Triisopropylsilylethynyl substituted benzodithiophene copolymers: synthesis, properties and photovoltaic characterization

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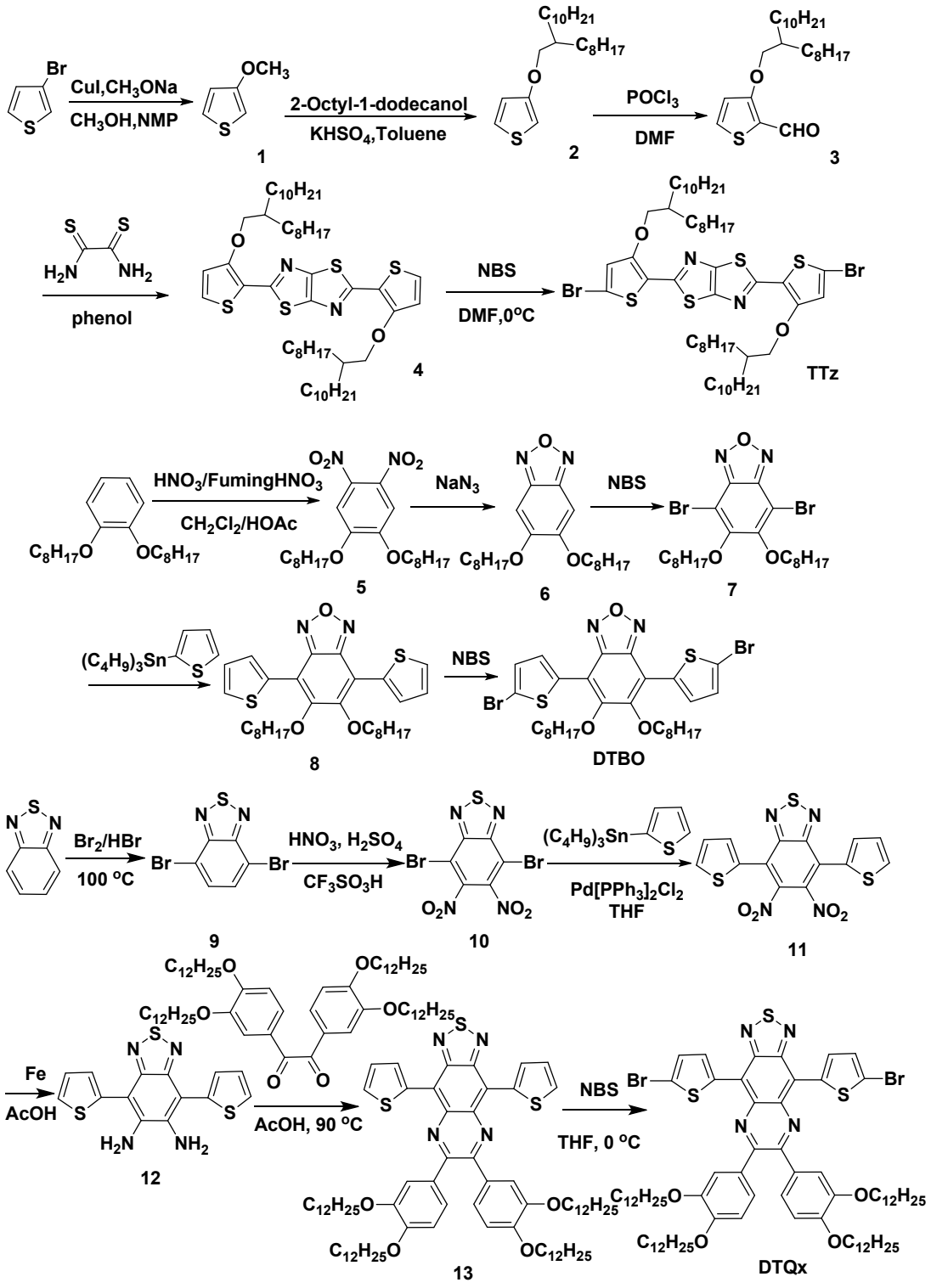
1. Synthetic procedure of acceptors



Scheme S1. Synthetic Route to Acceptors

3-Methoxy-thiophene (1). To a stirred solution of sodium methanolate (6.36 g, 118

mmol) in methanol (100 mL), N-methyl pyrrolidone (100 mL) and 3-bromothiophene (16 g, 100 mmol) were added into the mixture. The mixture was warmed to 110°C and then CuI (1.8 g, 9.6 mmol) was added in one portion and keep refluxed overnight. The reaction mixture was cooled to room temperature and water (100 mL) was added. The crude product was extracted with dichloromethane and the combined organic layers were washed with water and saturated aqueous NH_4Cl, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by distilled at reduced pressure with a distillation apparatus to give the *title* compound as colorless liquid (10 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.19-7.16 (m, 1H), 6.76-6.74 (m, 1H), 6.26-6.24 (m, 1H), 3.81 (s, 3H).

3-((2-Octyldodecyl)oxy)-thiophene (**2**)**.** To the mixture of compound **1** (5.26 g, 46.07 mmol) and potassium bisulfate (1.25 g, 9.21 mmol) in toluene (50 mL) was added 2-octyldodecan-1-ol (27.51 g, 92.15 mmol). The mixture was refluxed for 20 hours with nitrogen. Then the reaction was cooled to room temperature and quenched by water (50 mL). The resulting mixture was extracted with dichloromethane and the combined organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether to give the *title* compound as colorless liquid (8.70 g, 50%). ^{1}HNMR (500 MHz, $CDCl_3$, ppm) δ = 7.18 (dd, *J* = 5.2 Hz, *J* = 3.1 Hz, 1H), 6.78 (dd, *J* = 5.2 Hz, *J* = 1.5 Hz, 1H), 6.24 (dd, *J* = 3.1 Hz, *J* = 1.5 Hz, 1H), 3.85 (d, *J* = 5.7 Hz, 2H), 1.82-1.77 (m, 1H), 1.51-1.23 (m, 32H), 0.93 (t, *J* = 7.0 Hz, 6H).

3-((2-Octyldodecyl)oxy)-thiophene-2-carbaldehyde (3). Under nitrogen atmosphere, to the stirred solution of anhydrous DMF (40 mL) was slowly added $POCl_3$ (2.42 g, 15.76 mmol) at 0°C for 30 minutes. The reaction mixture was stirred for 3 hour after addition. Then compound **2** (5.00 g, 13.13mmol) was added to the mixture at 0°C and the reaction mixture was warmed to 70°C for 12 hours. The ice water was poured into reaction mixture at room temperature and then slowly neutralized it with 10% NaOH solution. The resulting mixture was extracted with dichloromethane and the combined organic layer was dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (8:1) to give the *title* compound as colorless liquid (4.03 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 10.00 (s, 1H), 7.62 (d, *J* = 5.4 Hz, 1H), 6.84 (d, *J* = 5.4 Hz, 1H), 4.03 (d, *J* = 5.6 Hz, 2H), 1.80 (dd, *J* = 12.1, *J* = 6.0 Hz, 1H), 1.46-1.20 (m, 32H), 0.88 (t, *J* = 6.8 Hz, 6H).

2,5-Bis(3-((2-octyldodecyl)oxy)thiophen-2-yl)thiazolo[5,4-d]thiazole (4). Compound **3** (3.0 g, 7.3 mmol), dithiooxamide (0.44 g, 3.6 mmol), and phenol (3.0 g, 34 mmol) were added to a round-bottom flask purged with nitrogen. The reaction mixture was refluxed at temperature 160°C for 3 hours. The crude product was purified by column chromatography on silica gel using petroleum ether/chloroform (3:2) to give the *title* compound as yellow solid (1.6 g, 30%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.32 (d, *J* = 5.5 Hz, 2H), 6.89 (d, *J* = 5.5 Hz, 2H), 4.14 (d, *J* = 4.8

Hz, 4H), 1.88-1.81 (m, 2H), 1.64-1.57 (m, 4H), 1.55-1.47 (m, 4H), 1.39-1.18 (m, 56H), 0.86 (t, *J* = 6.8 Hz, 12H).

2,5-Bis(5-bromo-3-((2-octyldodecyl)oxy)thiophen-2-yl)thiazolo[5,4-d]thiazole (TTz). NBS (700 mg, 2.9 mmol) was added to a solution of compound **4** (1.6 g, 1.8 mmol) dissolved in $CHCl_3$/AcOH (32/16 mL) at 0°C, then the reaction solution was stirred at room temperature overnight. The mixture was purified by column chromatography on silica gel using petroleum ether/chloroform (5:1) to give *title* compound as yellow solid (1.5 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 6.90 (s, 2H), 4.09 (d, *J* = 4.9 Hz, 4H), 1.87-1.79 (m, 2H), 1.62-1.44 (m, 8H), 1.39-1.19 (m, 56H), 0.86 (t, *J* = 6.9 Hz, 12H).

1,2-Dinitro-4,5-bis(octyloxy)benzene (5). HNO_3 (50 mL, 65%) was slowly added to the mixture of 1,2-bis(octyloxy)benzene (10 g, 29.9 mmol) dissolved in CH_2Cl_2/AcOH (100/100 mL) at 10°C. The reaction mixture was warmed to room temperature and stirred for 1 h. Fuming HNO_3 (50 mL) was added dropwise when the mixture was cooled to 10°C. After addition, the mixture was warmed to room temperature and stirred for 40 h. the mixture was quenched by ice-water. The resulting mixture was extracted with dichloromethane and the combined organic layer was dried ($MgSO_4$) and concentrated in vacuo. The crude product was recrystallized from ethanol to give *title* compound as yellow solid (10 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.29 (s, 2H), 4.10 (t, *J* = 6.5 Hz, 4H), 1.91-1.83 (m, 4H), 1.52-1.43

(m, 4H), 1.38-1.26 (m, 16H), 0.89 (t, J = 6.9 Hz, 6H).

5,6-Bis(octyloxy)benzo[c][1,2,5]oxadiazole (6). To the mixture of compound **5** (1.7 g, 4 mmol) and NaN_3 (1.3 g, 20 mmol) in toluene (50 mL) n-Bu_4NBr (260 mg, 0.8 mmol) was added. The reaction mixture was refluxed for 12h. Then PPh_3 (1.26 g, 4.8 mmol) was added and the mixture was refluxed for an additional 24 h. The resulting mixture was filtered through a short silica plug and an off-white solid was obtained by pressure evaporation. The crude product was recrystallized from ethanol to give *title* compound as white needles (1.3 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 6.80 (s, 2H), 4.06 (t, J = 6.5 Hz, 4H), 1.92-1.86 (m, 4H), 1.50-1.47 (m, 4H), 1.37-1.27 (m, 16H), 0.89 (t, J = 6.7 Hz, 6H).

4,7-Dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]oxadiazole (7). To a solution of compound **6** (6 g, 27 mmol) in CH_2Cl_2/AcOH (80/10 mL) was slowly added Br_2 (0.85 mL, 16.6 mmol). The reaction mixture was stirred for 3 days at room temperature. The mixture was quenched by NaOH solution (10 g in 200 mL). The resulting mixture was extracted with dichloromethane (3×50 mL), and the combined organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified with column chromatography on silica gel using petroleum ether/dichloromethane (1:9) to give pure *title* compound as a white solid (2.0 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 4.15 (t, J = 6.6 Hz, 4H), 1.90-1.82 (m, 4H), 1.53-1.47 (m, 4H), 1.40-1.27 (m, 16H), 0.90 (t, J = 6.5 Hz, 6H).

5,6-Bis(octyloxy)-4,7-di(thien-2-yl)benzo[c][1,2,5]oxadiazole (8). Under nitrogen atmosphere, to the mixture of compound **7** (665 mg, 1.25 mmol) and 2-tributylstannylthiophene (994 μL, 3.13 mmol) in dry toluene (10 mL) $Pd_2(dba)_3$ (46 mg, 0.05 mmol) and tri-o-tolylphosphine (122 mg, 0.40 mmol) were added. Then the reaction mixture was refluxed for 16 h. The reaction mixture was concentrated directly under vacuum, and purified by column chromatography on silica gel using petroleum ether/chloroform (1:10) to afford pure *title* compound as a yellow solid (470 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.46 (dd, *J* = 3.8 Hz, *J* = 1.1 Hz, 2H), 7.50 (dd, *J* = 5.1 Hz, *J* = 1.0 Hz, 2H), 7.22 (dd, *J* = 5.1 Hz, *J* = 3.9 Hz, 2H), 4.15 (t, *J* = 7.3 Hz, 4H), 2.02-1.97 (m, 4H), 1.46-1.43 (m, 4H), 1.33-1.22 (m, 16H), 0.90 (t, *J* = 7.0 Hz, 6H).

4,7-Bis(5-bromothien-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]oxadiazole (**DTBO**). In the dark, NBS (533 mg, 3 mmol) was added in one portion to a solution of compound **8** (810 mg, 1.5 mmol) in $CHCl_3$/AcOH (45/45 mL) and then the mixture was stirred at room temperature for 20 h. The reaction mixture was purified by column chromatography on silica gel eluting with petroleum ether/ chloroform (9:1) to afford *title* compound as an orange solid (1.4 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.25 (d, *J* = 4.2 Hz, 2H), 7.17 (d, *J* = 4.1 Hz, 2H), 4.15 (t, *J* = 7.3 Hz, 4H), 2.02-1.96 (m, 4H), 1.51-1.43 (m, 4H), 1.39-1.26 (m, 16H), 0.90 (t, *J* = 6.9 Hz, 6H).

4,7-Dibromobenzo[c][1,2,5]thiadiazole (9). 2,3,1-Benzothiadiazole (5.00 g, 36.72

mmol) was dissolved in HBr aqueous solution (100 mL, 47%). Bromine (17.60 g, 110.15 mmol) in HBr aqueous solution (50 mL of 47%) was slowly added to the solution. The mixture was refluxed overnight. After the mixture was cooled to room temperature, an aqueous solution of $Na_2S_2O_3 \cdot 5H_2O$ was added and the product was extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried with MgSO4, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel eluting with CH_2Cl_2 to give the *title* compound as pale yellow needles (8.50 g, 79%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.73 (s, 2H).

4,7-Dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole (10). Trifluoromethanesulfonic acid (7.5 mL) and HNO_3 (8 mL) were added dropwise to concentrated H_2SO_4 (10 mL) at 0°C. Compound **9** (2.00 g, 6.85 mmol) was added to the acid mixture at 0°C. The mixture was kept at room temperature for 4 h before being poured into ice-water (100 mL) and then extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried with$MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel with ethyl acetate:petroleum ether (1:10, v/v) as eluent to give the *title* compound as a pale yellow solid (1.58 g, 40%).

5,6-Dinitro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (11). $PdCl_2(PPh_3)_2$ (78.2 mg, 0.11 mmol) was added to a solution of 2-tributylstannylthiophene (2.40 g, 6.41 mmol) and **10** (1.07 g, 2.79 mmol) in anhydrous THF (40 mL). The reaction mixture was then heated at 80°C for 20 h. After cooling to room temperature, the

solvent was evaporated and the crude product was washed with hexane and dried to give the *title* compound as an orange solid (0.72 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.74 (d, J = 4.9 Hz, 2H), 7.52 (d, J = 3.5 Hz, 2H), 7.24 (dd, J = 5.0 Hz, J = 3.9 Hz, 2H).

4,7-Di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,6-diamine (12). Iron dust (1.23 g, 20.01mmol) was added to a solution of compound **11** (0.72 g, 1.83mmol) in acetic acid (50 mL). The mixture was heated at 80°C for 5 h before being cooled to room temperature, poured into the water, and extracted with ether. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation to give the *title* compound as a brown solid (0.51 g, 84%). ^{1}HNMR (500 MHz, $CDCl_3$, ppm) δ 7.56 (dd, J = 5.2, J = 1.0 Hz, 2H), 7.37 (dd, J = 3.5, J = 1.0 Hz, 2H), 7.26 (m, 2H), 4.40 (s, 4H).

6,7-Bis(3,4-bis(dodecyloxy)phenyl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (13). Compound **12** (510mg, 1.54 mmol) and 1,2-bis(3,4-bis(dodecyloxy)phenyl)ethane-1,2-dione (1.61 g, 1.70 mmol) were dissolved in acetic acid (80 mL). The reaction mixture was purged with nitrogen and heated at 90°C for 12 h. After cooling to room temperature, the mixturewas then poured intowater and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel with ethyl acetate:petroleum ether (1:20, v/v) as eluent

to give the *title* compound as a purple black solid (1.10 g, 50%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.99 (d, *J* = 2.9 Hz, 2H), 7.63 (d, *J* = 4.0 Hz, 2H), 7.60 (d, *J* = 1.8 Hz, 2H), 7.34-7.30 (m, 4H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 4H), 4.00 (t, *J* = 6.7 Hz, 4H), 1.89-1.78 (m, 9H), 1.51-1.42 (m, 8H), 1.40-1.22 (m, 64H), 0.90-0.86 (m, 12H).

6,7-Bis(3,4-bis(dodecyloxy)phenyl)-4,9-bis(5-bromothiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (DTQx). NBS (168 mg, 0.95 mmol) in one portion was added to a solution of compound **13** (534 mg, 0.43 mmol) in anhydrous THF (100 mL). The mixture was stirred in the dark at 0°C overnight. The mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was concentrated via rotary evaporation. The crude residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20 v/v) to give the *title* compound as a purple black solid (538 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.74 (d, *J* = 4.2 Hz, 2H), 7.69 (d, *J* = 1.4 Hz, 2H), 7.13 (d, *J* = 4.2 Hz, 2H), 7.05 (dd, *J* = 8.3 Hz, *J* = 1.6 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 4.17 (t, *J* = 6.3 Hz, 4H), 4.06 (t, *J* = 6.5 Hz, 4H), 1.95-1.84 (m, 8H), 1.61-1.48 (m, 8H), 1.44-1.20 (m, 64H), 0.92-0.85 (m, 12H).

2. ^{1}H-NMR Spectra of acceptors and polymers

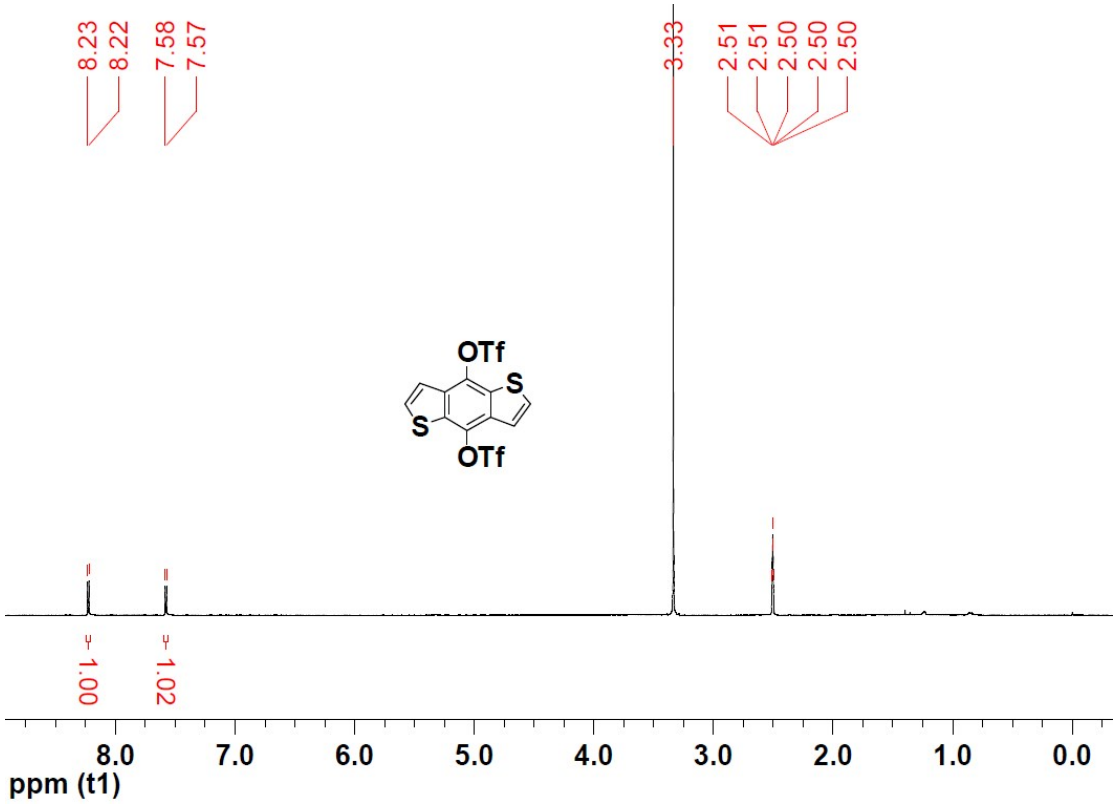


Figure S1. ^{1}H NMR spectrum of **1** in DMSO-d_6 solution

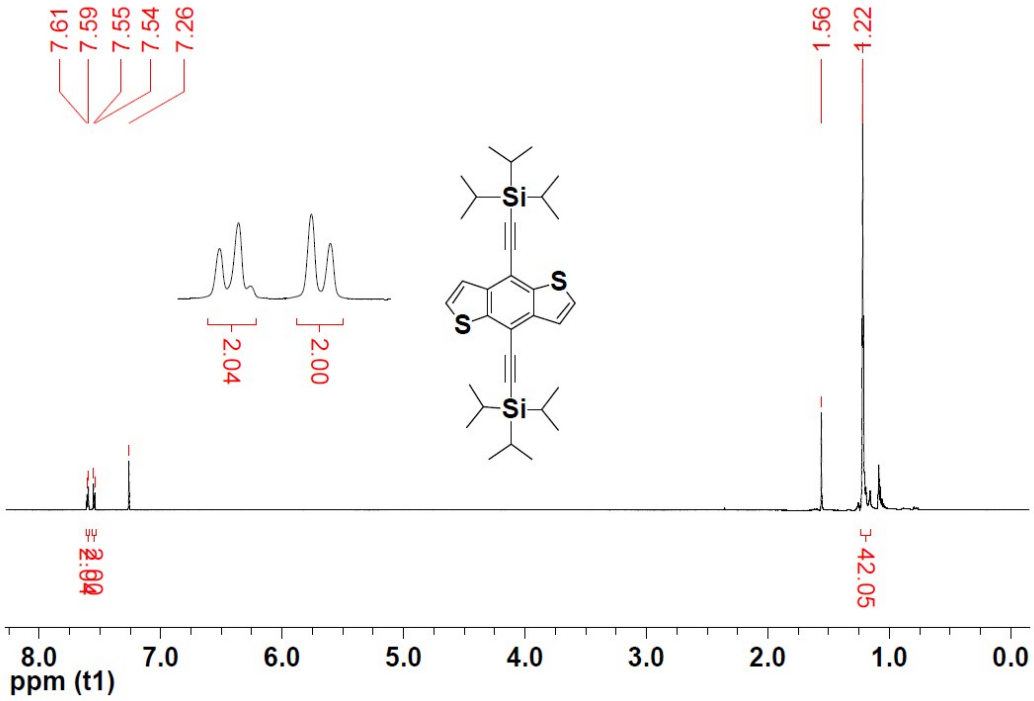


Figure S2. ^{1}H NMR spectrum of **2** in $CDCl_3$ solution

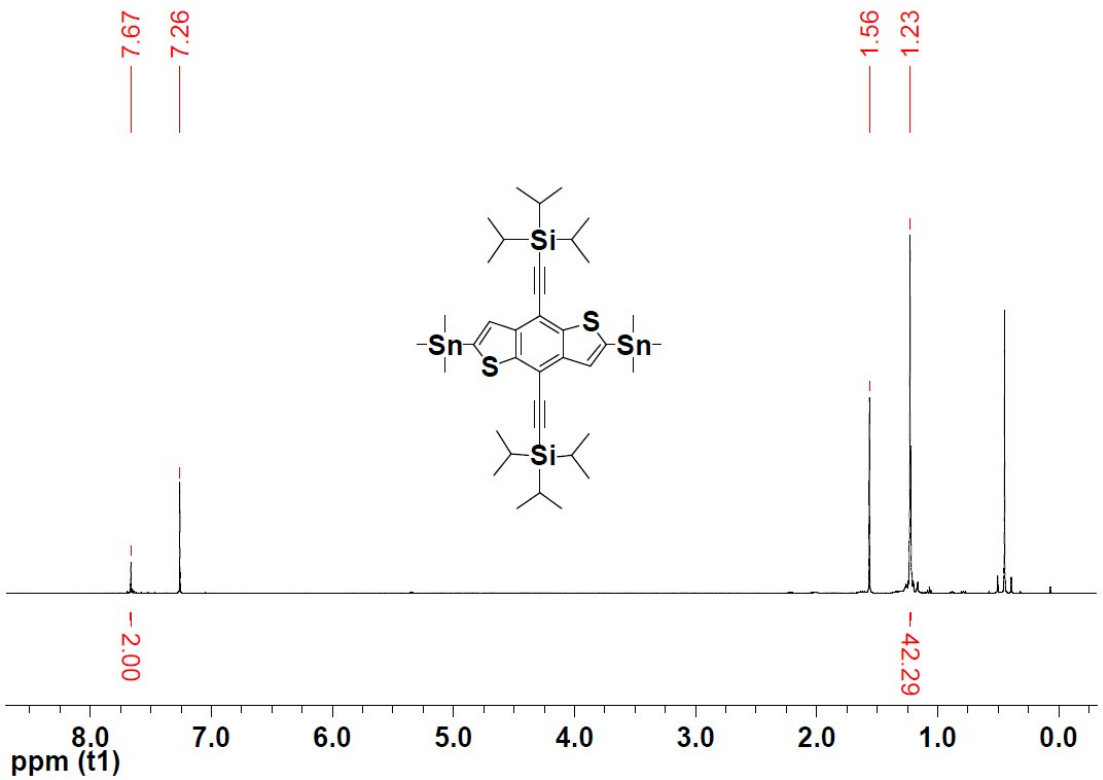


Figure S3. ^{1}H NMR spectrum of **TIPSBDT** in $CDCl_3$ solution

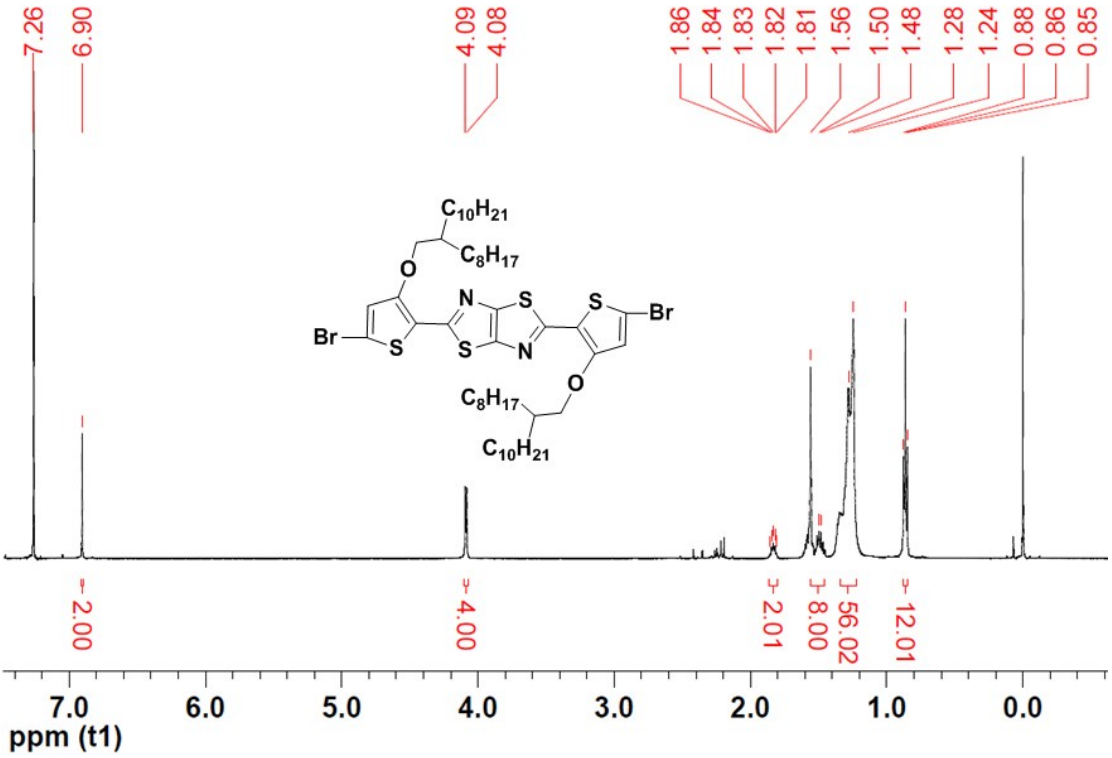


Figure S4. ^{1}H NMR spectrum of **TTz** in $CDCl_3$ solution

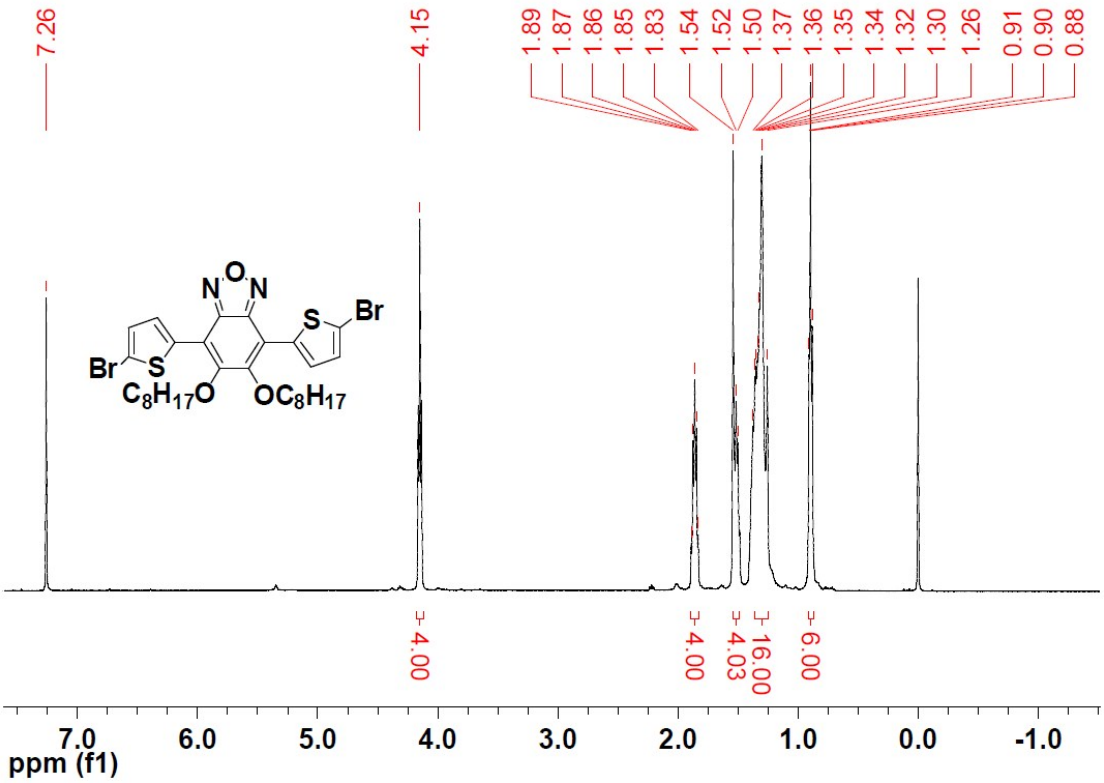


Figure S5. ^{1}H NMR spectrum of **DTBO** in $CDCl_3$ solution

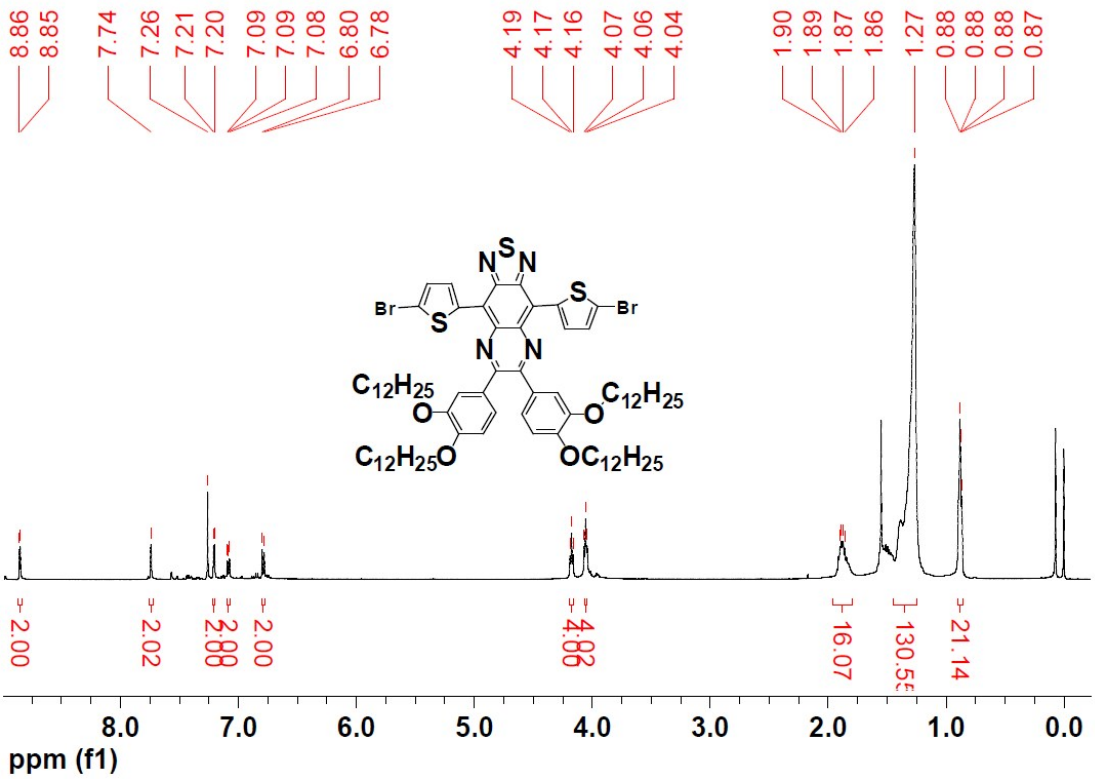


Figure S6. ^{1}H NMR spectrum of **DTQx** in $CDCl_3$ solution

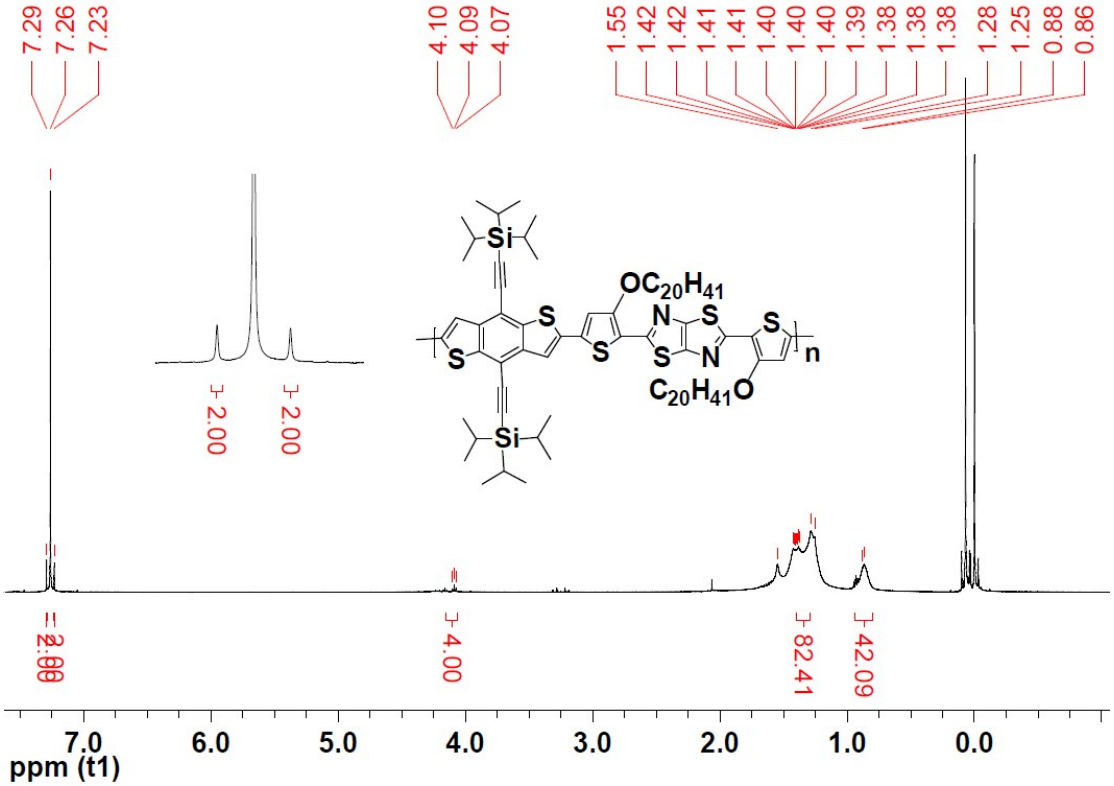


Figure S7. ^{1}H NMR spectrum of **PTIPSBDT-TTz** in $CDCl_3$ solution

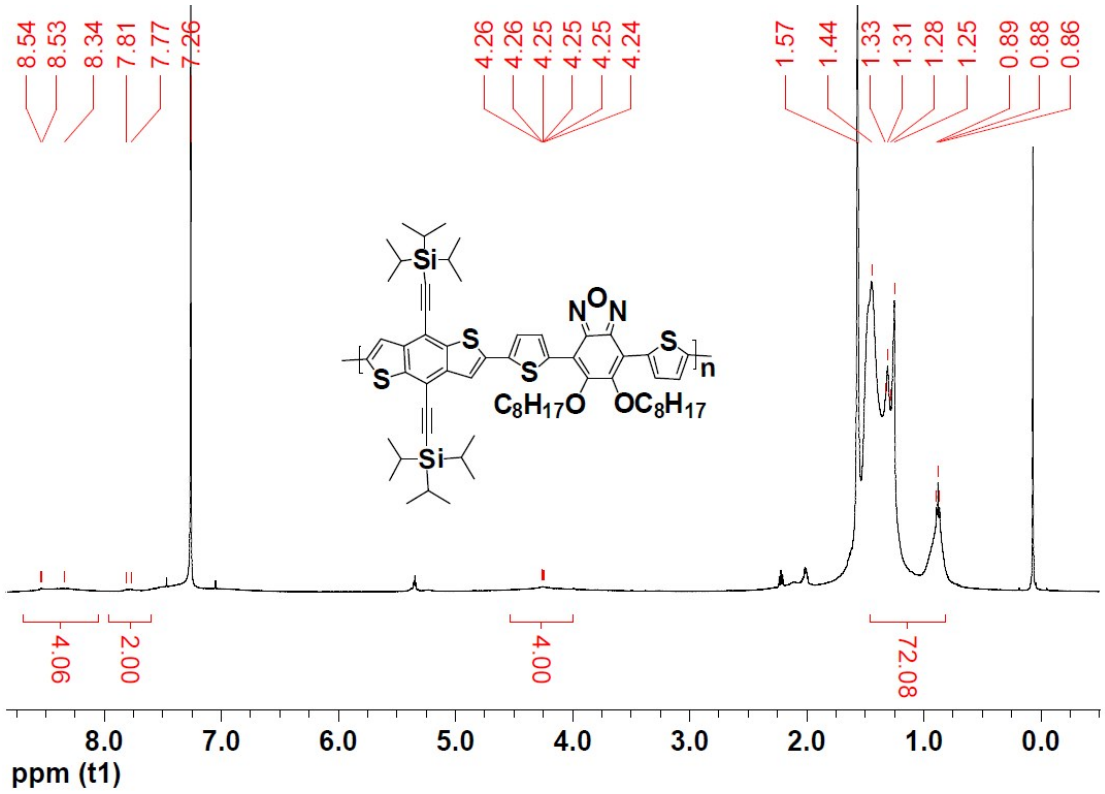


Figure S8. ^{1}H NMR spectrum of **PTIPSBDT-DTBO** in $CDCl_3$ solution

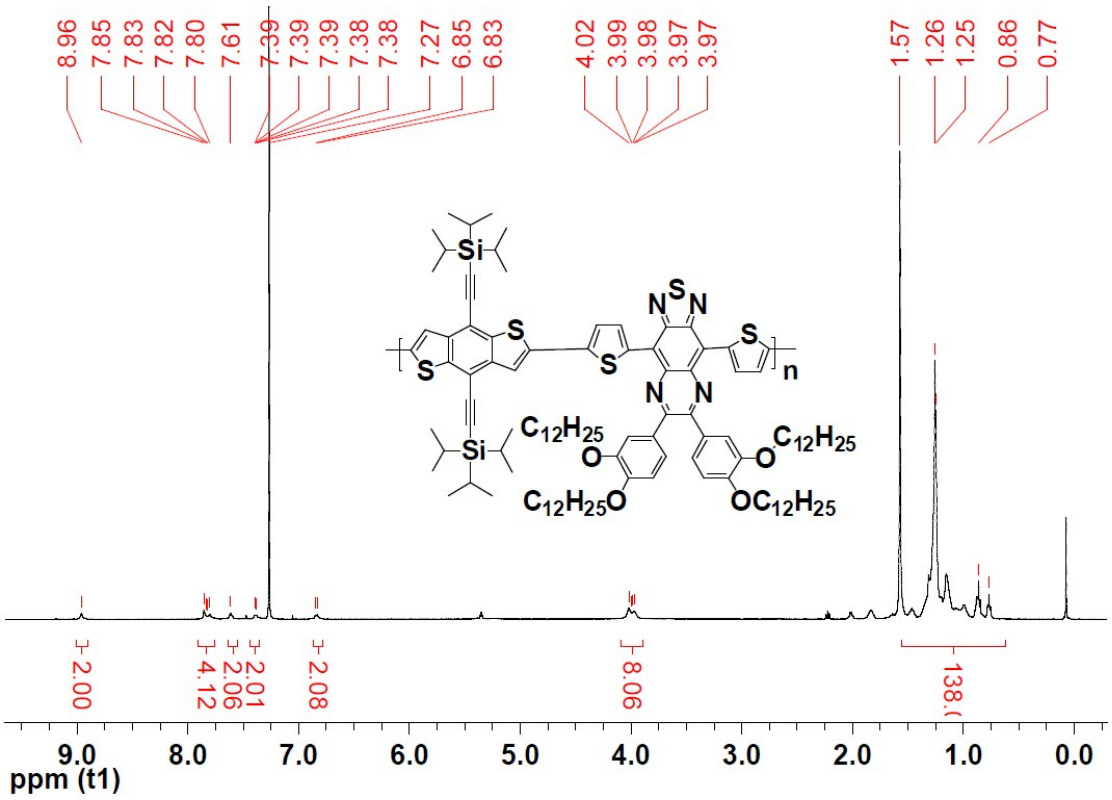


Figure S10. ^{1}H NMR spectrum of **PTIPSBDT-DTQx** in $CDCl_3$ solution.

3. TGA analysis

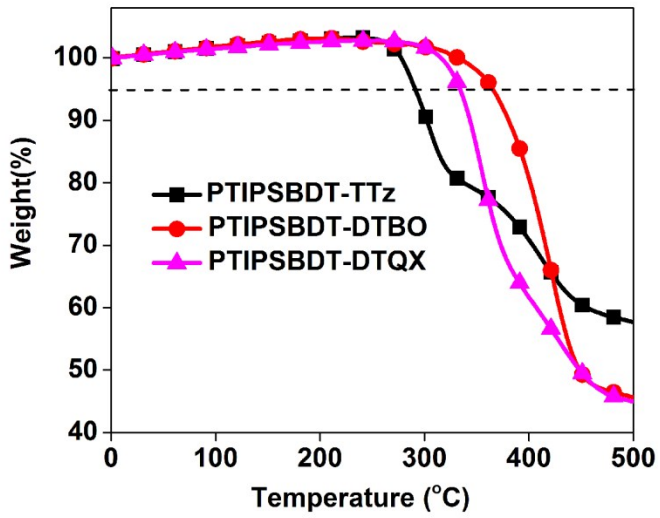


Figure S11. TGA curves of polymers with 10°C min^{-1} heating rate under nitrogen.

4. Device parameters for polymer:$PC_{71}BM$ cells processed from CF solutions

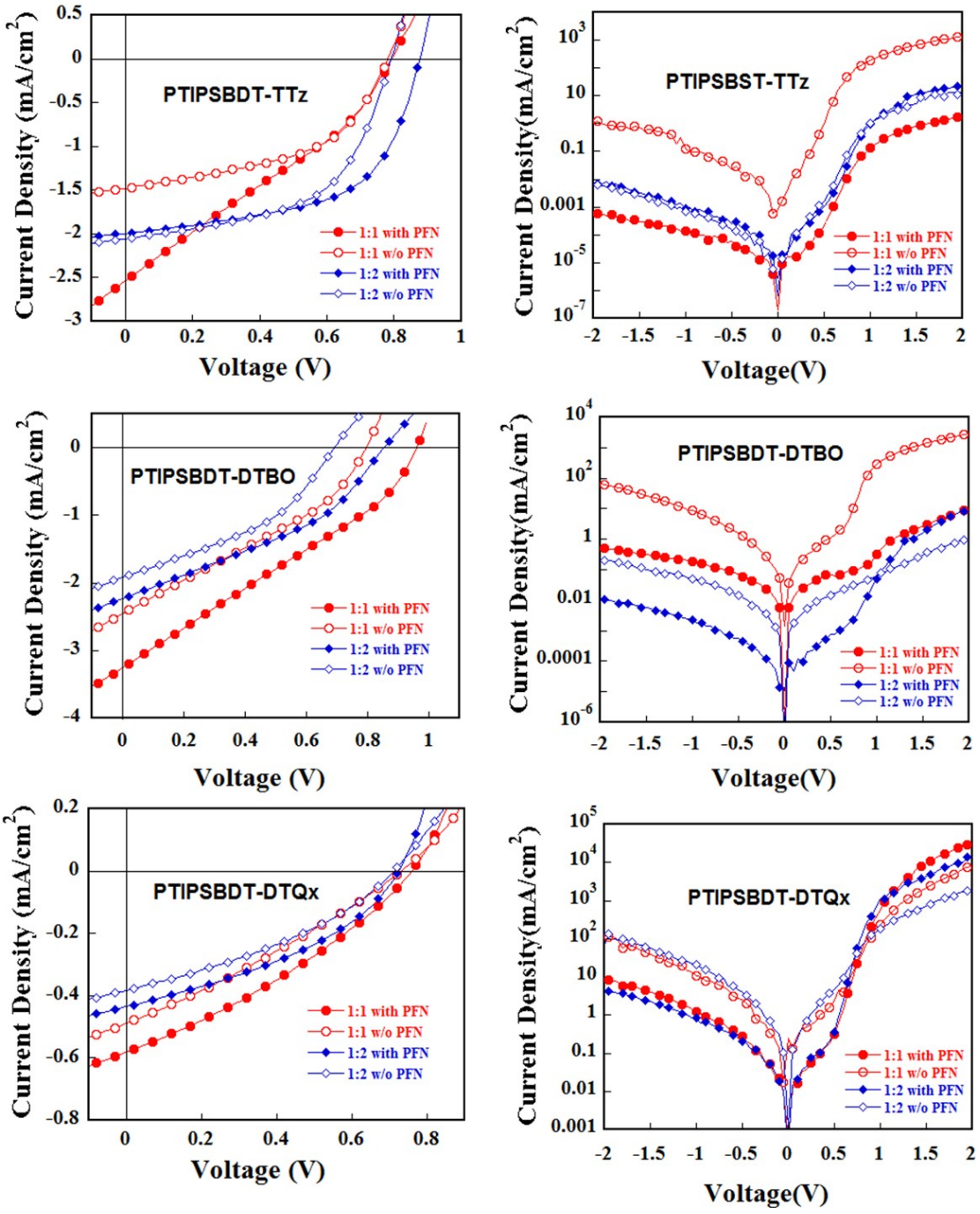


Figure S12. *J-V* characteristics of copolymer:$PC_{71}BM$ devices spin-coated from CF with or w/o PFN layer

Table S1. Comparison of the photovoltaic properties of co-polymer/$PC_{71}BM$-based devices with or w/o PFN layer under different ratios

Active Layers	D:A [wt%]	PFN	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
PTIPSBDT-TTz：$PC_{71}BM$	1:1	with	0.79	2.54	29.8	0.60
		w/o	0.78	1.48	49.7	0.57
	1:2	with	0.88	2.00	56.7	1.00
		w/o	0.79	2.06	54.5	0.89
P2：$PC_{71}BM$	1:1	with	0.96	3.25	29.1	0.91
		w/o	0.80[a]	2.45	31.7	0.62
	1:2	with	0.85	2.23	36.5	0.69
		w/o	0.69	1.92	38.9	0.52
P4：$PC_{71}BM$	1:1	with	0.76	0.58	31.8	0.14
		w/o	0.73	0.49	28.9	0.10
	1:2	with	0.72	0.44	37.9	0.12
		w/o	0.71	0.38	35.0	0.10