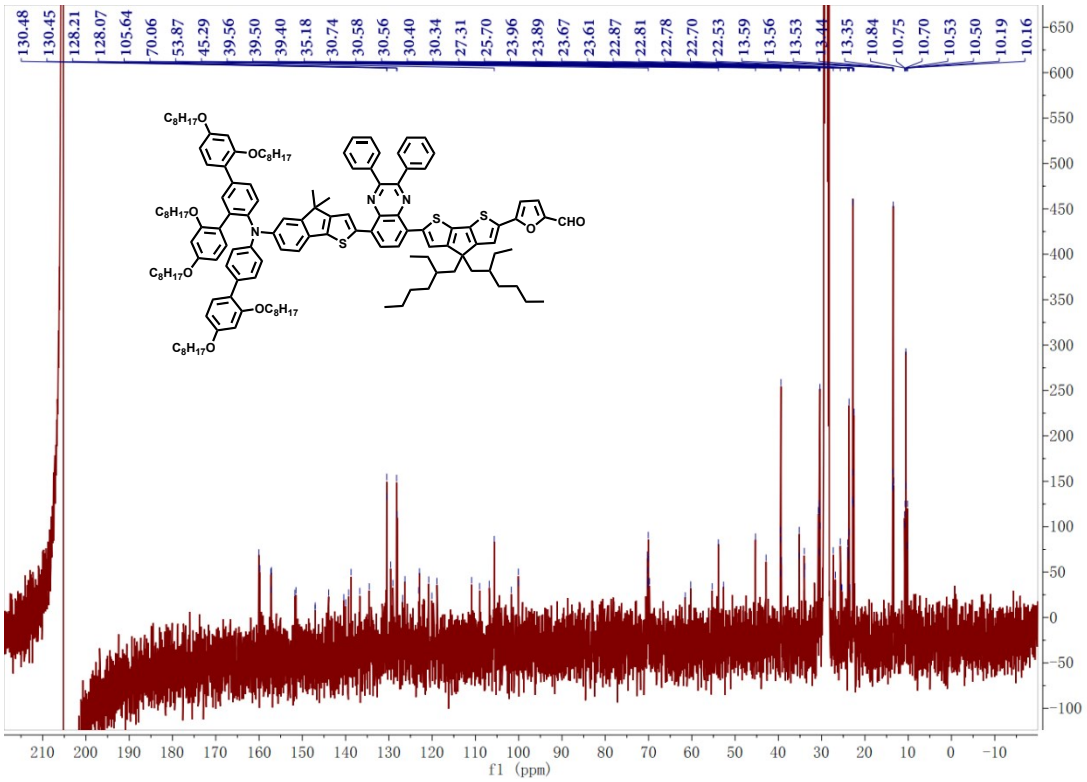


Fig. S26 ^{1}C NMR spectrum of compound **5c** in acetone-d_6.

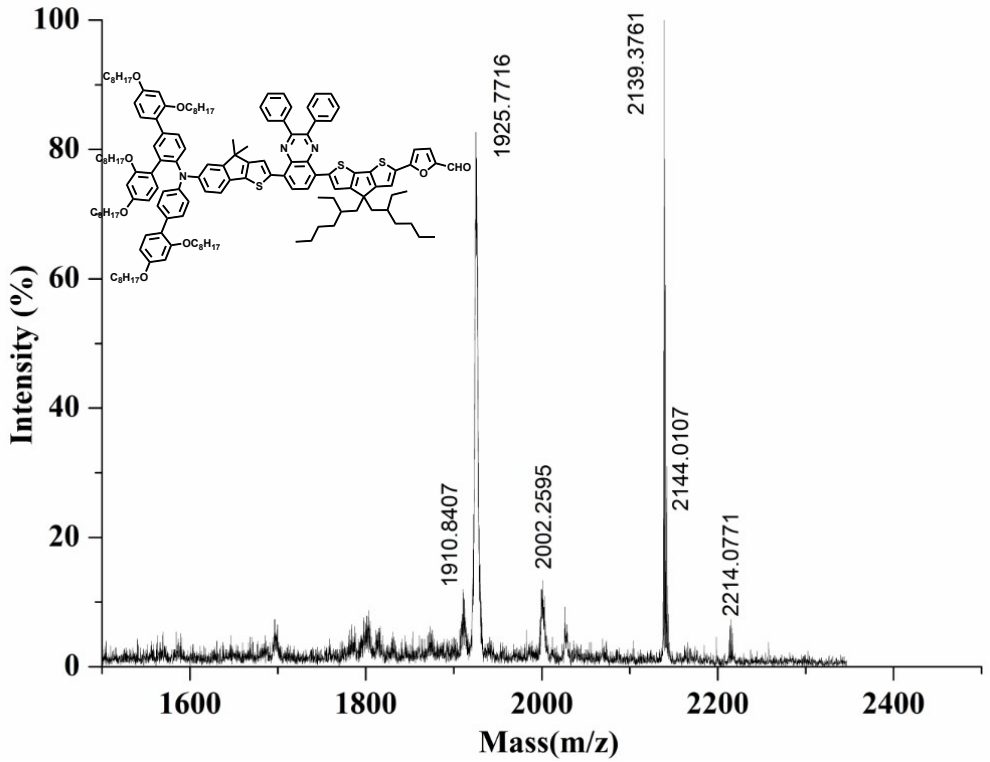


Fig. S27 HRMS of compound **5c.**

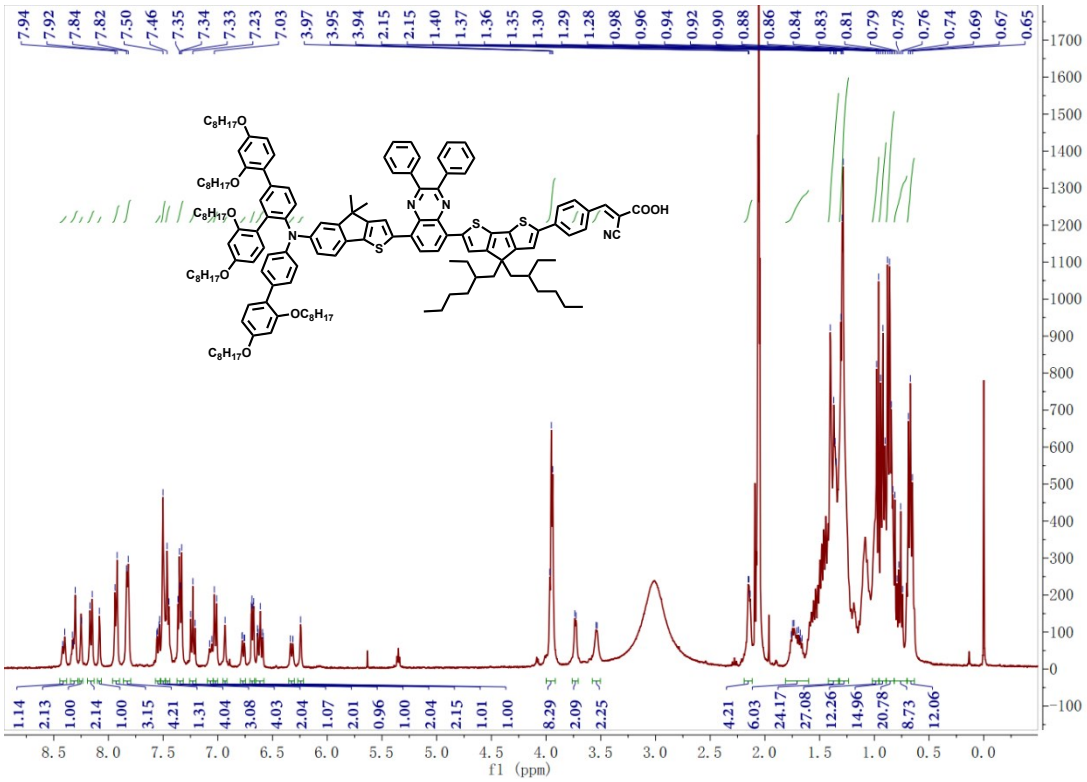


Fig. S28 [1]H NMR spectrum of compound **SD1** in acetone-d_6.

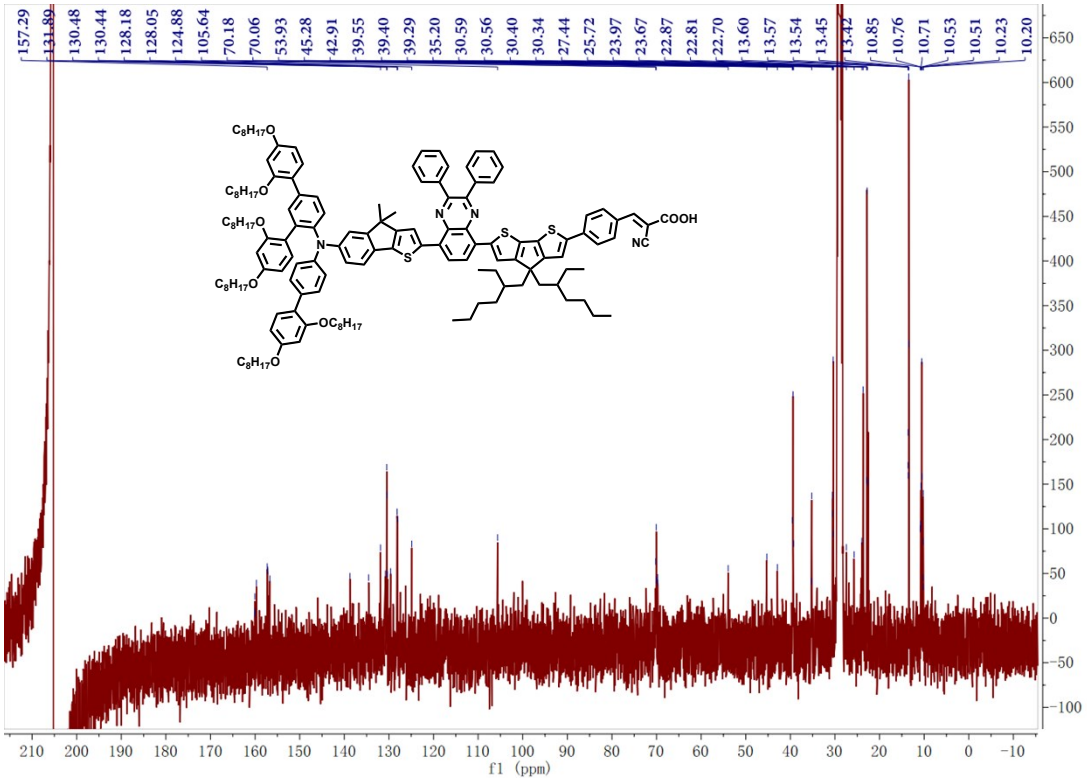


Fig. S29 [1]C NMR spectrum of compound **SD1** in acetone-d_6.

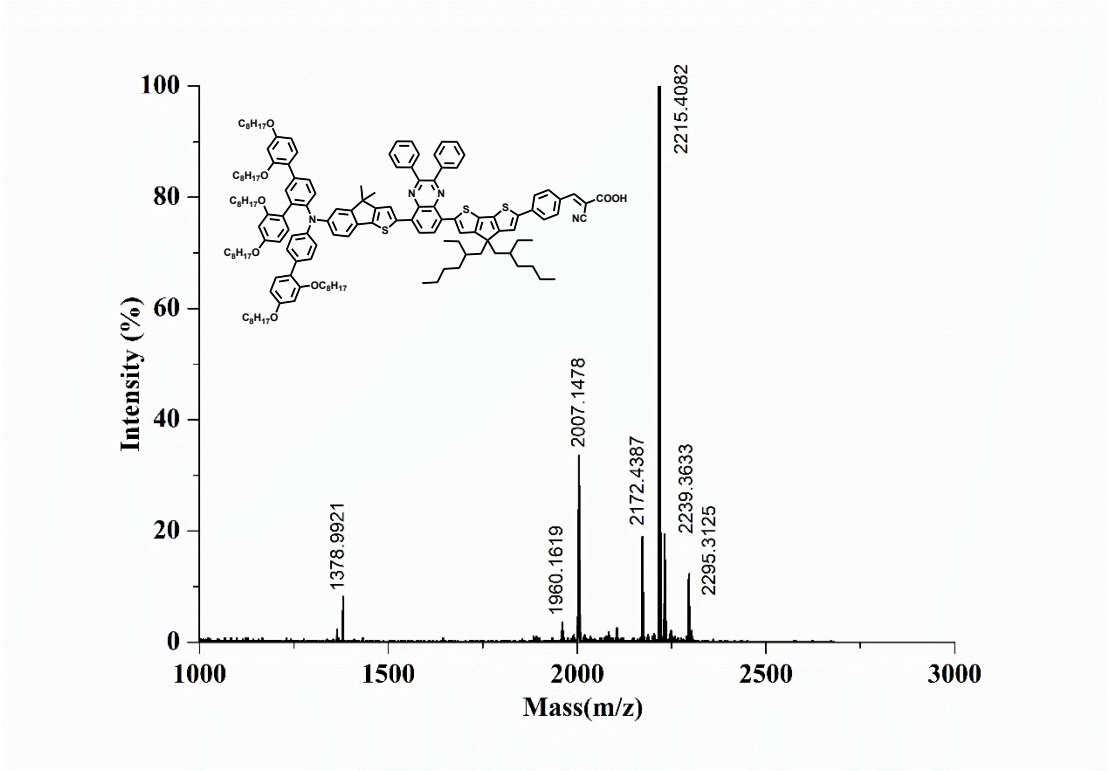


Fig. S30 HRMS of compound **SD1.**

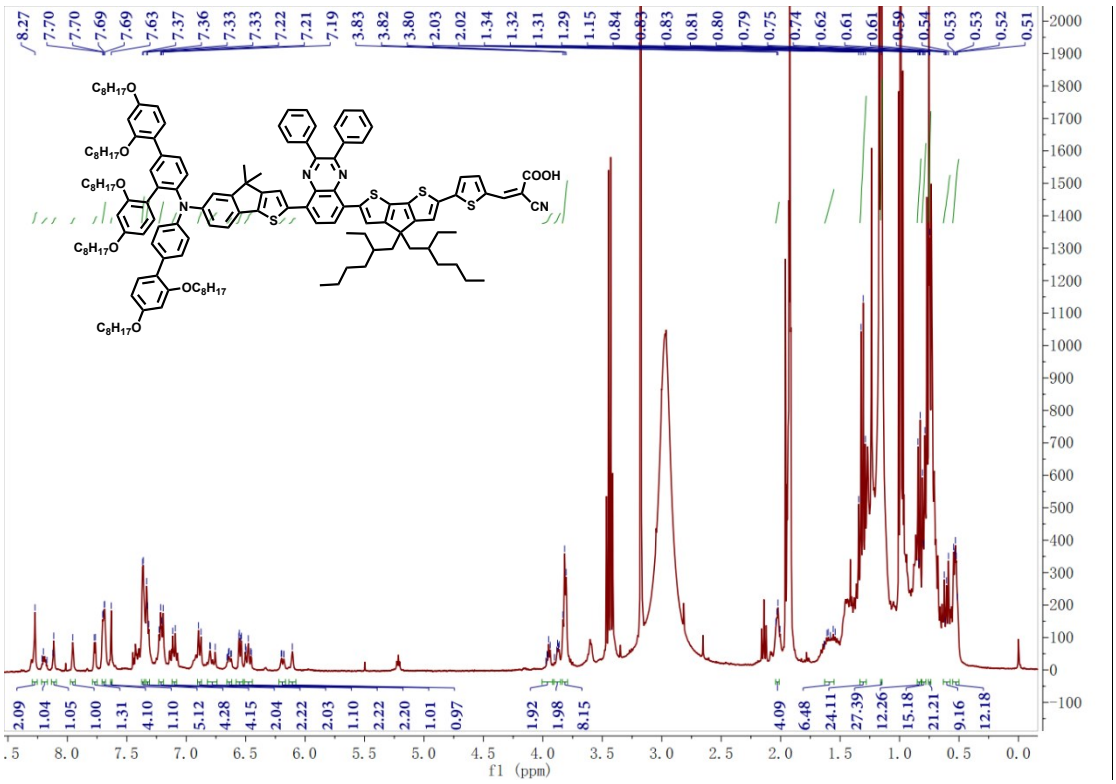


Fig. S31 ^{1}H NMR spectrum of compound **SD2** in acetone-d_6.

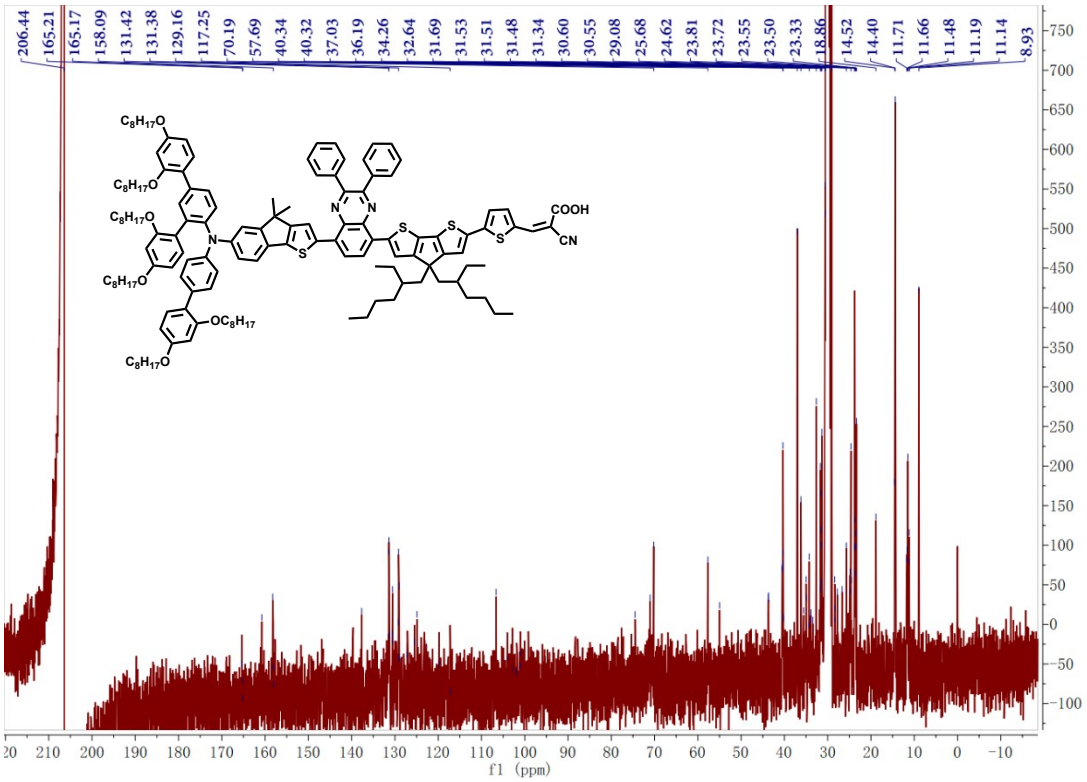


Fig. S32 ^{1}C NMR spectrum of compound **SD2** in acetone-d_6.

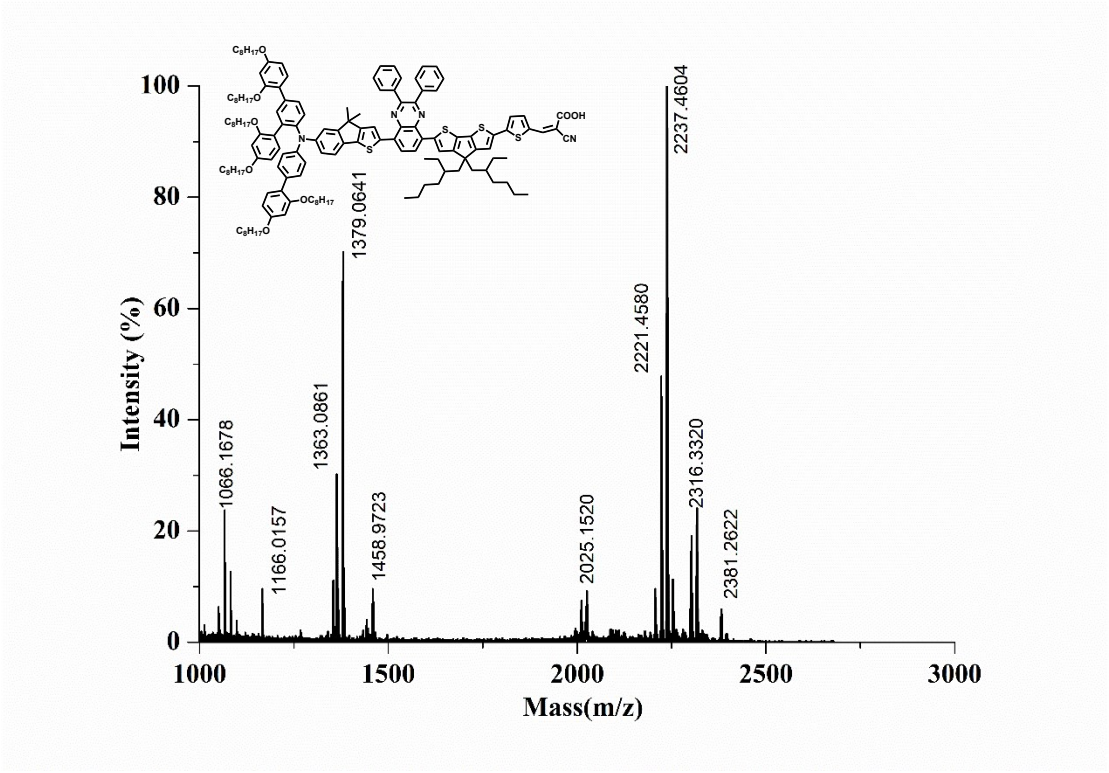


Fig. S33 HRMS of compound **SD2.**

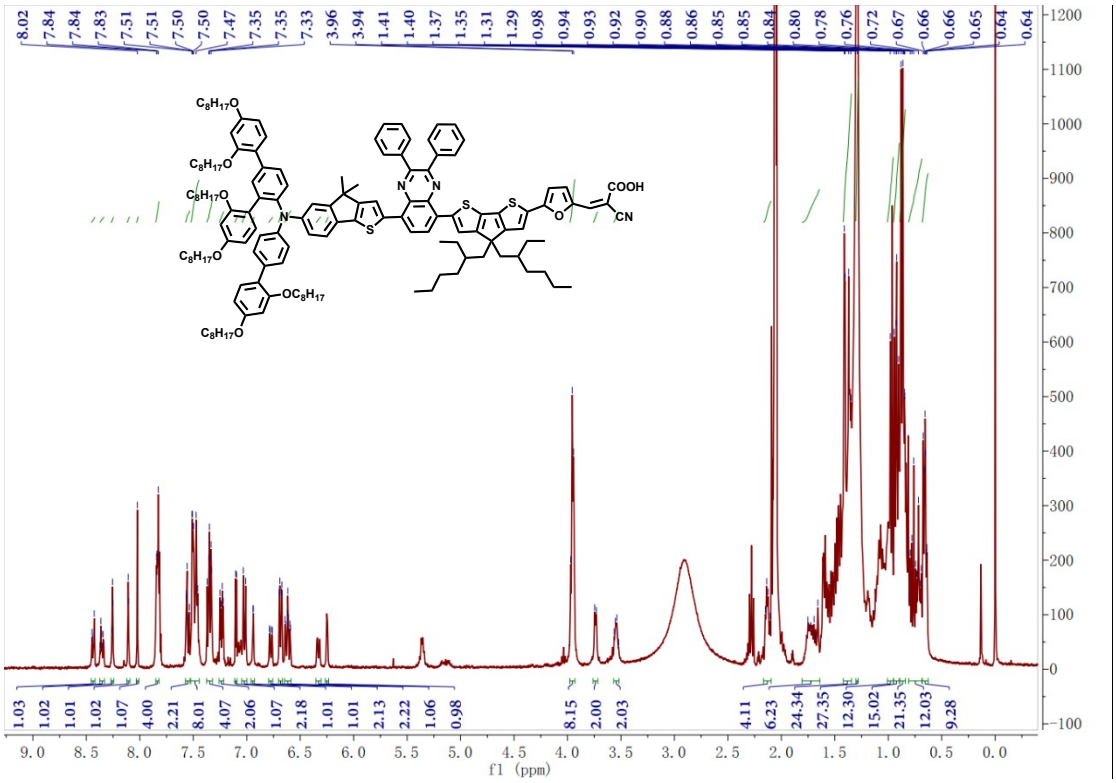


Fig. S34 [1]H NMR spectrum of compound **SD3** in acetone-d_6.

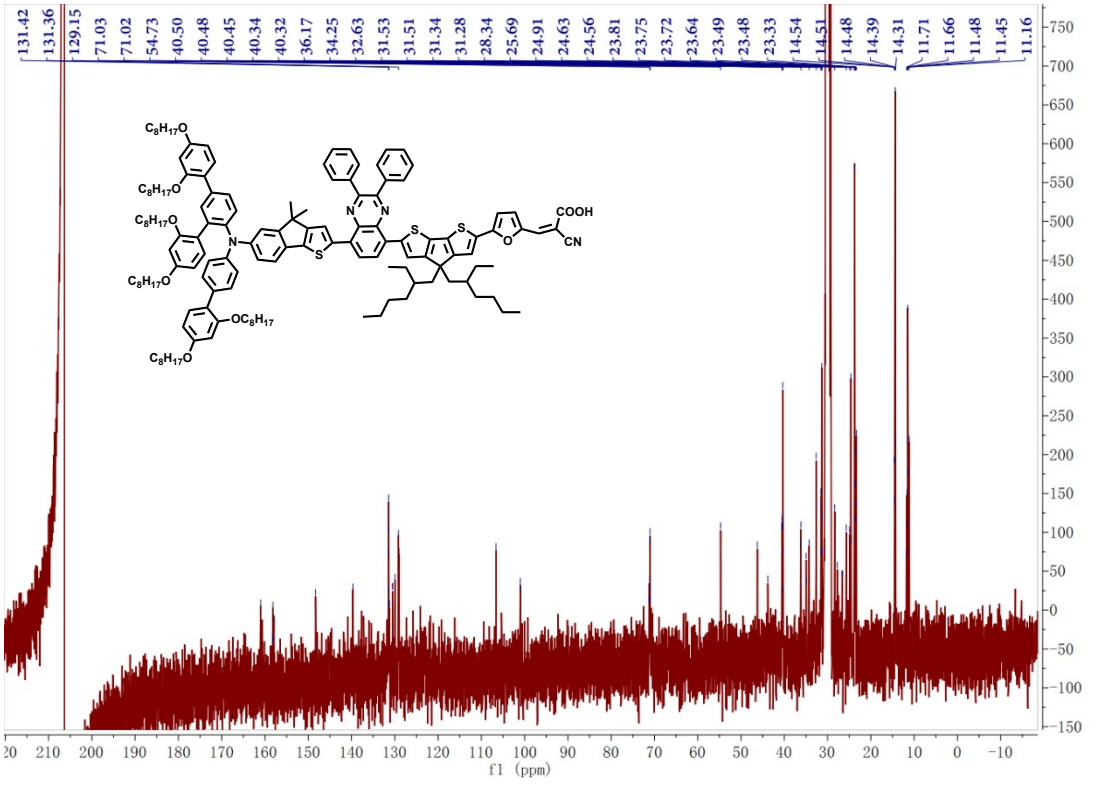


Fig. S35 [1]C NMR spectrum of compound **SD3** in acetone-d_6.

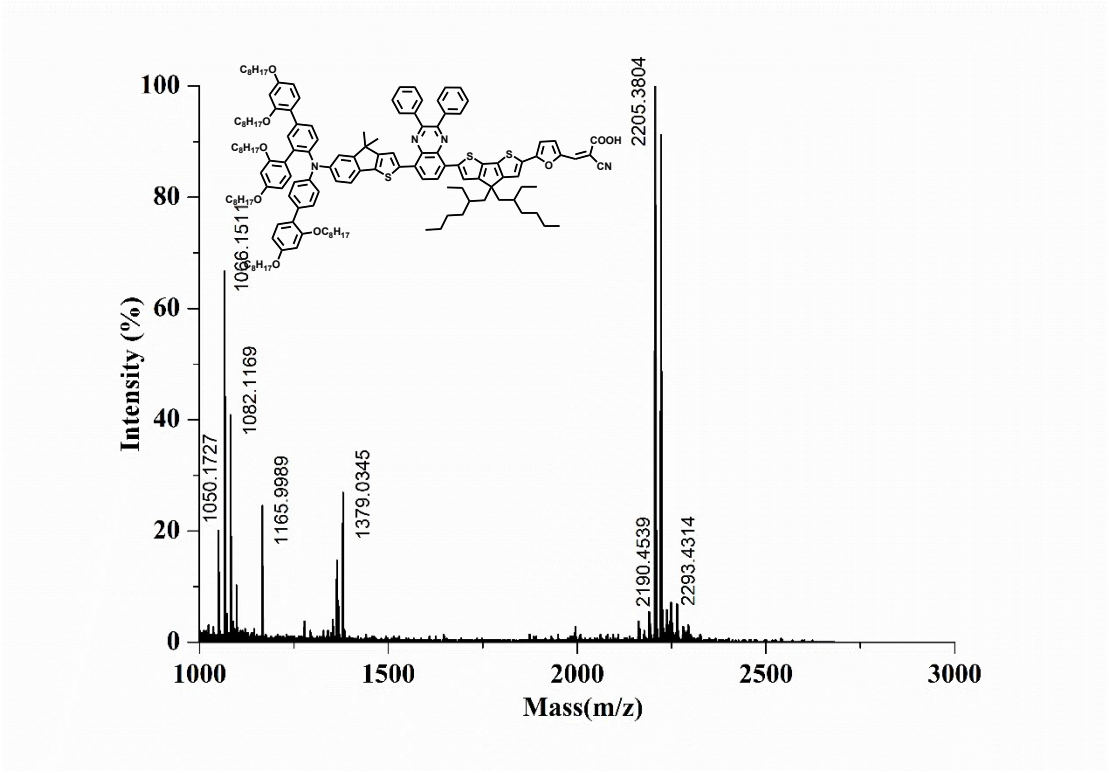


Fig. S36 HRMS of compound **SD3.**

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