Electronic Supplementary Information

Design and photovoltaic characterization of dialkylthio benzo[1,2-b:4,5-b']dithiophene polymers with different accepting units

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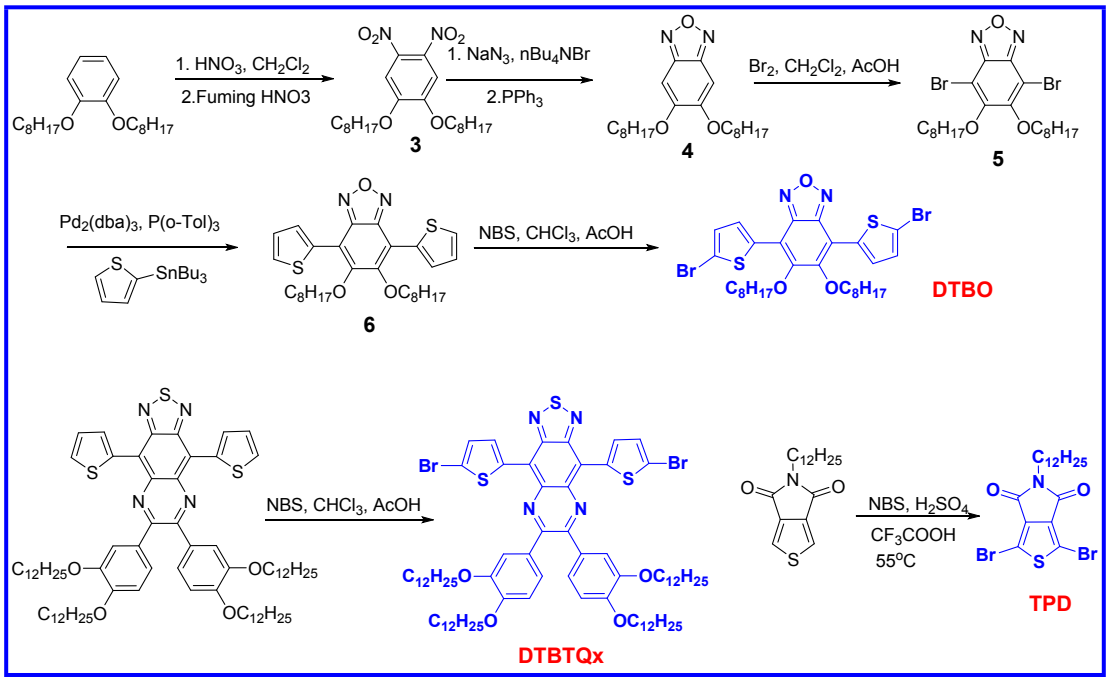
1. Synthesis of momoners

All chemicals and solvents were purchased from Sigma-Aldrich Co. and used without further purification. Toluene, THF, dichloromethane and diethyl ether were freshly distilled before use. The monomers DTBTQx,[1] DTBO[2] and TPD[3] were synthesized according to the procedures in literature illustrated in Scheme S1.



Scheme S1. Synthesis of monomers DTBO, DTBTQx and TPD**.**

1,2-Dinitro-4,5-bis(octyloxy)benzene (3). 65% HNO_3 was added dropwise to a 10°C cooled mixture solution of 1,2-bis(octyloxy)benzene (10 g, 29.9 mmol), CH_2Cl_2 (140 mL) and AcOH (140 mL). The reaction mixture was warmed to rt and stirred for 1 h. The mixture was then cooled to 10°C before fuming HNO_3 (50 mL) was added. Before being poured into ice-water, the mixture was warmed to room temperature and stirred for 40 h. The CH_2Cl_2 layer was separated and the aqueous phase extracted with CH_2Cl_2. The organic phases were combined, washed sequentially with water, sat. $NaHCO_3$ (aq), and brine, then over dried with $MgSO_4$ and concentration. The crude product was recrystallized from EtOH. Yield: 10 g (80%), yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) 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 (4). Compound **3** (1.7 g, 4 mmol), NaN_3 (1.3 g, 20 mmol), and n-Bu_4NBr (260 mg, 0.8 mmol) was added in 20ml toluene and refluxed for 12h. Then PPh_3 (1.26 g, 4.8 mmol) was added and the

mixture heated under reflux for an additional 24 h. The reaction system was cooled to room temperature and filtered through a short silica plug; the solvent was removed by pressure evaporation and an off-white solid was obtained. The final solid was recrystallized in ethanol, and yielded 1.3 g (60%) of the target compound 5. ^{1}H NMR (500 MHz, $CDCl_3$) 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 (5). Br_2 (0.85 mL, 16.6 mmol) were added sequentially to a solution of compound **4** (1.5 g, 4.0 mmol) in CH_2Cl_2 (80 mL) and AcOH (10 mL). The resulting mixture was stirred for 3 days at room temperature and then poured into then poured into aqueous NaOH solution (10 g in 200 mL). The aqueous phase was extracted with CH_2Cl_2; the combined organic extracts were washed with brine and concentrated under reduced pressure and purified through column chromatography on silica gel eluting with dichloromethane: petroleum ether (1:9, v/v) to yield a white solid 6 (2.0 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) 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 (6). Compound **5** (665 mg, 1.25 mmol), $Pd_2(dba)_3$ (46 mg, 0.05 mmol), tri-o-tolylphosphine (122 mg, 0.40 mmol) and 2-tributylstannylthiophene (994 μL, 3.13 mmol) was added into a round bottom flask purged with nitrogen. Dry toluene (10 mL) was then added to leave the reaction mixture heated under reflux for 16 h under N_2. The reaction mixture was concentrated directly under vacuum, and purified by column chromatography on silica gel eluting with chloroform: petroleum ether (1:10, v/v) afforded the title product as a yellow solid (470 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.46 (dd, *J* = 3.8, 1.1 Hz, 2H), 7.50 (dd, *J* = 5.1, 1.0 Hz, 2H), 7.22 (dd, *J* = 5.1, 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).[1] NBS (533 mg, 3 mmol) was added in one portion to a solution of **6** (810 mg, 1.5 mmol) in $CHCl_3$ (45 ml) and glacial AcOH (45 mL) and then the mixture was stirred at room temperature for 20 h in the dark. The reaction mixture was concentrated directly onto Celite under vacuum, and purified by column chromatography on silica gel eluting with chloroform:petroleum ether (1:9, v/v) to

afford **M3** as an orange solid (1.4 g, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 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).

6,7-Bis(3,4-bis(dodecyloxy)phenyl)-4,9-bis(5-bromothiophen-2-yl)-[1,2,5] thiadiazolo[3,4-g]quinoxaline (**DBTQx**). To a solution of 6,7-bis(3,4-bis(dodecyloxy)-phenyl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]-quinoxaline (534 mg, 0.43 mmol) in anhydrous THF (100 mL) was added with N-bromosuccinimide (NBS) (168 mg, 0.95 mmol) in one portion. The mixture was stirred in the dark at 0°C overnight. The mixture was then poured into water and extracted with extracted by 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 pure DTBTQx as a purple black solid (538 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) 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, 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, 8), 1.61-1.48 (m, 8H), 1.44 – 1.20 (m, 64H), 0.92-0.85 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.77, 150.79, 150.61, 149.10, 137.15, 133.51, 132.88, 130.32, 129.31, 124.56, 119.89, 115.41, 111.95, 69.37, 69.07, 31.94, 29.71, 29.39, 26.34, 26.13, 25.99, 22.69, 14.10.

2. NMR spectra

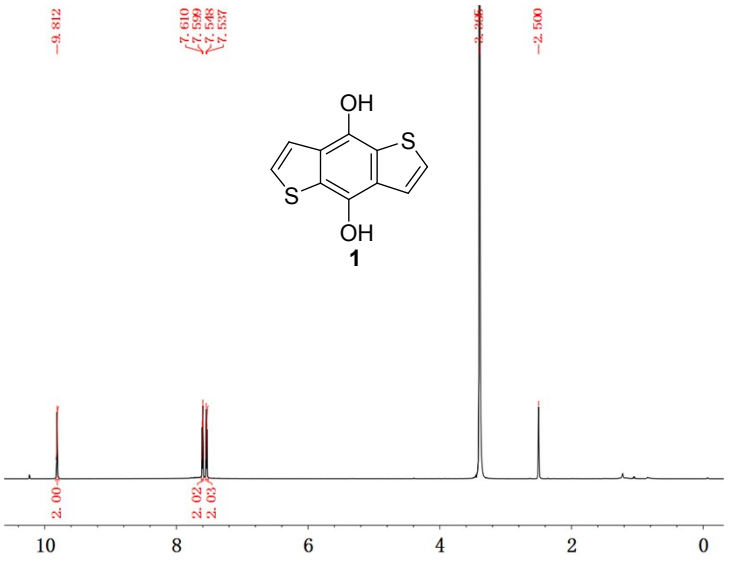


Figure S1. ^{1}H NMR spectrum of compound **1.**

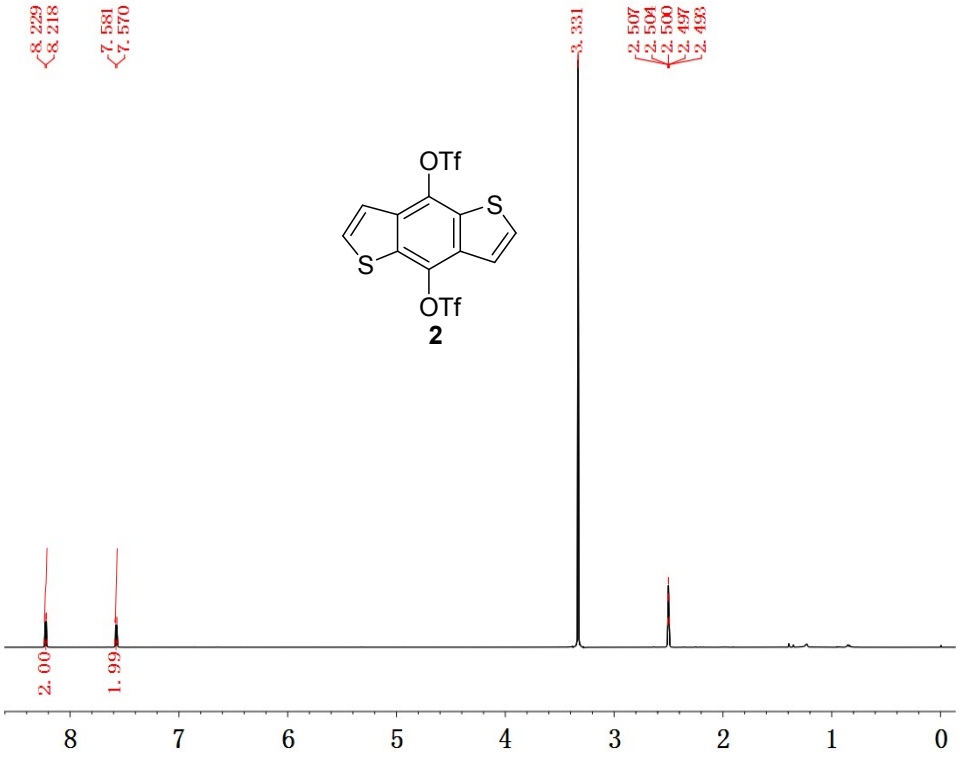


Figure S2. [1]H NMR spectrum of compound **2.**

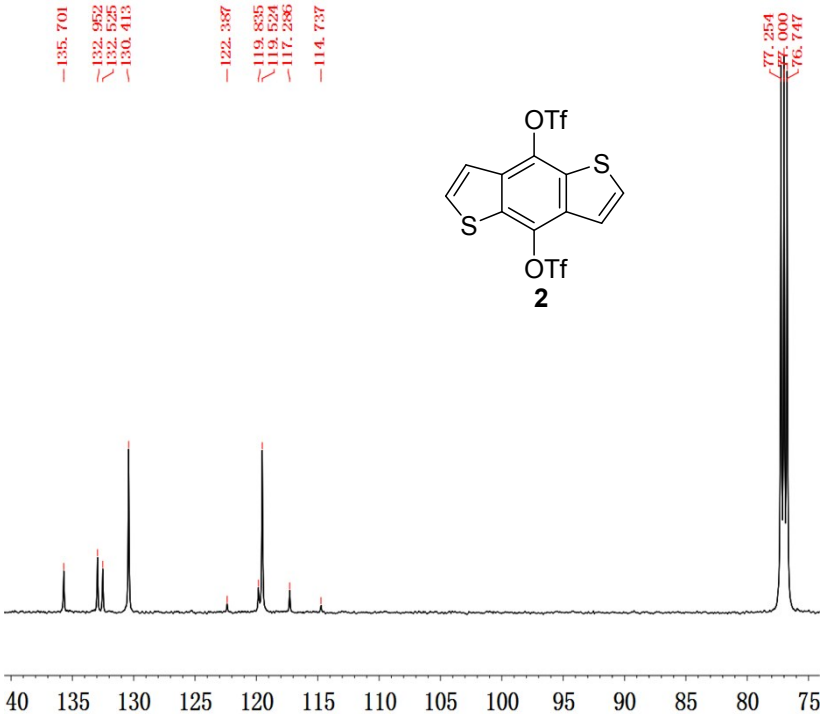


Figure S3. [13]C NMR spectrum of compound **2.**

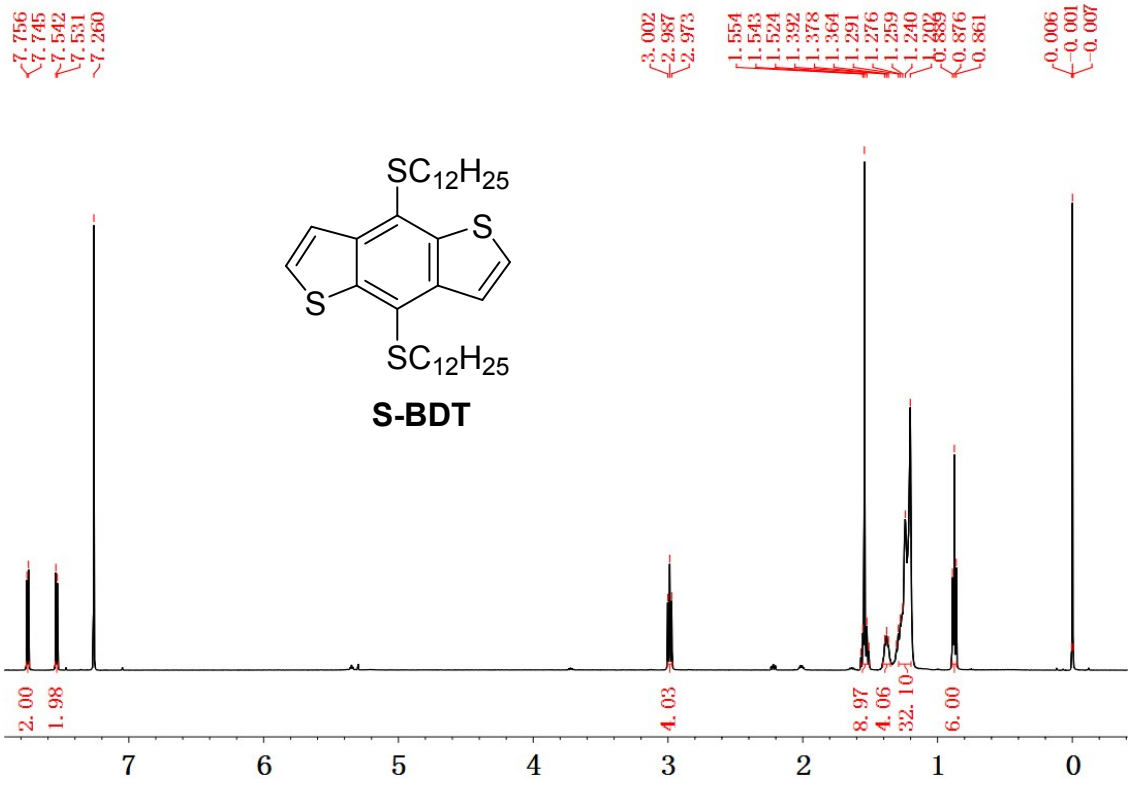


Figure S4. [1]H NMR spectrum of **S-BDT.**

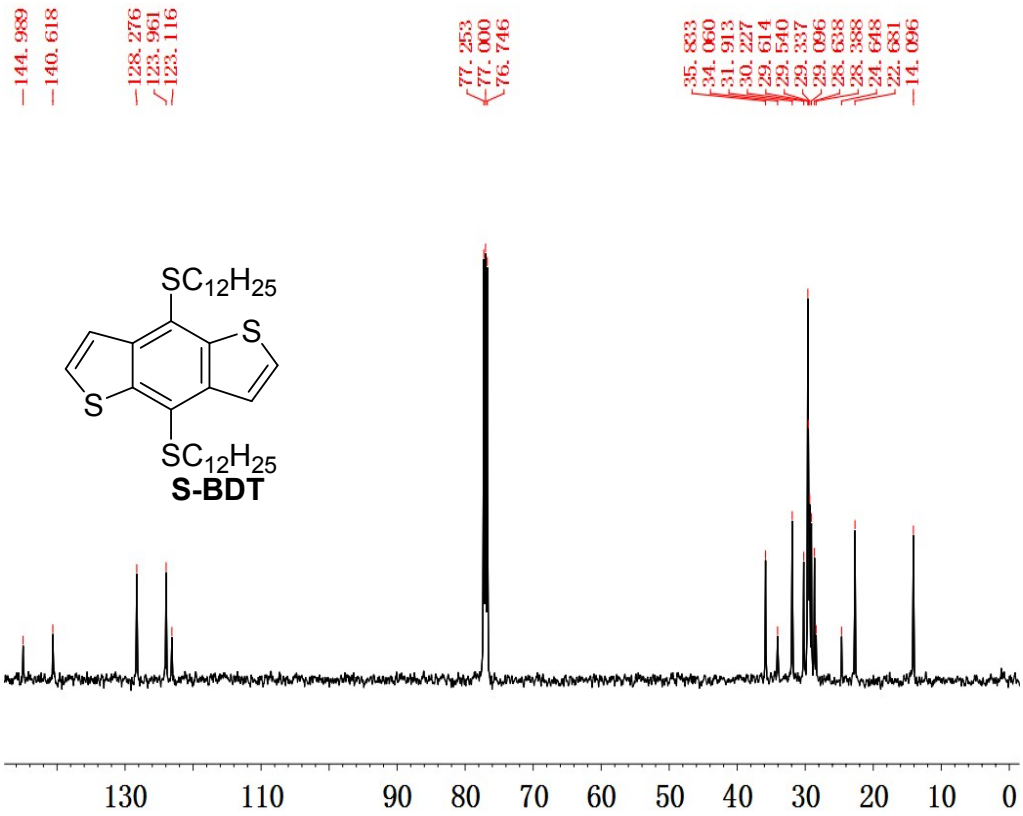


Figure S5. [13]C NMR spectrum of **S-BDT.**

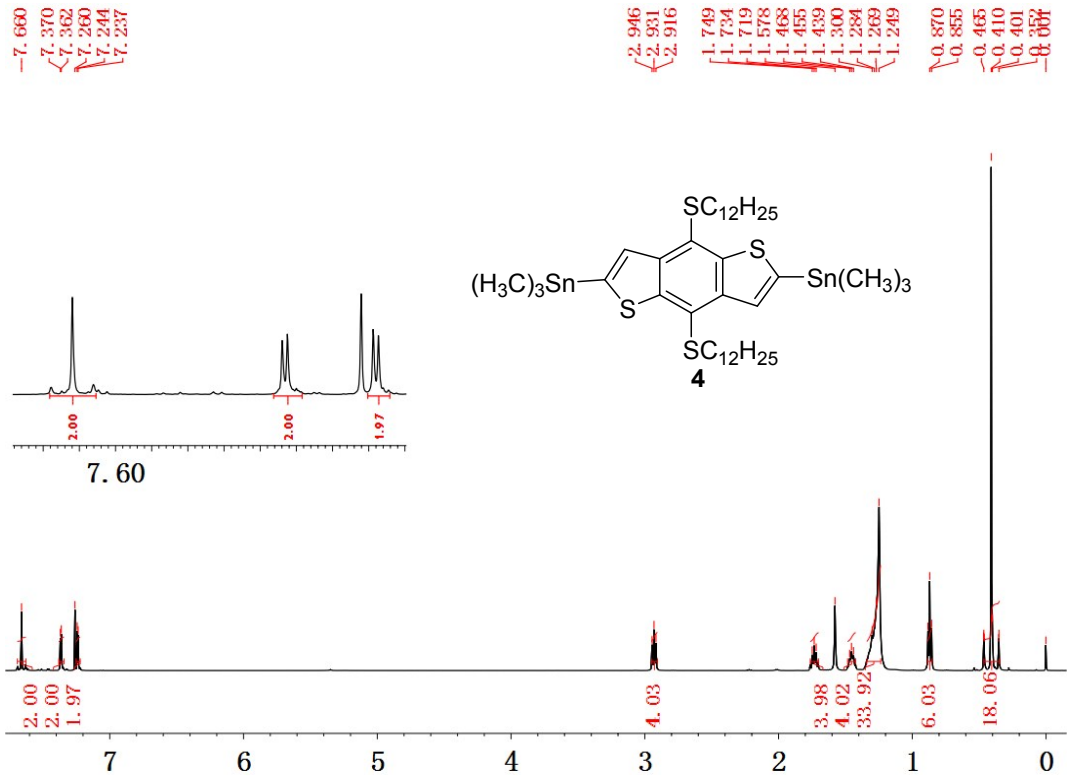


Figure S6. ^{1}H NMR spectrum of **M1.**

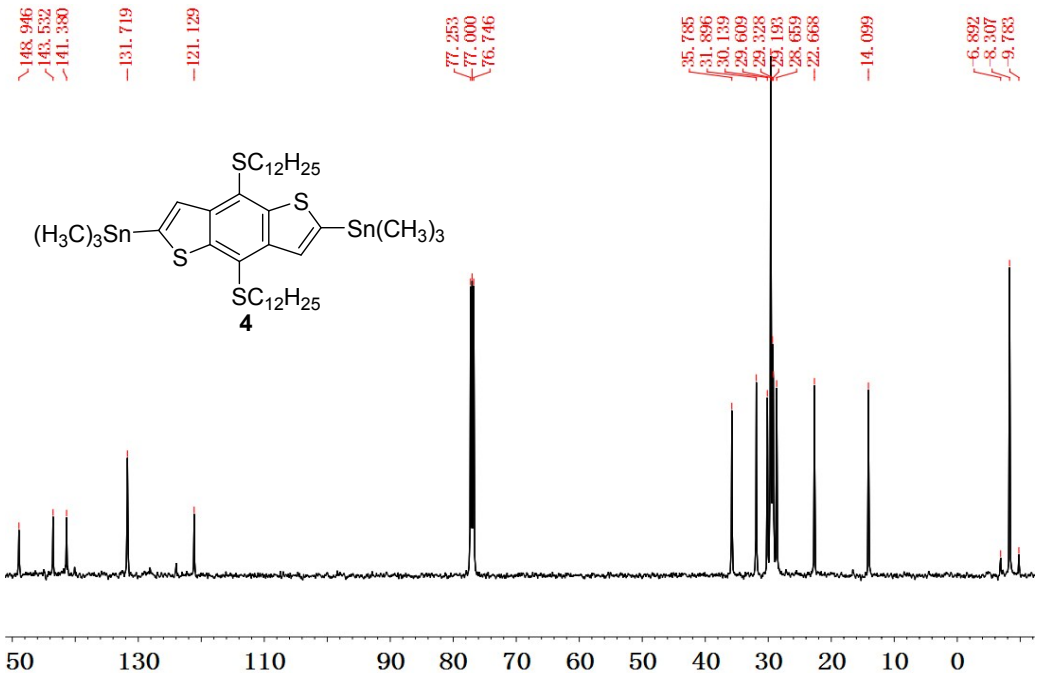


Figure S7. ^{13}C NMR spectrum of **M1.**

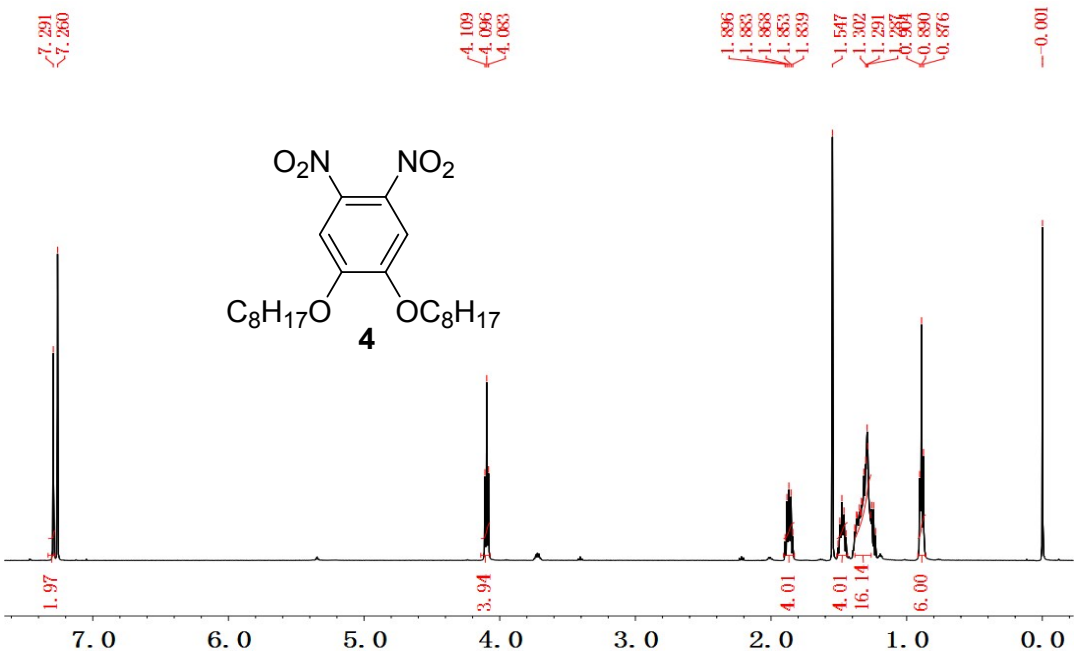


Figure S8. [1]H NMR spectrum of compound **4.**

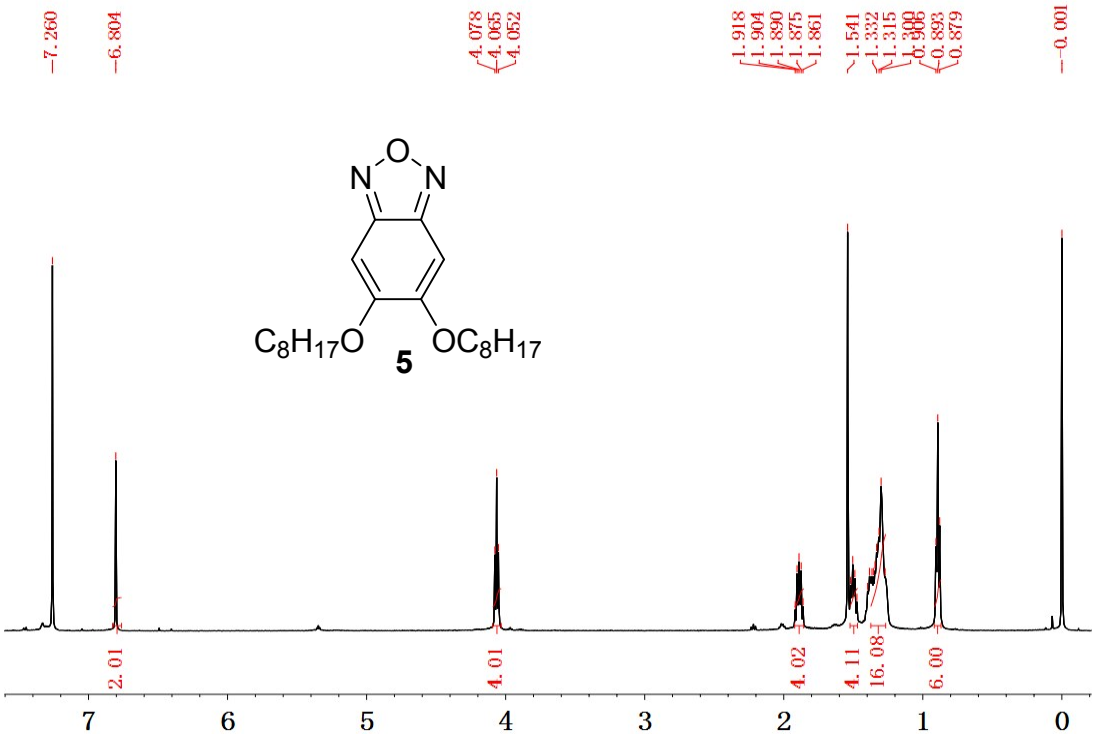


Figure S9. [1]H NMR spectrum of compound **5.**

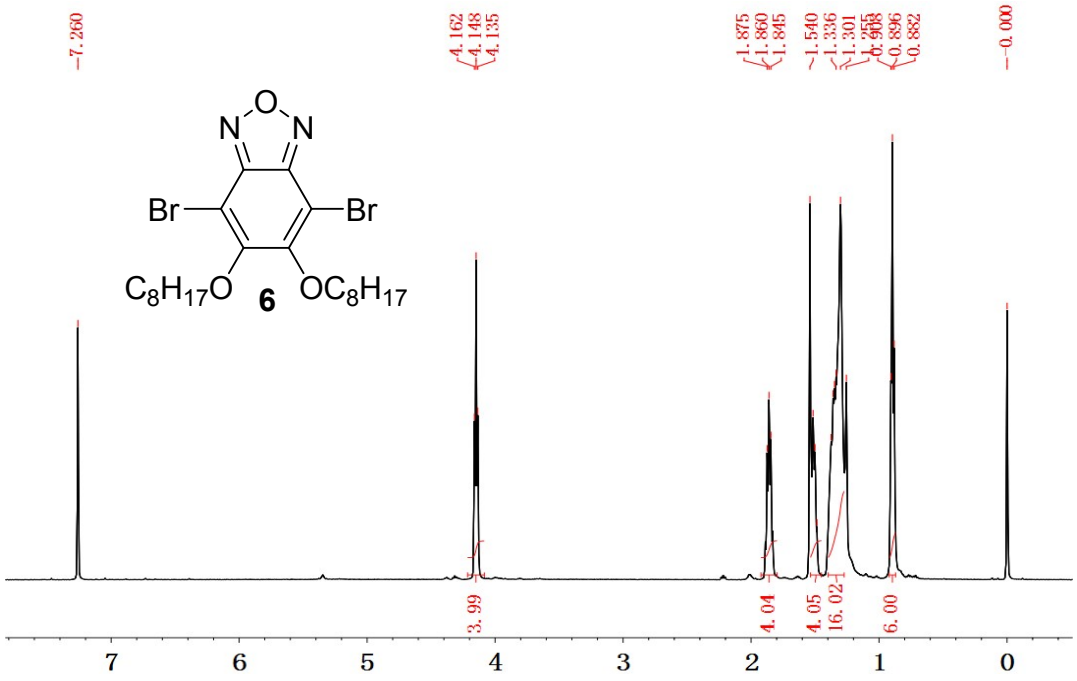


Figure S10. ^{1}H NMR spectrum of compound **6.**

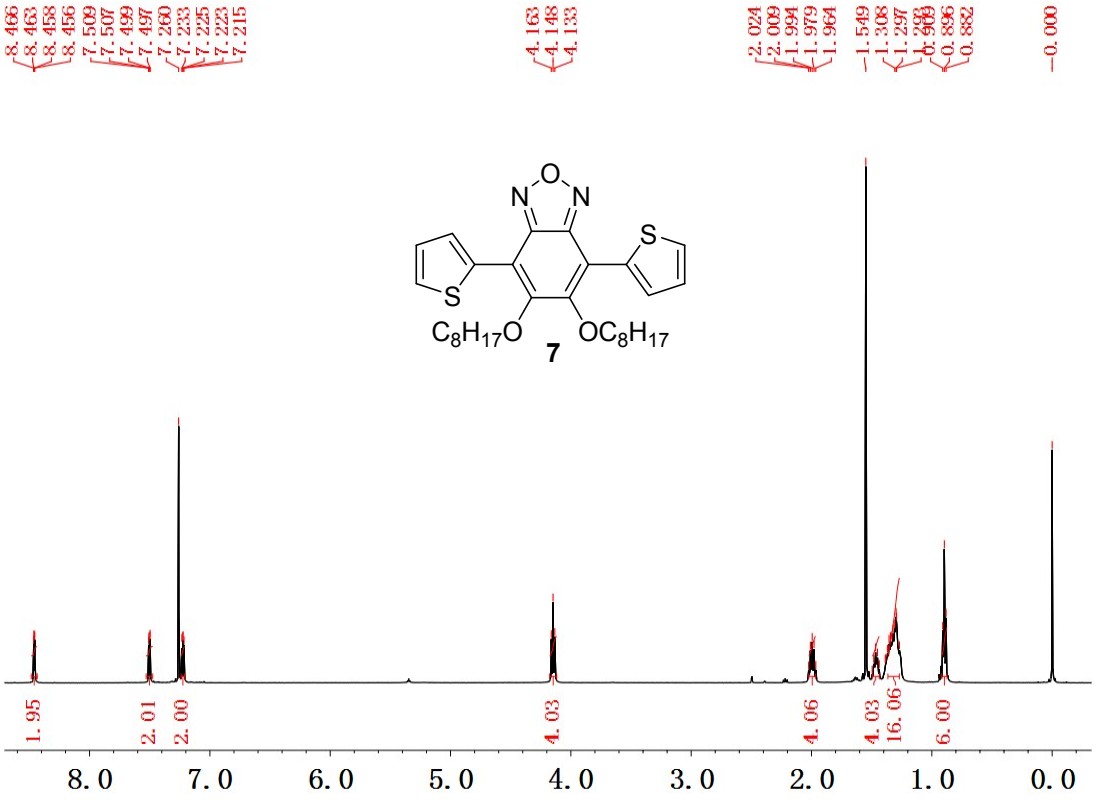


Figure S11. ^{1}H NMR spectrum of compound **7.**

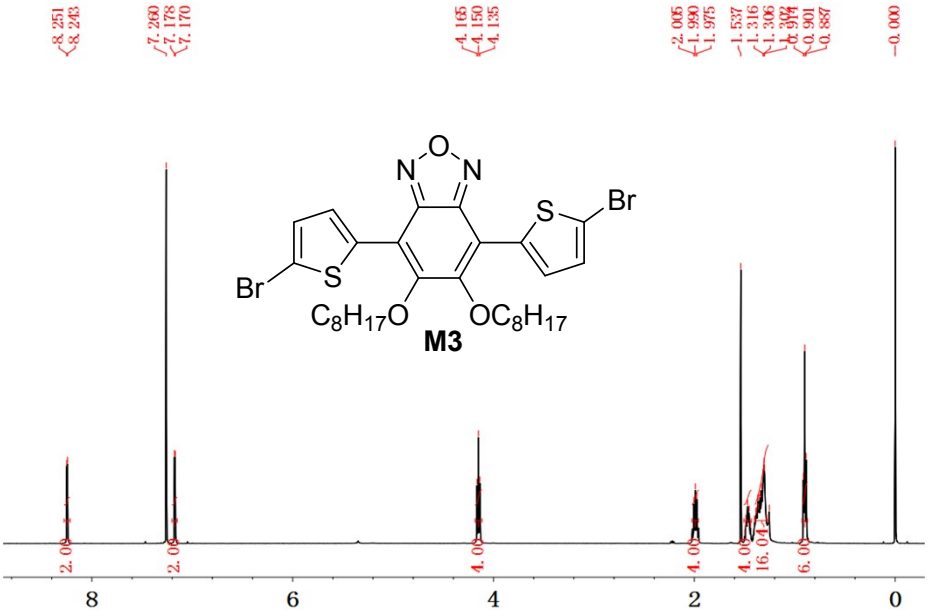


Figure S12. [1]H NMR spectrum of **M3.**

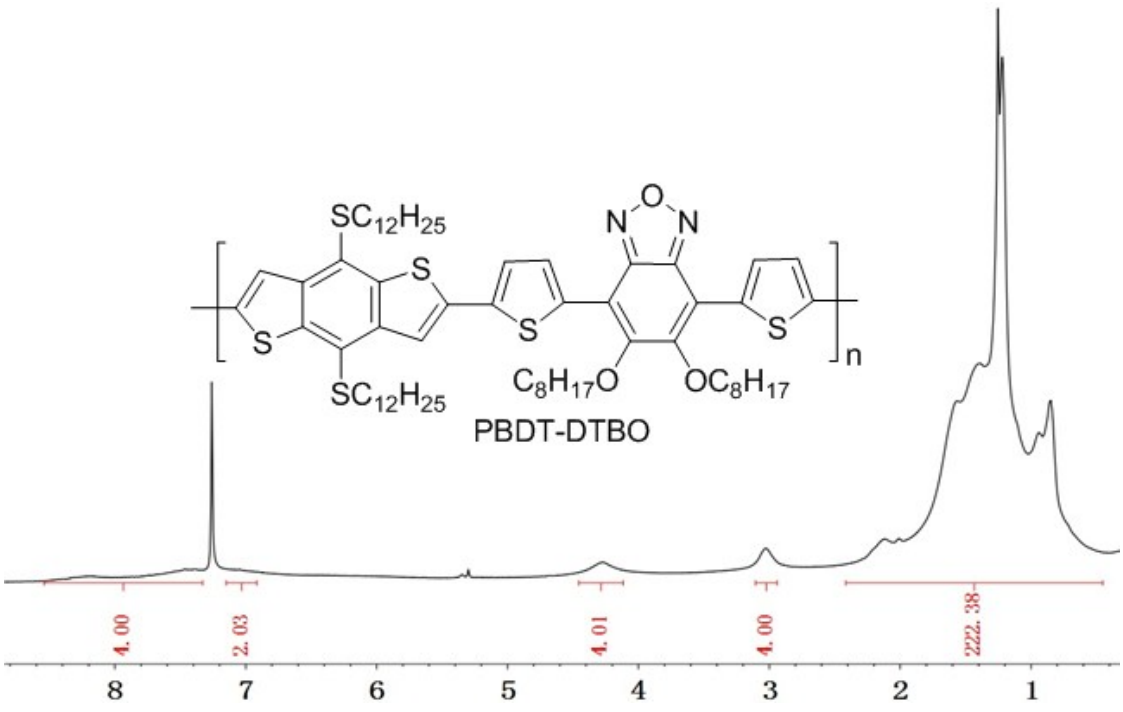


Figure S13. [1]H NMR spectrum of PBDT-DTBO.

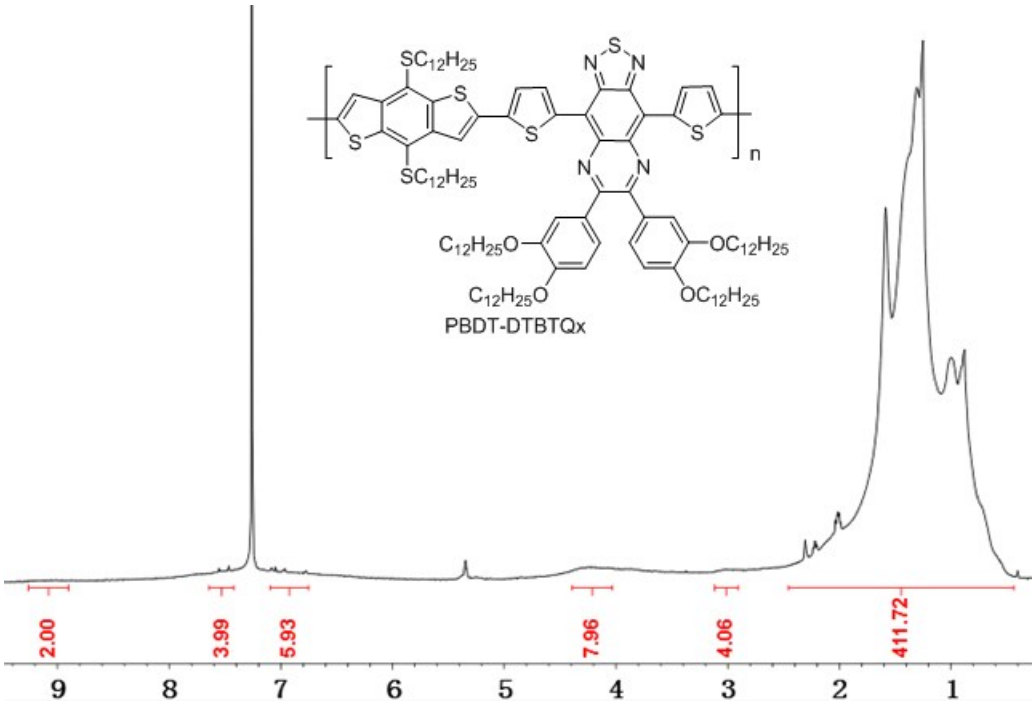


Figure S14. ^{1}H NMR spectrum of PBDT-DTBTQx.

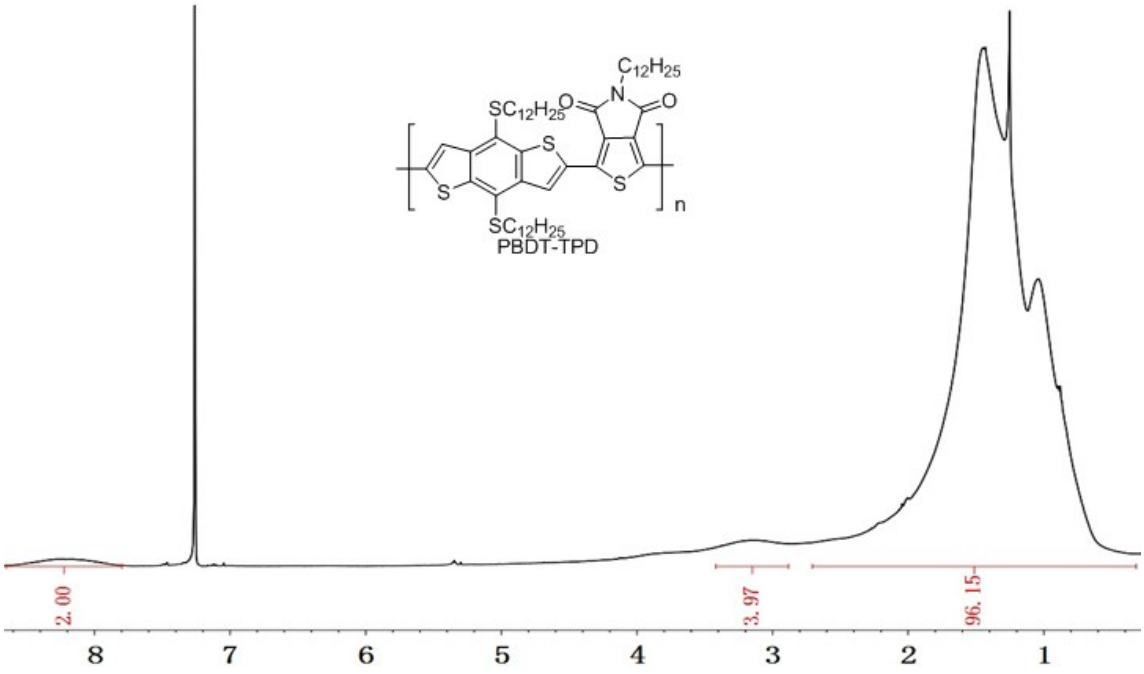


Figure S15. ^{1}H NMR spectrum of **PBDT-TPD.**

3. Thermal properties of polymers and electrochemical calculation

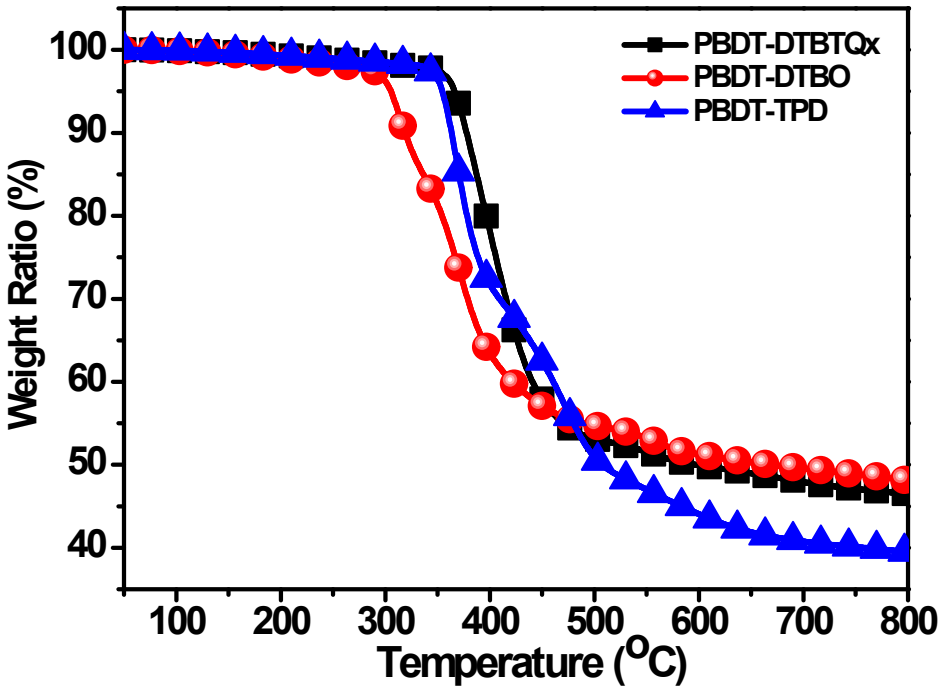


Fig.S16. TGA traces of polymers at heating rate of 10°C/min under an inert atmosphere.

The potential of ferrocene 0.40 V vs SCE is used as internal standard. According to the following equations we calculate the HOMO level of the polymers from the onset oxidation potentials (E_{ox}^{onset}) and the LUMO levels using HOMO and E_g^{opt}, on the basis of 4.8 eV below vacuum for the energy level of Fc/Fc^+.

HOMO = $-e(E_{ox}^{onset} + 4.4)$ (eV);

LUMO = HOMO + E_g^{opt} (eV)

4. Complete PSC devices data

Table S1 Photovoltaic performance of polymer:PCBM devices

Polymer:PCBM	Processing solvent	D/A	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%][g]
PBDT-DTBTQx/$PC_{61}BM$						
	o-DCB	1:1	0.45	0.90	53.6	0.22 (0.21±0.01)
	o-DCB	4:5	0.48	0.95	53.3	0.24 (0.23±0.01)
	o-DCB +1%DIO	4:5	0.45	1.00	50.1	0.23 (0.21±0.02)
	CF+1%DIO	4:5	0.46	0.92	49.1	0.21 (0.20±0.01)
PBDT-TPD/$PC_{61}BM$						
	CF	1:1	0.64	3.11	41.4	0.82 (0.80±0.02)
	CF+3%DIO	1:1	0.74	2.85	38.7	0.82 (0.81±0.01)
	CF+3%DIO[a]	1:1	0.65	1.99	52.8	0.68 (0.67±0.01)
	CF+3%DIO[b]	1:1	0.76	1.65	47.7	0.60 (0.59±0.01)
	CF+3%DIO[c]	1:1	0.75	3.00	41.2	0.93 (0.91±0.02)
	CF+5%DIO	1:1	0.78	2.02	38.4	0.61 (0.60±0.01)
	CF+3%DIO	3:2	0.75	2.12	38.4	0.61 (0.60±0.01)
	o-DCB+1%DIO	1:1	0.78	2.08	32.6	0.53 (0.52±0.01)
	***o*-DCB+3%DIO**	**1:1**	**0.80**	**4.95**	**32.2**	**1.28** (1.26±0.03)
PBDT-DTBO/$PC_{61}BM$						
	CF	**1:1**	**0.83**	**7.38**	**59.5**	**3.64** (3.60±0.04)
	CF[a]	**1:1**	**0.83**	**8.13**	**62.9**	**4.24** (4.19±0.05)
	CF[b]	1:1	0.81	6.35	55.9	2.87 (2.83±0.04)
	CF[e]	1:1	0.83	7.38	47.3	2.90 (2.84±0.07)
	CF[a,c]	1:1	0.80	8.10	59.8	3.88 (3.82±0.06)
	CF+3%DIO	1:1	0.80	6.27	46.1	2.31 (2.28±0.05)
	CF+3%DIO	1:2	0.74	6.08	40.8	1.84 (1.81±0.04)
	CF+3%DIO[d]	1:1	0.70	4.62	44.5	1.44 (1.42±0.02)
	o-DCB+1%DIO	1:1	0.73	5.77	39.3	1.66 (1.62±0.04)
	CB+1%DIO	1:1	0.77	4.21	43.9	1.42 (1.39±0.03)
PBDT-DTBO/$PC_{71}BM$						
	CF	1:1	0.70	12.77	45.1	4.03 (3.98±0.05)
	CF[c]	1:1	0.73	13.75	44.9	4.51 (4.46±0.06)
	CF+1%DIO[c]	**1:1**	**0.83**	**10.24**	**66.3**	**5.63** (5.52±0.12)
	CF+1%DIO[f]	**1:1**	**0.83**	**9.69**	**66.5**	**5.35** (5.25±0.10)
	CF+3%DIO	1:1	0.84	9.41	58.8	4.65 (4.59±0.06)
	CF+5%DIO	1:1	0.84	8.63	57.2	4.15 (4.12±0.04)
	CF+1%DIO	1:2	0.81	8.27	66.2	4.43 (4.38±0.05)
	CF+3%DIO	1:2	0.81	9.34	66.5	5.03 (4.98±0.06)
	CF+1%DIO	1:3	0.81	6.60	59.2	3.16 (3.14±0.02)
	CF+1%DIO[c]	1:3	0.81	6.83	60.9	3.37 (3.34±0.03)

[a]annealing at 50°C, [b]annealing at 100°C, [c]spin-coating at 1200 rpm, [d]spin-coating at 1300 rpm, [e]concentration at 30 mg/mL, [f]spin-coating at 1500 rpm, [g]values in parenthesses are avaerage values and variances of 20 devices.

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References

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[2] Jiang, J-M.; Yang, P-A.; Chen, H-C.; Wei, K-H. *Chem. Commun.* **2011**, *47*, 8877-88979.

[3] Zhu, E.; Ni, B.; Zhao, B.; Hai, J.; Bian, L.; Wu, H.; Tang, W. *Macromol. Chem. Phys.* **2014**, *215*, 227.