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Electronic Supplementary Information

Thieno[3,2-*b*]thiophene-based Conjugated Polymers for Solution-processable Neutral Black Electrochromism

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Summary of Previous Research Works

Table S1 Summary of Black Electrochromic Polymers in Previous Research Works.

Polymer	Synthesis	$L^*a^*b^*$	A_{max} (a.u.)[a]	ΔT_{int} (%)	λ_{test} (nm)	ΔT (%)	$t_{switching}$ (s)[b]	CE (cm^2 C^{-1})
P1[1]	Oxidative	Neutral: 45,0,–18 Ox: 85,–5,–5	0.9	-	636	40	2~5	-
P2[2]	Electrochemical	Neutral: 14.3,0.29,0.35 Ox: 39.2,0.29,0.33	-	-	522	15.3	2~3	-
P3[3]	Stille coupling	Neutral.: 46,3,–11 Ox: 82,–8,–6	0.45	-	540	47	2~10	-
P4[4]	Stille coupling	-	-	-	600	23	0.7	-
P5[5]	Electrochemical	Neutral: 45.1,2.97,–11.6 Ox: 71.3,–6.12,–12.5	0.46	-	500	39	5~10	-
P6-1[6]	Stille coupling	Neutral: 49,–3,–2 Ox: 60,–2,–4	0.62	17.2	736	26.4	Ox: 61.38[c] Red: 2.00[d]	200
P6-2[6]	Stille coupling	Neutral.: 50,0,–6 Ox: 61,–2,–6	0.63	13.6	790	23.0	Ox: 33.99[c] Red: 3.07 [d]	130

Table S1 (continued)

Polymer	Synthesis	*L*a*b**	A_{max} (a.u.)[a]	ΔT_{int} (%)	λ_{test} (nm)	ΔT (%)	$t_{switching}$ (s)[b]	CE ($cm^2\ C^{-1}$)
P6-3[6]	Stille coupling	Neutral: 53,0,–7 Ox: 65,–2,–5	0.61	13.3	785	15.2	Ox: 72.91 [c] Red: 14.57 [d]	107
P7[7]	Direct arylation	Neutral: 45,5,3 Ox: 88,–4,–3	-	51.7	-	-	-	-
P8[8]	Electro-chemical	Neutral: 4,–2,0 Ox: 51,–5,12	-	-	700	32	1.15	121.3
P9-1[9]	Stille coupling	Neutral: 36.99,0.45,–4.52 Ox: 52.63,–4.07,–5.81	-	-	520	21.0	1.90	155.97
P9-2[9]	Stille coupling	Neutral: 29.90,2.21,–3.94 Ox: 38.0,–1.23,–6.70	-	-	510	20.6	0.72	167.61

[a] A_{max} are the optical densities of the polymer films used in the performance tests; [b] $t_{switching}$ are the times required to reach 95% of the full responses; [c] Switching time from the neutral to the oxidized state; [d] Switching time from the oxidized to the neutral state.

Synthesis

Synthesis of precursors and monomers

Tetrabromothieno[3,2-*b*]thiophene (**1**), 3,6-dibromothieno[3,2-*b*]thiophene (**2**), and 3,6-dimethoxythieno[3,2-*b*]thiophene (TTOMe) and 4,7-dibromo-2,1,3-benzothiadiazole (BTBr) were synthesized according to reported procedures.[10-12]

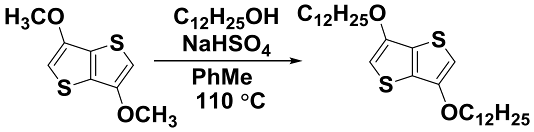
4,7-Dibromo-2,1,3-benzothiadiazole (BTBr): Yield: 5.7 g (95 %). ^{1}H NMR (300 MHz, CDCl3, ppm): δ 7.73 (s, 2H).

Tetrabromothieno[3,2-*b*]thiophene (1): Pale yellow solid. Yield: 84.6 g (93 %). ^{13}C NMR spectrum was difficult to record because of poor solubility in common organic solvents. GC-MS revealed a single peak. MS (*m/z*): 455.7 [M+].

3,6-Dibromothieno[3,2-*b*]thiophene (2): Yield: 11.9 g (90 %). ^{1}H NMR (300 MHz, CDCl3, ppm): δ 7.34 (s, 2H).

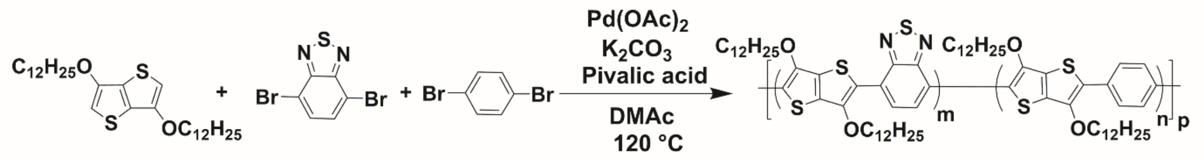
3,6-Dimethoxythieno[3,2-*b*]thiophene (TTOMe): Yield: 4.9 g (75 %). ^{1}H NMR (300 MHz, CDCl3, ppm): δ 6.26 (s, 2H), 3.92 (s, 6H).

3,6-Bis(dodecyloxy)thieno[3,2-*b*]thiophene (TTOC12): A solution of 3,6-dimethoxy-thieno[3,2-*b*]thiophene (1.00 g, 5.00 mmol), 1-dodecanol (3.73 g, 20 mmol), and $NaHSO_4$ (60 mg, 0.50 mmol) in anhydrous toluene (25 mL) was heated to 110 ℃ for 15 h. After cooling to r.t., the solution was poured into methanol and the precipitate was collected by filtration. The pale blue crude product was dissolved in CH_2Cl_2 and washed with a saturated aqueous NaHCO3 and water. The organic layer was separated and the solvent was evaporated to give pale blue solid. It was recrystallized from chloroform and ethanol to afford white solid of pure TTOC12. Yield: 2.44 g (68.5 %). ^{1}H NMR (400 MHz, CDCl3, ppm) δ 6.23 (s, 2H), 4.05 (t, *J* = 6.6 Hz, 4H), 1.85 – 1.77 (m, 4H), 1.50 – 1.23 (m, 36H), 0.88 (t, *J* = 6.9 Hz, 6H).

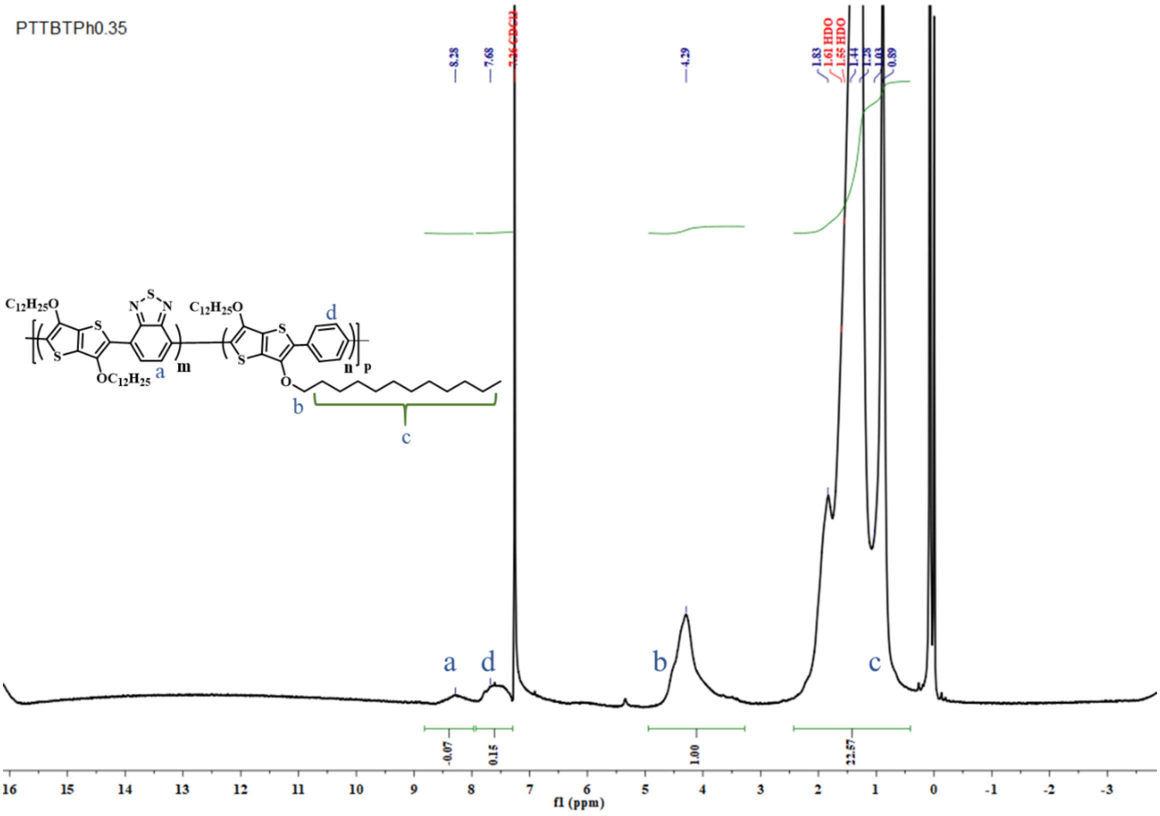


Typical direct arylation polycondensation procedure for PTTBTPhx
（PTTBTPh0.35 as example, x=0.35, y=0.65）

PTTBTPh0.35: Under nitrogen atmosphere, 3,6-bis(dodecyloxy)thieno[3,2-*b*]thiophene (100 mg, 0.20 mmol), 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (20.6 mg, 0.07 mmol) and 1,4-dibromobenzene (30.7 mg, 0.13 mmol) were dissolved in anhydrous *N*,*N*-dimethylacetamide (DMAc) (10 mL). Then $Pd(OAc)_2$ (1.8 mg, 0.008 mmol), K_2CO_3 (70 mg, 0.4 mmol) and pivalic acid (6 mg, 0.06 mmol) were added and the mixture was stirred with heating at 120 °C for 12 h under N_2 atmosphere. The mixture was cooled to room temperature, poured into a large amount of MeOH, and the precipitate was filtered off. The crude product was purified by Soxhlet extraction, sequentially with MeOH, acetone, hexane, and $CHCl_3$. The $CHCl_3$ fraction was concentrated and precipitated into MeOH. The dark black solid was filtered off and dried under vacuum. Yield: 95 mg (78 %). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.52 (br, s), 7.81 (br, s), 4.34 (br, s), 1.86 – 1.27 (br, m), 0.90 (br, s). GPC analysis: M_n = 9,657 g mol^{-1}; M_w = 18,063 g mol^{-1}; PDI = 1.87.



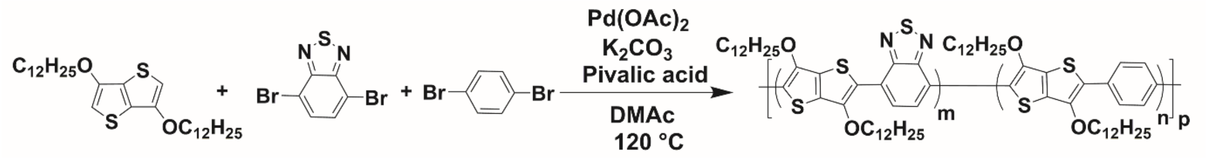
1 (eq.) **x=0.35 (eq.)** **y=0.65 (eq.)** **PTTBTPh0.35**



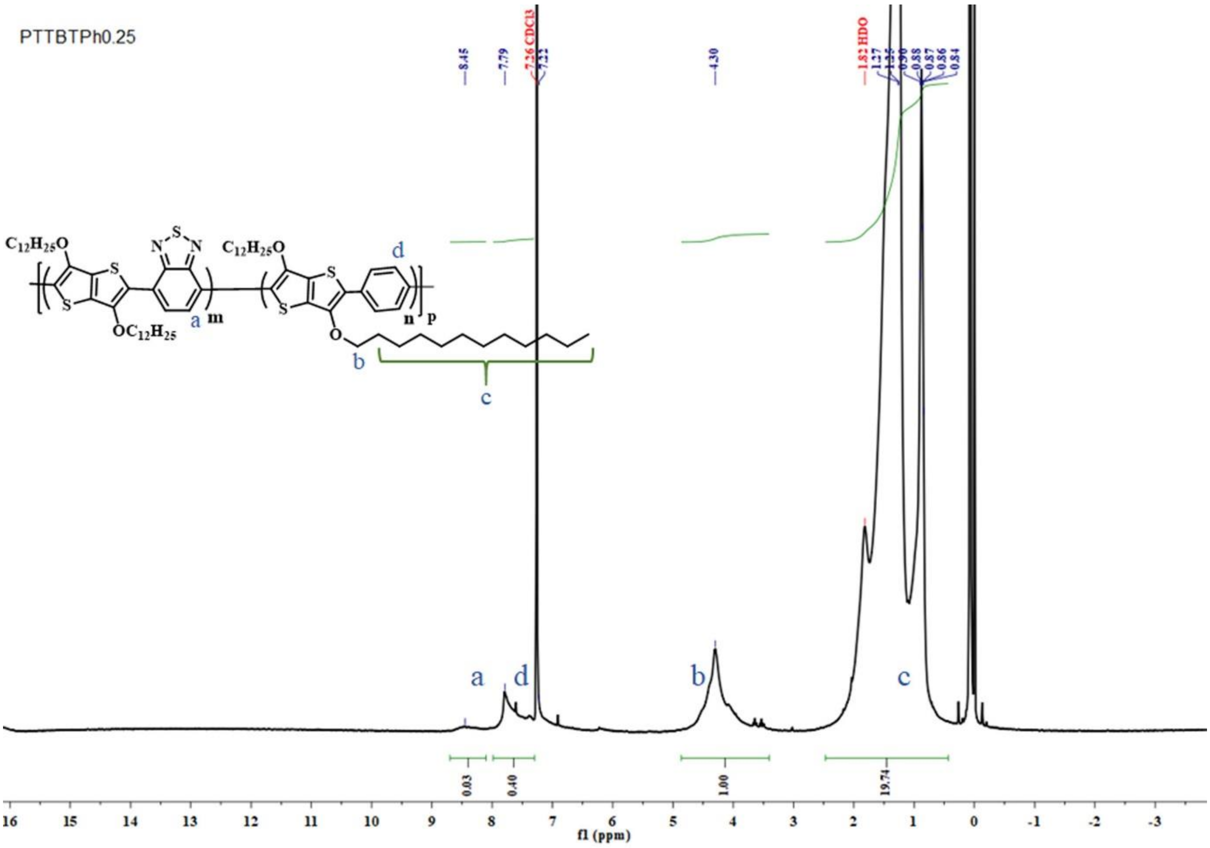
PTTBTPh0.25: Dark black solid, 76 % yield (91 mg).

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.52 (br, s), 7.82 (br, s), 4.33 (br, s), 1.85 – 1.27 (br, m), 0.90 (br, s).

GPC analysis: M_n = 9,451 g mol^{-1}; M_w = 14,947 g mol^{-1}; PDI = 1.58.



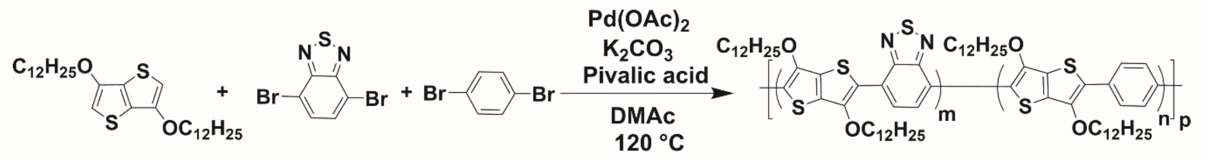
1 (eq.) **x=0.25 (eq.)** **y=0.75 (eq.)** **PTTBTPh0.25**



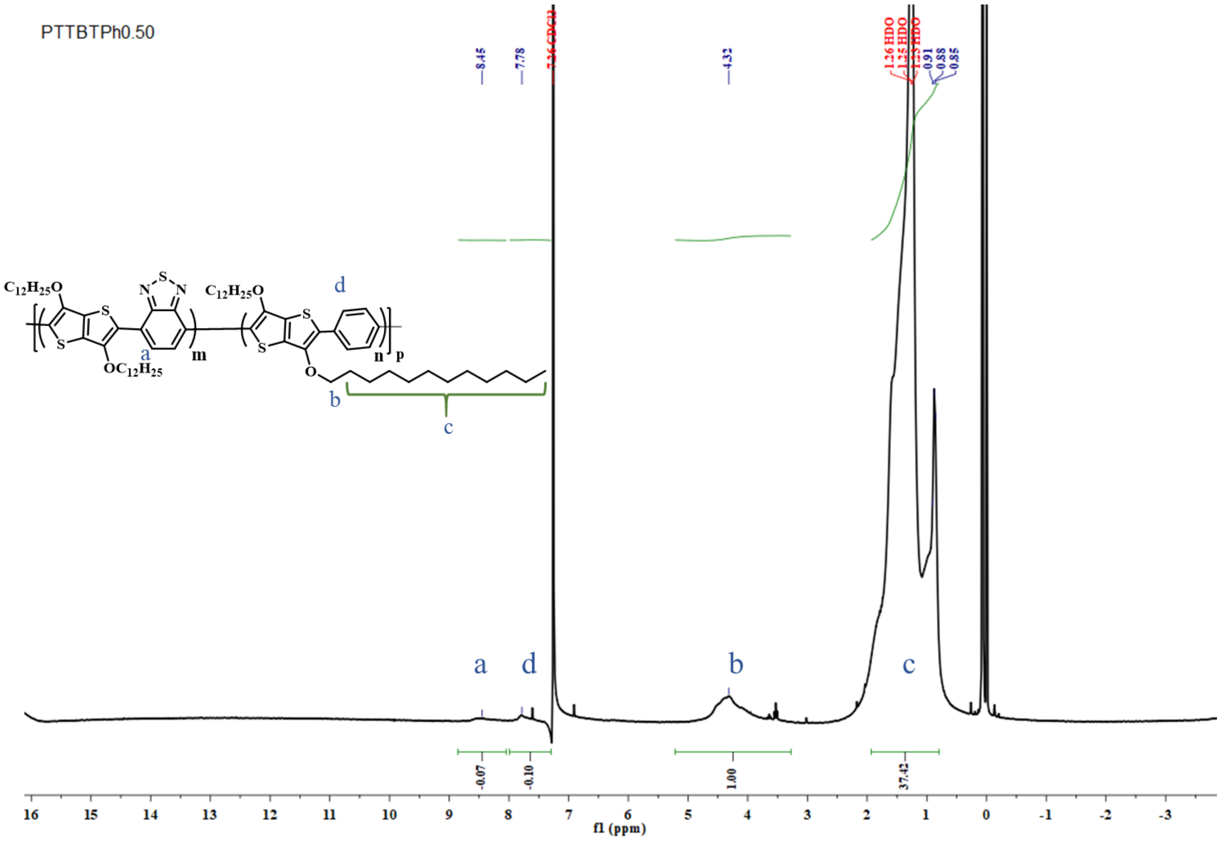
PTTBTPh0.50: Dark black solid, 81 % yield (99 mg).

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.52 (br, s), 7.83 (br, s), 4.36 (br, s), 1.88 – 1.27 (br, m), 0.90 (br, s).

GPC analysis: M_n = 8,040 g mol^{-1}; M_w = 11,535 g mol^{-1}; PDI = 1.43.

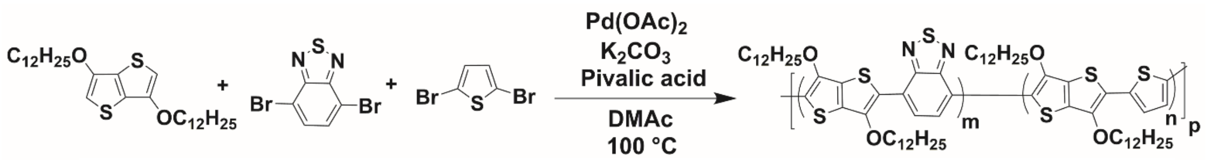


1 (eq.) **x=0.50 (eq.)** **y=0.50 (eq.)** **PTTBTPh0.50**

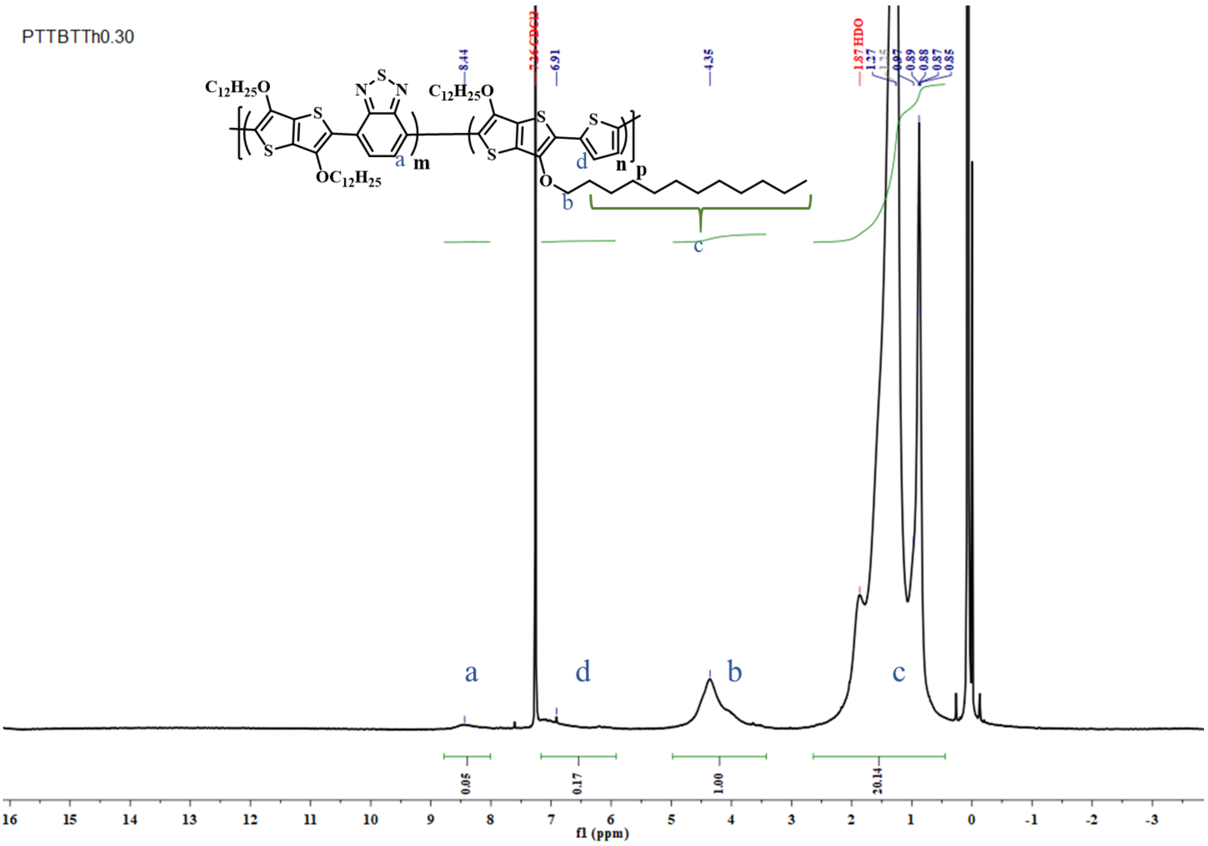


Typical direct arylation polycondensation procedure for PTTBTThx (PTTBTTh0.30 as example, x=0.3, y=0.7):

PTTBTTh0.30: Under nitrogen atmosphere, 3,6-bis(dodecyloxy)thieno[3,2-*b*]thiophene (100 mg, 0.20 mmol), 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (18 mg, 0.06 mmol), 2,5-dibromothiophene (34 mg, 0.14 mmol) were dissolved in anhydrous *N*,*N*-dimethylacetamide (DMAc) (10 mL). Then $Pd(OAc)_2$ (1.8 mg, 0.008 mmol), K_2CO_3 (70 mg, 0.4 mmol) and pivalic acid (6 mg, 0.06 mmol) were added and the mixture was stirred with heating under reflux at 100 °C for 12 h under N_2 atmosphere. The mixture was cooled to room temperature, poured into a large amount of MeOH, and the precipitate was filtered off. The crude product was purified by Soxhlet extraction, sequentially with MeOH, acetone, hexane, and $CHCl_3$. The $CHCl_3$ fraction was concentrated and precipitated into MeOH. The dark black solid was filtered off and dried under vacuum. Yield: 88 mg (73 %). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.46 (br, s), 7.11 (br, s), 4.36 (br, s), 1.90 – 1.27 (br, m), 0.90 (br, s). GPC analysis: M_n = 10,970 g mol^{-1}; M_w = 13,818 g mol^{-1}; PDI = 1.26.



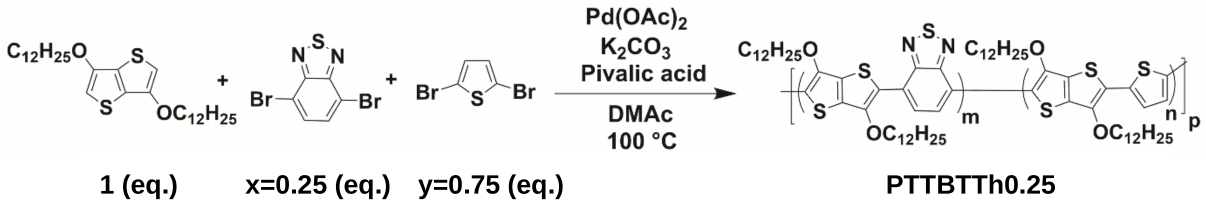
1 (eq.) **x=0.30 (eq.)** **y=0.70 (eq.)** **PTTBTTh0.30**

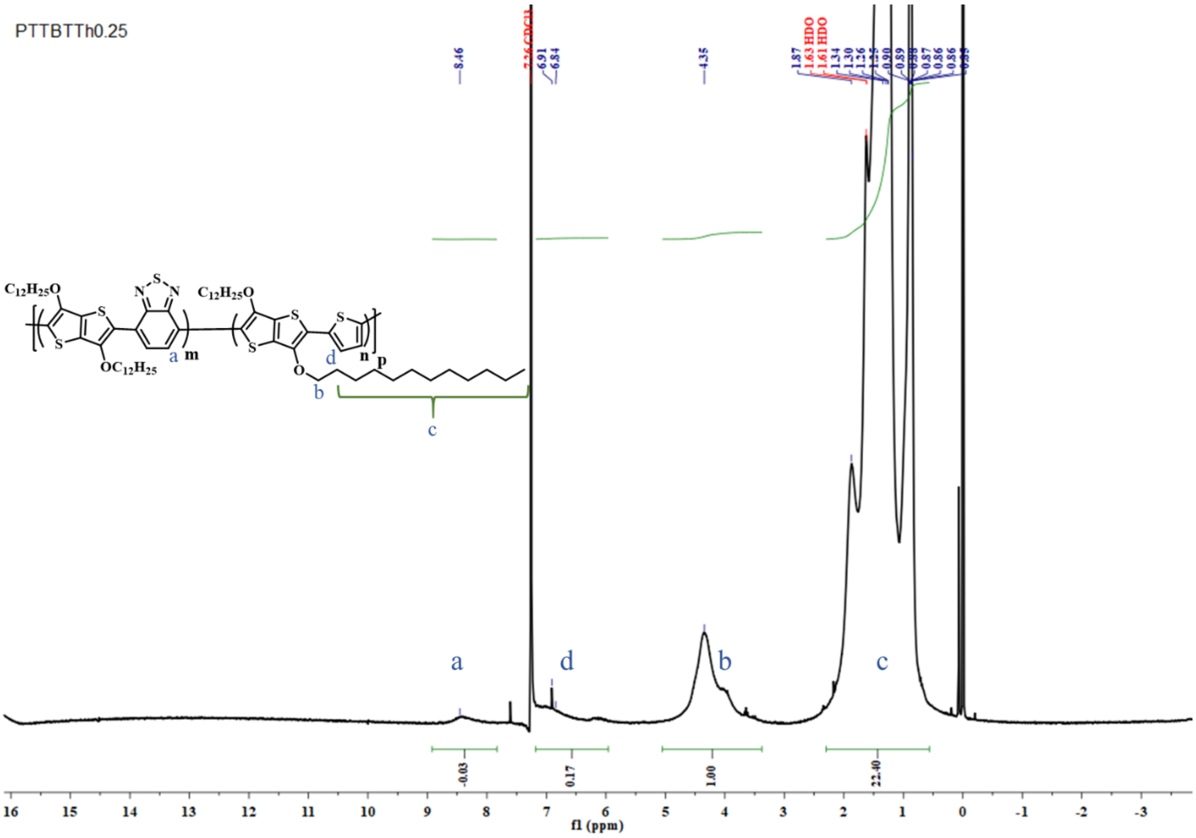


PTTBTTh0.25: Dark black solid, 77 % yield (93 mg).

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.46 (br, s), 7.11 (br, s), 4.36 (br, s), 1.90 – 1.27 (br, m), 0.90 (br, s).

GPC analysis: M_n = 8,478 g mol^{-1}; M_w = 12,392 g mol^{-1}; PDI = 1.46.

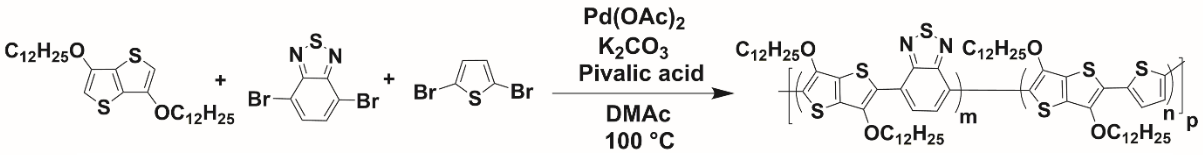




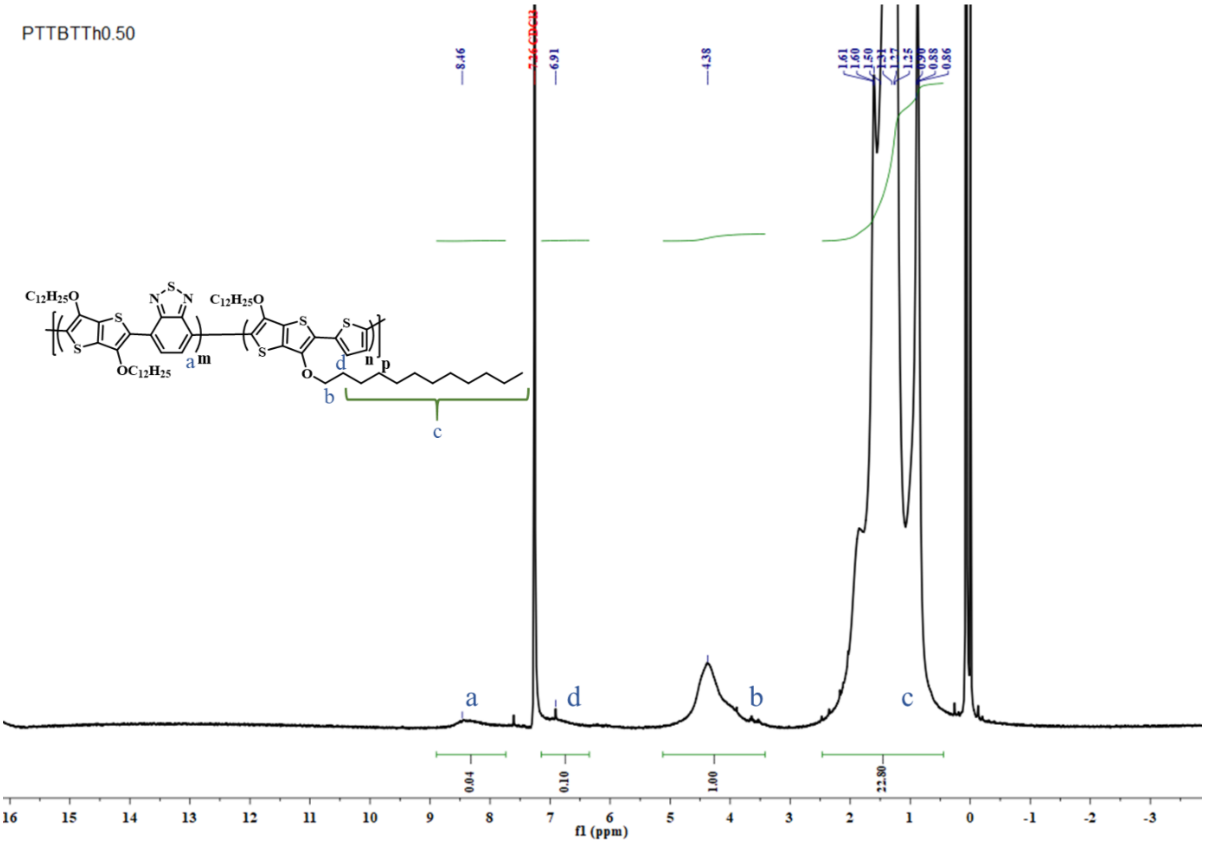
PTTBTTh0.50: Dark black solid, 69 % yield (85 mg).

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.44 (br, s), 7.00 (br, s), 4.41 (br, s), 1.88 – 1.27 (br, m), 0.90 (br, s).

GPC analysis: M_n = 8,652 g mol^{-1}; M_w = 13,172 g mol^{-1}; PDI = 1.52.



1 (eq.) **x=0.50 (eq.)** **y=0.50 (eq.)** **PTTBTTh0.50**



Neutrality of Black Polymers

Colorimetry coordinates (a^*b^*) of black copolymers (including PTTBTPh0.35 and PTTBTTh0.30) in the neutral states have been summarized in Figure S1, and the neutrality has been investigated by calculating the distances from their colorimetry coordinates to the coordinate (0,0) (ΔN_{ab}^* in Table S2).

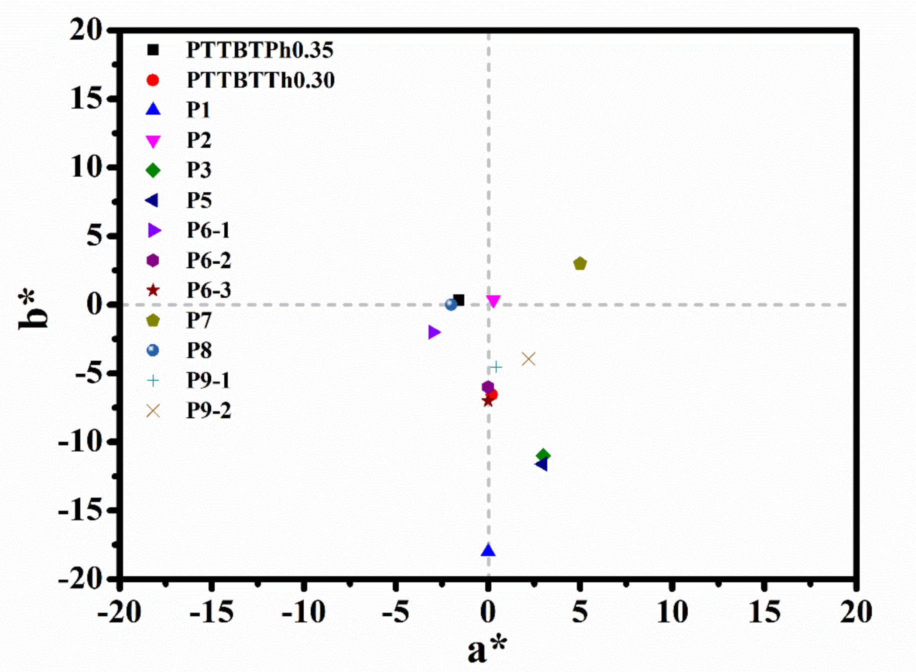


Fig. S1 Colorimetry coordinates (a^*b^*) of black copolymers in the neutral states.

Table S2 Neutrality of Neutral Black Polymers

Polymers	(a^*b^*)	ΔN^*_{ab} [a]
PTTBTPh0.35	(–1.59, 0.32)	1.62
PTTBTTh0.30	(0.20, –6.56)	6.56
P1	(0, –18)	18.0
P2	(0.29, 0.35)	0.45
P3	(3, –11)	11.4
P5	(2.97, –11.6)	12.0
P6-1	(–3, –2)	3.61
P6-2	(0, –6)	6.0
P6-3	(0, –7)	7.0
P7	(5, 3)	5.83
P8	(–2, 0)	2.0
P9-1	(0.45, –4.52)	4.54
P9-2	(2.21, –3.94)	4.52

[a] $\Delta N^*_{ab} = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2}$

Morphology

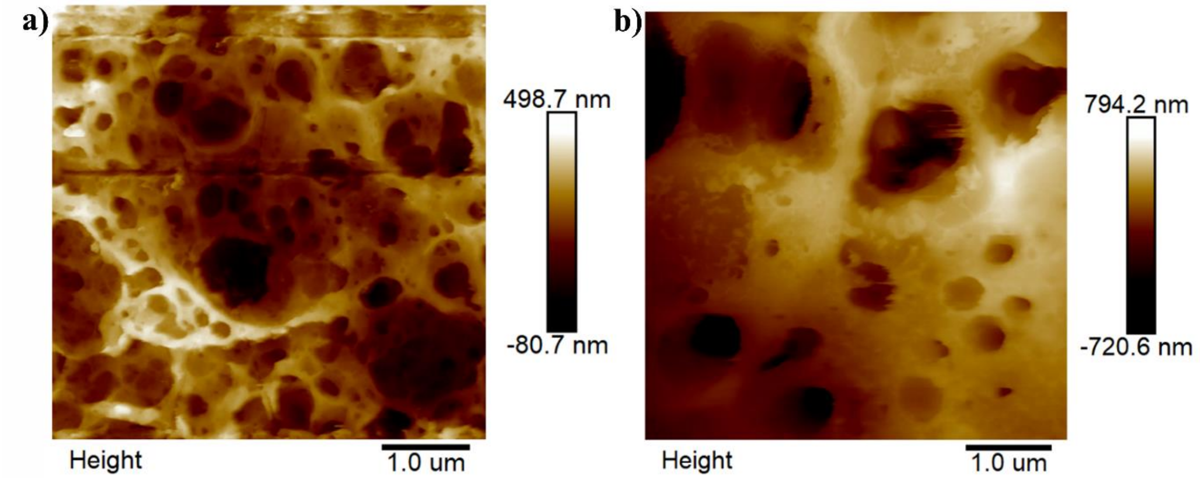


Fig. S2 AFM images of a) PTTBTPh0.35 and b) PTTBTTh0.30 spray-coated on ITO-coated glass slides.

Electrochemical properties of homopolymers

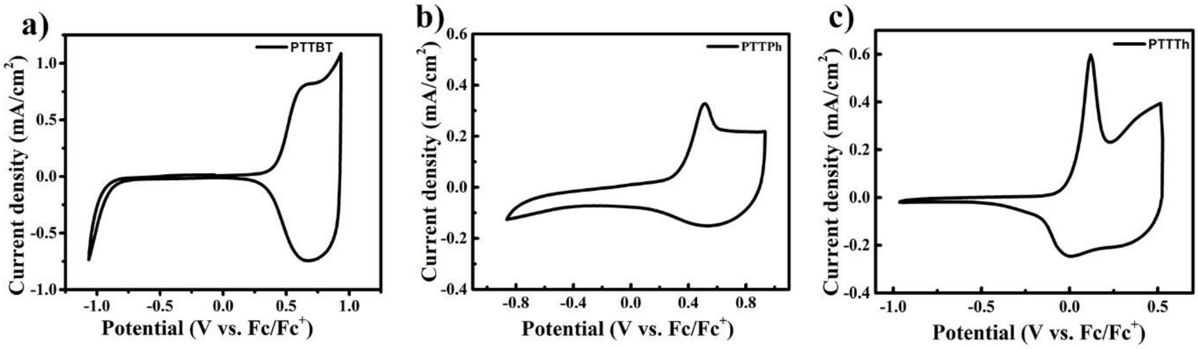


Fig. S3 Cyclic voltammograms of homopolymers PTTBT, PTTPh and PTTTh spray-coated on the Pt disk electrode in 0.1 M TBAPF$_6$/ACN, recorded *vs.* Ag/Ag$^+$ reference electrode and re-calculated to the Fc/Fc$^+$ scale; scan rate 100 mV s^{-1}.

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