Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Highly Regioselective Pd/C-Catalyzed Direct Arylation toward Thiophene-based π-Conjugated Polymers

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Experimental

Materials

2-Bromo-3-hexylthiophene was synthesized by bromination of 3-hexylthiophene. **P3HT$_{GM}$** was synthesized by Grignard metathesis polymerization by using 2-bromo-5-iodo-3-hexylthiophene, isopropyl magnesium chloride (2.0 M THF solution, Aldrich), lithium chloride (Wako Chemical Inc.), and 1,2-bis(diphenylphosphinoethane)nickel(II) dichloride (TCI) in THF. Solvents and reagents for direct arylation and Suzuki-Miyaura reaction were used as received. Thiophene (Wako Chemical Inc.), 2,2'-bithiophene (TCI), 2,7-dibromo-9,9-dioctylfluorene (TCI), potassium carbonate (KANTO), pivalic acid (TCI), palladium acetate (Wako Chemical Inc.) palladium 10% on carbon wetted with 55% water (TCI), and palladium hydroxide 20% on carbon wetted with 55% water (TCI), palladium acetate (Wako Chemical Inc.), 2,5-dibromothiophene (Aldrich), 3,4-dibromothiophene (Aldrich), 9,9-dioctylfluorene-2,7-diboronic acid (Aldrich), 2,5-thiophenediboronic acid (Aldrich), 2,2'-bithiophene-5,5'-diboronic acid (1,2-ethanediol)ester

(Aldrich), tris(dibenzylideneacetone) dipalladium(0) (Aldrich), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) (Aldrich), and tricyclohexylphosphonium tetrafluoroborate (Aldrich) were obtained from commercial sources shown in parentheses.

General procedure for Direct Arylation Polycondensation

Polycondensation of 2-bromo-3-hexylthiophene (1) using Pd/C or $Pd(OH)_2/C$

A mixture of 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol), pivalic acid (102 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), and palladium on carbon (0.025 mmol) in 2 mL of solvent was stirred at 100-120 °C for 48 h under argon. The reaction mixture was filtrated to remove insoluble materials including the heterogeneous catalyst used. The filtrate was poured into a large amount of methanol. The precipitated polymer, P3HT, was separated by filtration, washed with methanol, and then dried under vacuum.

P3HT$_{\mathbf{DA}}$: Purple black powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.8 (*Ar-H*, br), 2.8 ($CH_2(CH_2)_4CH_3$, br), 1.8-0.7 ($CH_2(CH_2)_6CH_3$, br). Anal. Calcd. for $(C_{10}H_{14}S)_n$: C, 72.23; H, 8.49. Found: C, 73.18; H, 8.05.

Polycondensation of 2-bromo-3-hexylthiophene (1) using $Pd(OAc)_2$

A mixture of 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol), pivalic acid (102 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), and $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) in 2 mL of solvent was stirred at 100 °C for 48 h under argon. The reaction mixture was filtrated to remove insoluble materials. The filtrate was poured into a large amount of methanol. The precipitated polymer, P3HT, was separated by filtration, washed with methanol, and then dried under vacuum. The resulting insoluble polymer, networked P3HT, which was precipitated from the reaction mixture during polymerization, was separated by washing with a large amount of THF, water, and methanol and then dried under vacuum.

Polycondensation between thiophene (2a) and 2,7-dibromo-9,9-dioctylfluorene (3)

A mixture of thiophene (28 mg, 0.33 mmol), 2,7-dibromo-9,9-dioctylfluorene (164 mg, 0.30 mmol), pivalic acid (61 mg, 0.60 mmol), K_2CO_3 (249 mg, 1.8 mmol), and a palladium source (0.0075 mmol of Pd) in 1 mL of dry *N*,*N*-dimethylacetoamide was stirred at 100 °C for 48 h under argon. The reaction mixture was filtrated to remove insoluble materials including the heterogeneous catalyst used. The filtrate was poured into a large amount of methanol. The precipitated polymer, **PTF**, was separated by filtration, washed with methanol, and then dried under vacuum.

PTF: Yellow powder. Yield: 57% (80 mg). GPC: M_n = 6700, M_w/M_n = 2.64. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.9-7.3 (*Ar-H*, br), 2.08 ($C\mathit{H_2}(CH_2)_6CH_3$, br), 1.25-0.77 ($CH_2(C\mathit{H_2})_6C\mathit{H_3}$, br). Anal. Calcd. for $(C_{33}H_{22}S)_n$: C, 84.20; H, 8.99. Found: C, 79.70; H, 8.61.

Polycondensation between 2,2'-bithiophene (2b) and 2,7-dibromo-9,9-dioctylfluorene (3)

A mixture of 2,2'-bithiophene (50 mg, 0.30 mmol) 2,7-dibromo-9,9-dioctylfluorene (164 mg, 0.30 mmol), pivalic acid (61 mg, 0.60 mmol), K_2CO_3 (249 mg, 1.8 mmol), and a palladium source (0.0075 mmol of Pd) in 1 mL of dry *N*,*N*-dimethylacetoamide was stirred at 100 °C for 48 h under argon. The reaction mixture was filtrated to remove insoluble materials including the heterogeneous catalyst used. The filtrate was poured into a large amount of methanol. The precipitated polymer, **PBF**, was separated by filtration, washed with methanol, and then dried under vacuum.

PBF: Yellow powder. Yield: 73% (121 mg). GPC: M_n = 10900, M_w/M_n = 3.02. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7-6.9 (*Ar-H*, br), 2.06 ($CH_2(CH_2)_6CH_3$, br), 1.25-0.77 ($CH_2(CH_2)_6CH_3$, br). Anal. Calcd. for $(C_{37}H_{24}S)_n$: C, 80.38; H, 8.02. Found: C, 76.88; H, 7.56.

Synthesis of PTF$_{SC}$

2,5-Dibromothiophene (73 mg, 0.30 mmol), 9,9-dioctylfluorene-2,7-diboronic acid (144 mg, 0.30 mmol), $Pd_2(dba)_3$-$CHCl_3$ (15.5 mg, 10 mol%), S-Phos (49 mg, 40 mol%), and tetrabutylammonium bromide (3 mg) were dissolved in 1 mL of dry *N*,*N*-dimethylformamide under argon. To the solution, 1 mL of 2M K_2CO_3 aq was added. After stirred at 100 °C for 48 h, the reaction mixture was poured into a large amount of methanol. The precipitated polymer was collected by filtration, and then dissolved in tetrahydrofuran. The polymer solution was poured into a large amount of methanol. The reprecipitated polymer was collected by filtration, and then dried under vacuum.

PTF$_{SC}$: Yellow powder. Yield: 59% (83 mg). GPC: M_n = 7600, M_w/M_n = 2.10. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.9-7.3 (*Ar-H*, br), 2.08 ($CH_2(CH_2)_6CH_3$, br), 1.25-0.77 ($CH_2(CH_2)_6CH_3$, br).

2,5-Thiophene-diboronic acid (52 mg, 0.30 mmol), 2,7-dibromo-9,9-dioctylfluorene (164 mg, 0.30 mmol), $Pd_2(dba)_3$-$CHCl_3$ (15.5 mg, 10 mol%), S-Phos (49 mg, 40 mol%), and tetrabutylammonium bromide (3 mg) were dissolved in 1 mL of dry *N*,*N*-dimethylformamide under argon. To the solution, 1 mL of 2M K_2CO_3 aq were added. After stirred at 100 °C for 48 h, the reaction mixture was poured into a large amount of methanol. The precipitated polymer was collected by filtration, and then ~~re~~dissolved in tetrahydrofuran. The polymer solution was poured into a large amount of methanol. The reprecipitated polymer was collected by filtration, and then dried under vacuum to give as a powder. Yield: trace (<1.0 mg). GPC: M_n = 2100, M_w/M_n = 1.18.

Synthesis of PBF$_{SC}$

2,2'-Bithiophene-5,5'-diboronic acid bis(ethanediol)ester (125 mg, 0.30 mmol), 2,7-dibromo-9,9-dioctylfluorene (164 mg, 0.30 mmol), $Pd_2(dba)_3$-$CHCl_3$ (15.5 mg, 10 mol%), S-Phos (49 mg, 40 mol%), and tetrabutylammonium bromide (3 mg) were dissolved in 1 mL of dry toluene under argon. To the solution, 1 mL of 2 M K_2CO_3 aq was added. After stirred for 48 h at 100 °C, the reaction mixture was poured into a large amount of methanol. The precipitated polymer was collected by filtration, and then dissolved in tetrahydrofuran. The polymer solution was poured into a large amount of methanol. The reprecipitated polymer was collected by filtration, and then dried under vacuum.

PBF$_{SC}$: Yellow powder. Yield: 14% (23 mg). GPC: M_n = 2300, M_w/M_n = 1.83. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7-6.9 (*Ar-H*, br), 2.06 ($CH_2(CH_2)_6CH_3$, br), 1.25-0.77 ($CH_2(CH_2)_6CH_3$, br).

Synthesis of b-PTF

3,4-Dibromothiophene (73 mg, 0.30 mmol), 9,9-dioctylfluorene-2,7-diboronic acid (144 mg, 0.30 mmol), $Pd_2(dba)_3$-$CHCl_3$ (15.5 mg, 10 mol%), S-Phos (49 mg, 40 mol%), and tetrabutylammonium bromide (3 mg) were dissolved in 1 mL of toluene under argon. To the solution, 1 mL of 2 M K_2CO_3 aq was added. After stirred at 100 °C for 48 h, the reaction mixture was poured into a large amount of methanol. The precipitated polymer was collected by filtration, and then dissolved in tetrahydrofuran. The polymer solution was poured into a large amount of methanol. The reprecipitated polymer was collected by filtration, and then dried under vacuum.

b-PTF: Yellow powder. Yield: 75% (106 mg). GPC: M_n = 5600, M_w/M_n = 1.73. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.5-7.0 (*Ar-H*, br), 1.68 ($CH_2(CH_2)_6CH_3$, br), 1.25-0.77 ($CH_2(CH_2)_6CH_3$, br). ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.7, 142.5, 139.6, 135.3, 127.8, 123.6, 123.4, 119.3, 54.9, 40.5, 31.9, 31.8, 30.0, 29.5, 29.4, 29.3, 23.8, 22.7, 22.6, 14.1, 14.0.

Measurements

Liquid-state ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-300 spectrometer. Elemental analyses were performed on a Thermo Finnigan Flash EA1112 CHN-O analyzer. UV-vis absorption spectra were obtained on an Ocean Optics USB4000-XR1 fiber spectrometer with DH2000-BAL tungsten halogen light source. Fluorescence spectra were obtained on an Ocean Optics USB4000 fiber spectrometer with PX-2 pulsed xenon light source. Powder XRD analysis was performed by JEOL JDX-3530 X-ray diffractometer system. DSC analysis was performed by a Shimadzu DS-60, which measured during heating from room temperature to 400 ^{o}C at heating rate of 10 ^{o}C/min in nitrogen. TGA analysis was performed by a Shimadzu TA-60, which measured during heating from room temperature to 600 ^{o}C at heating rate of 20 ^{o}C/min in nitrogen.

Table S1. Direct Arylation Polycondensation of **1**

				P3HT				
entry	solvent	[Pd]	time	M_n [a]	M_w/M_n [a]	HT	yield	insoluble part
			(h)	(kDa)		(%) [b]	(%) [b]	(%) [e]
1	DMAc	**Pd/C**	48	5.7	1.36	94	52	-
2	DMAc	**Pd/C**	72	7.8	1.28	95	65	-
3	DMAc	**Pd/C**	96	7.8	1.32	96	71	-
4	DMAc	**Pd(OAc)$_2$**	48	5.0	1.52	70 [d]	< 3	71
5	toluene	**Pd/C**	48	**-**	**-**	**-**	0	-
6	THF	**Pd/C**	48	**-**	**-**	**-**	0	-
7	NMP	**Pd/C**	48	11.4	1.71	97	78	-
8	NMP	**Pd/C** f	48	9.0	1.74	95	80	-
9 [g]	DMAc	**Pd/C**	48	15.7	2.24	93	42	-
10 [g]	NMP	**Pd/C**	48	15.6	3.29	93	34	-
11 [h]	NMP	**Pd/C**	48	16.3	3.17	97	91	-
12	DMAc	**Pd(OH)$_2$/C**	48	14.8	3.20	96	99	-
13	NMP	**Pd(OH)$_2$/C**	48	18.9	3.01	96	99	-
14 [h]	NMP	**Pd(OH)$_2$/C**	48	19.3	2.29	89	38	-
15	NMP	**Pd(OH)$_2$/C**	18	18.4	3.11	97	99	-
16	NMP	**Pd(OH)$_2$/C** [f]	18	9.4	2.03	95	86	-
17	NMP	**Pd(OH)$_2$/C**	8	7.0	1.54	90	71	-
18	NMP	**Pd(OAc)$_2$**	8	6.7	2.80	66 [d]	10	55
19	NMP	**Pd(OAc)$_2$** [i]	8	5.4	1.89	60 [d]	6	62
20	NMP	**Pd(OAc)$_2$** [j]	18	-	-	-	<1	*quant.*

Conditions: 2-bromo-3-hexylthiophene (1.0 mmol), [Pd] (2.5 mol%), PivOH (1.0 mmol), K$_2$CO$_3$ (3.0 mmol), solvent (2.0 mL), 100°C, under argon. [a] Estimated by GPC measurements (eluent: THF, standard: polystyrene). [b] Estimated by ^{1}H NMR. [c] Insoluble in methanol. [d] Bent and branched structures were included. [e] Insoluble P3HT was obtained. [f] 1.25 mol%. [g] Tricyclohexylphosphonium tetrafluoroborate (10.0 mol%) was used as ligand. [h] 120 °C. [i] 5.0 mol%. [j] Pd(OAc)$_2$ (2.5 mol%) and activated carbon (2.5 x 5 mol%).

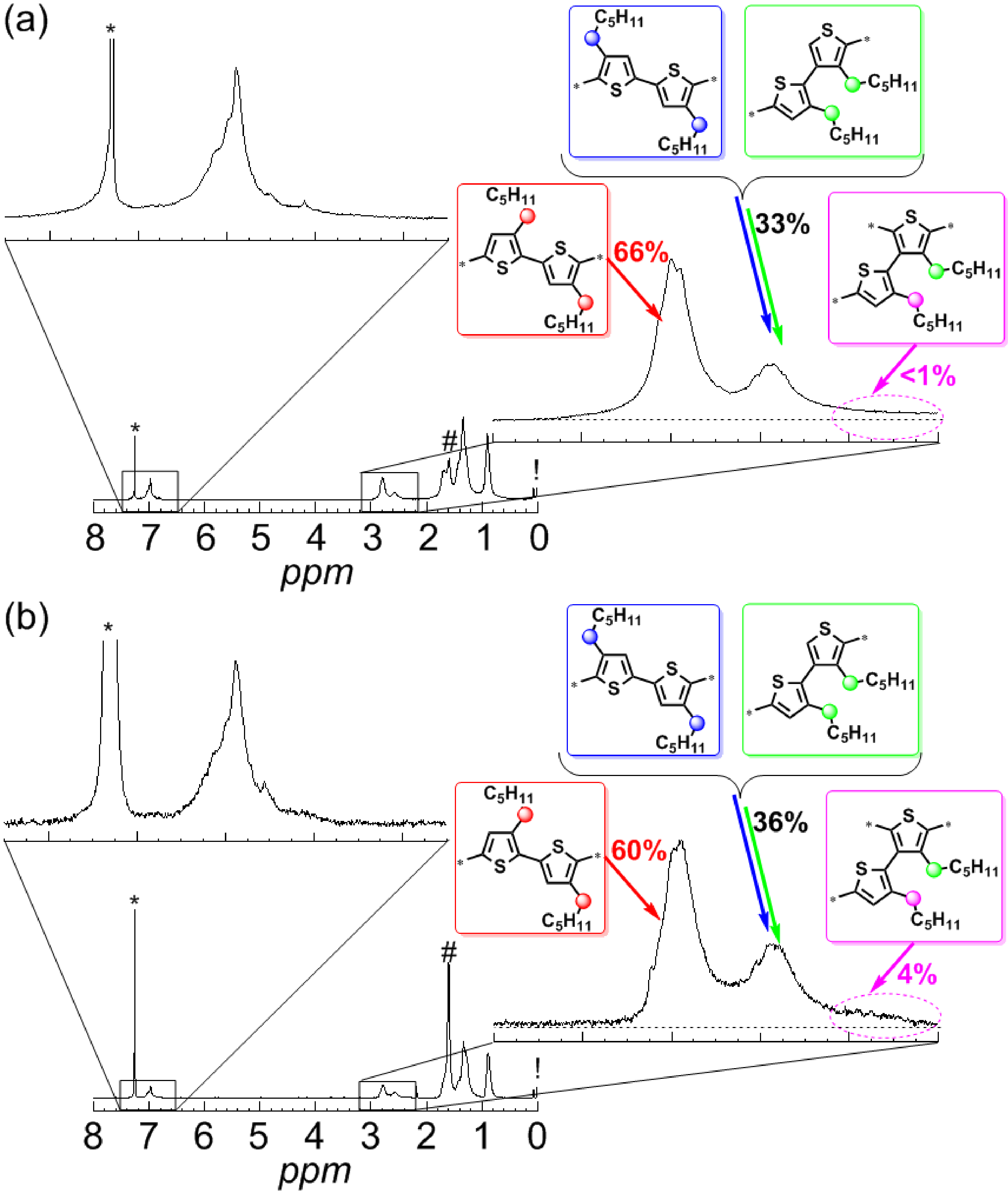


Figure S1. ^{1}H NMR spectra of **b-P3HTa** (Table 1, entry 18) (a) and **b-P3HTb** (Table 1, entry 19) (b) in $CDCl_3$. Symbols, !, #, and *, indicate TMS, H_2O, and solvent peaks, respectively.

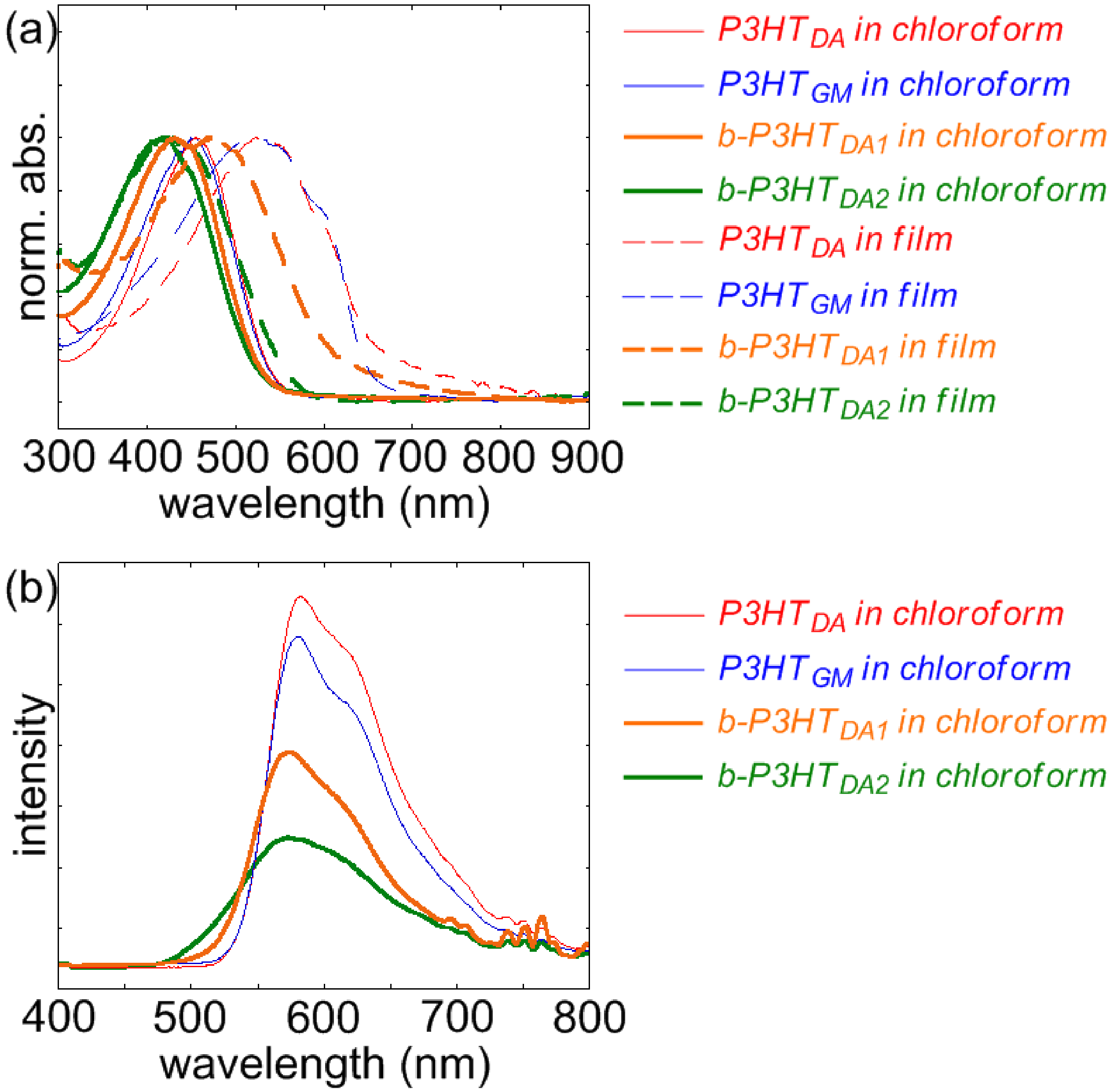


Figure S2. (a) UV-vis absorption spectra of **P3HT$_{DA}$** (red line), **P3HT$_{GM}$** (blue line), and **b-P3HTs** (bold line) in chloroform (solid line) and in film spin-coated from a toluene solution (dashed line). (b) Fluorescence spectra of **P3HT$_{DA}$** (red line), **P3HT$_{GM}$** (blue line), and **b-P3HTs** (bold line) in a dilute (1.0 x 10^{-6} M) chloroform solution.

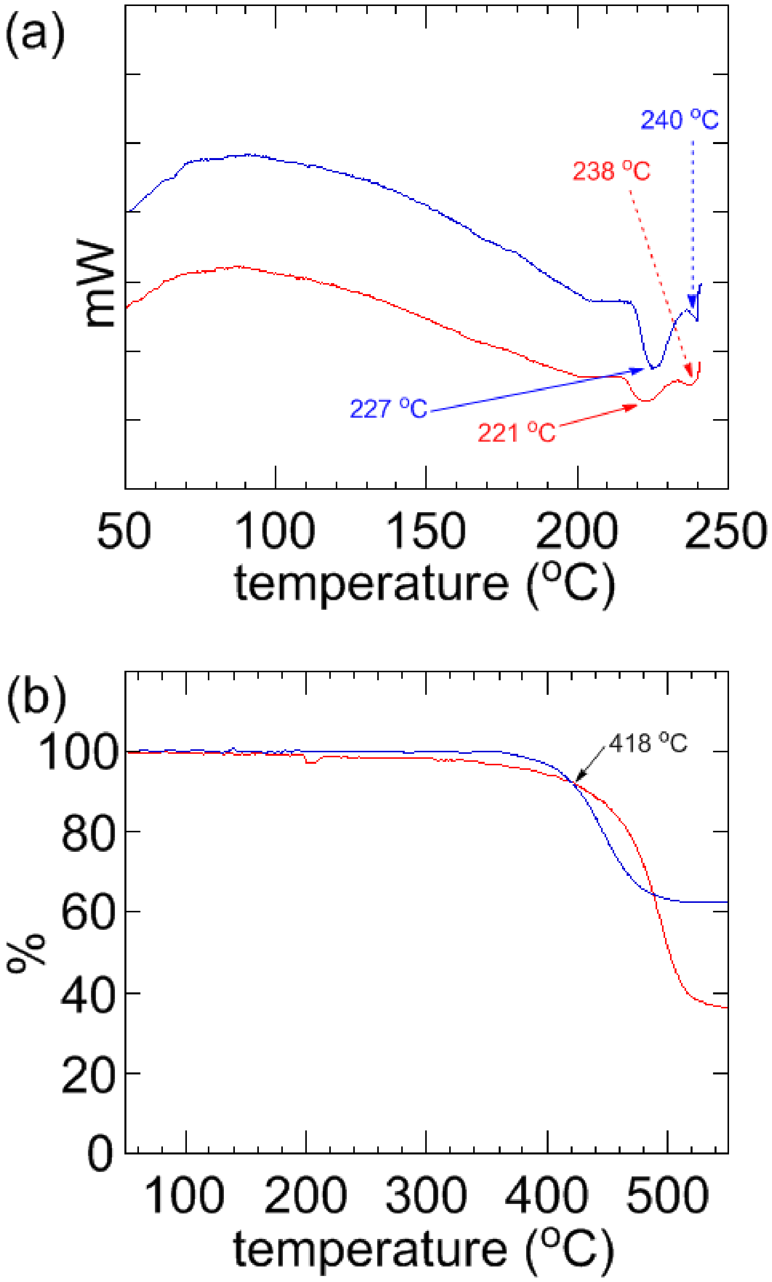


Figure S3. (a) DSC traces of **P3HT$_{\mathbf{DA}}$** (red line) and **P3HT$_{\mathbf{GM}}$** (blue line). (b) TGA data of **P3HT$_{\mathbf{DA}}$** (red line) and **P3HT$_{\mathbf{GM}}$** (blue line).

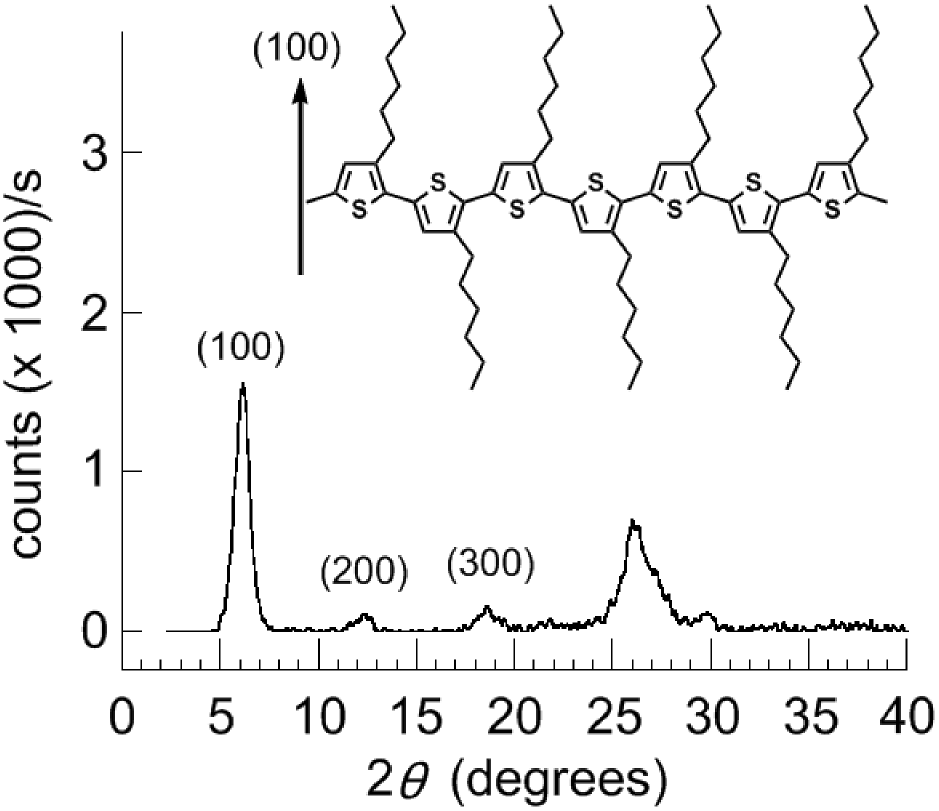


Figure S4. Powder XRD pattern of **P3HT$_{\mathbf{DA}}$** film on Pt plate.

Scheme S1

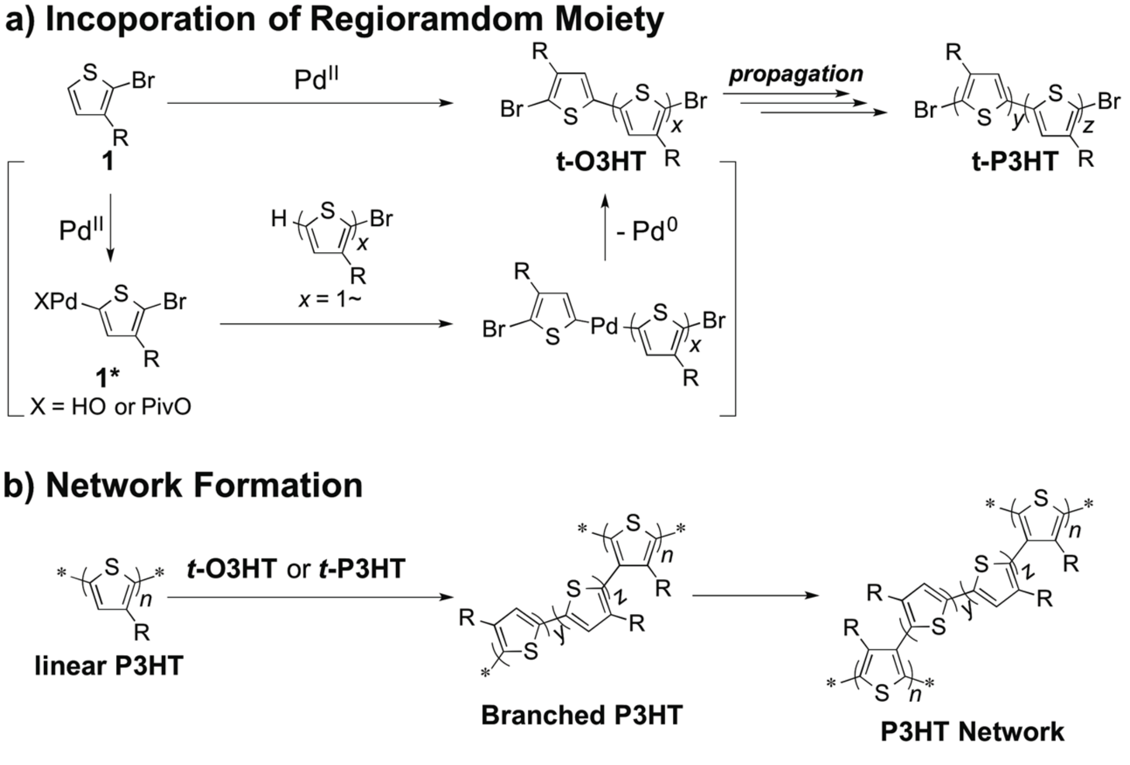
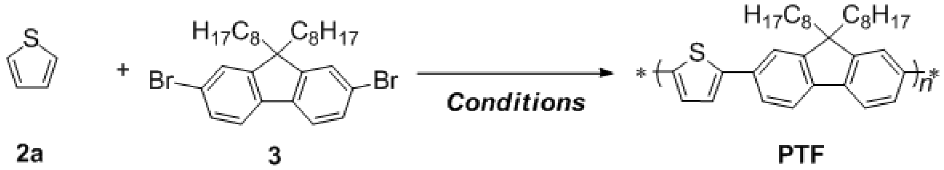


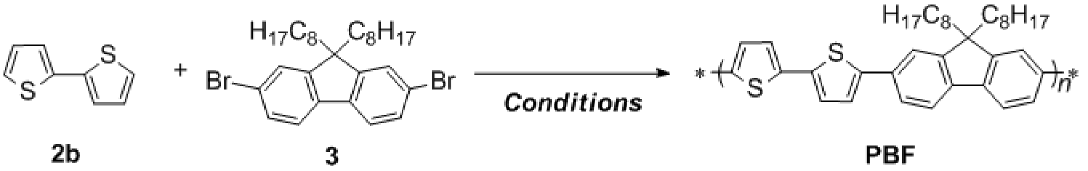
Table S2. Direct Arylation Polycondensation of **2a** with **3**



			PTF			
entry	solvent	[Pd]	M_n (kDa) [a]	M_w/M_n [a]	yield (%) [b]	insoluble part (%) [c]
1	DMAc	**Pd/C**	6.6	2.29	57	-
2	NMP	**Pd/C**	2.6	1.31	65	-
3	DMAc	**Pd(OH)$_2$/C**	5.9	1.94	33	-
4	DMAc	**Pd(OAc)$_2$**	7.5	1.59	<1	63

Conditions: **2a** (0.33 mmol) and **3** (0.30 mmol), [Pd] (2.5 mol%), PivOH (0.60 mmol), K_2CO_3 (1.8 mmol), solvent (1.0 mL), 100°C, under argon. [a] Estimated by GPC measurements (eluent: THF, standard: polystyrene). [b] Insoluble in methanol. [c] Products insoluble in common organic solvents.

Table S3. Direct Arylation Polycondensation of **2b** and **3**



		PBF			
entry	[Pd]	M_n (kDa) [a]	M_w/M_n [a]	yield (%) [b]	insoluble part (%) [c]
1	**Pd/C**	10.9	3.02	73	-
2	**Pd(OAc)$_2$**	5.9	1.87	7	130 [d]

Conditions: **2b** (0.30 mmol) and **3** (0.30 mmol), [Pd] (2.5 mol%), PivOH (0.60 mmol), K_2CO_3 (1.8 mmol), solvent (1.0 mL), 100°C, under argon. [a] Estimated by GPC measurements (eluent: THF, standard: polystyrene). [b] Insoluble in methanol. [c] Products insoluble in common organic solvents. [d] Insoluble part may include inorganic salts.

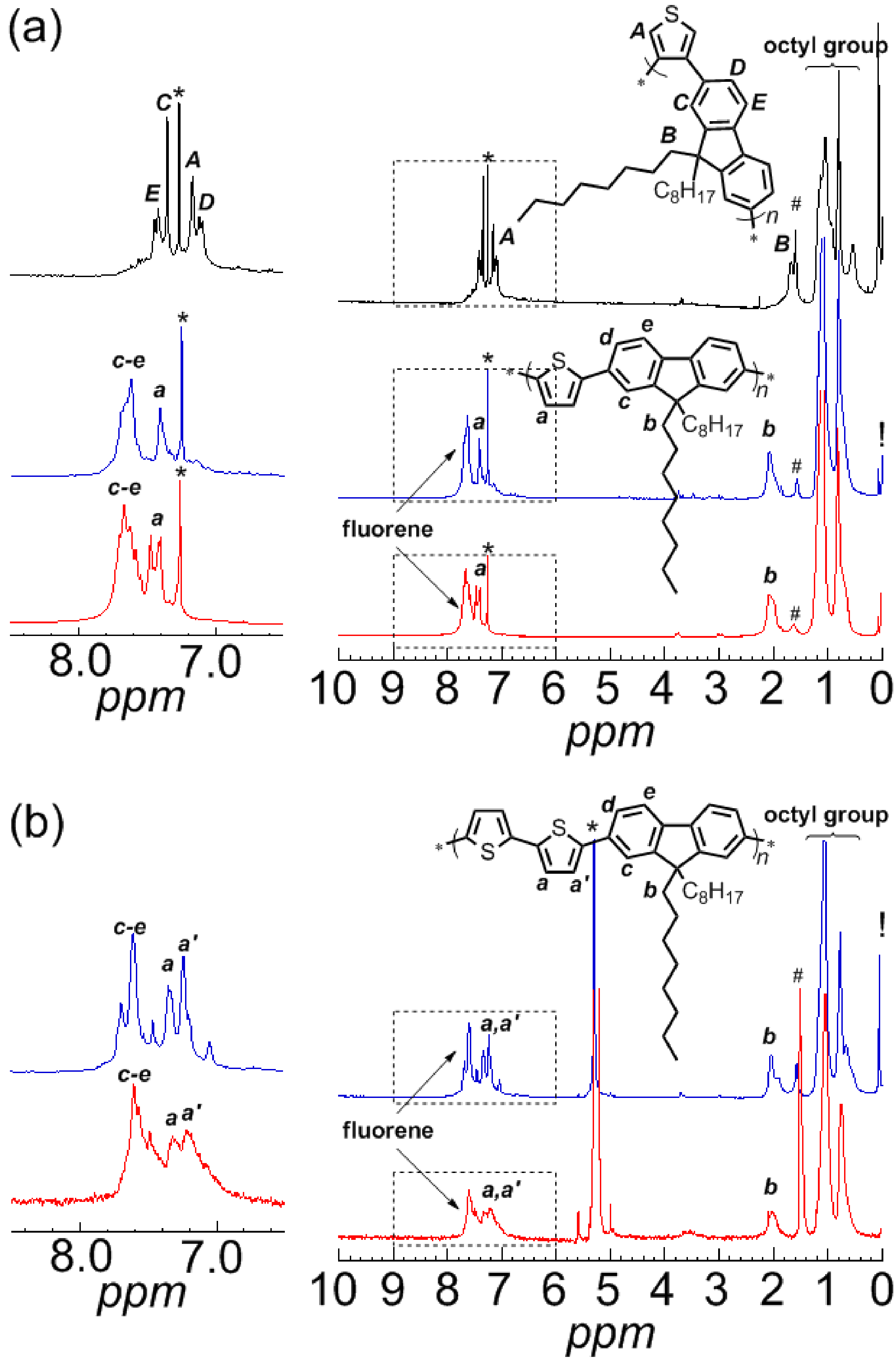


Figure S5. (a) ^{1}H NMR spectra of **PTF$_{\mathrm{DA}}$** (red line) and **PTF$_{\mathrm{SC}}$** (blue line) in $CDCl_3$. (b)^{1}H NMR spectra of **PBF$_{\mathrm{DA}}$** (red line) and **PBF$_{\mathrm{SC}}$** (blue line) in CD_2Cl_2. Symbols, !, #, and *, indicate TMS, H_2O, and solvent peaks, respectively.

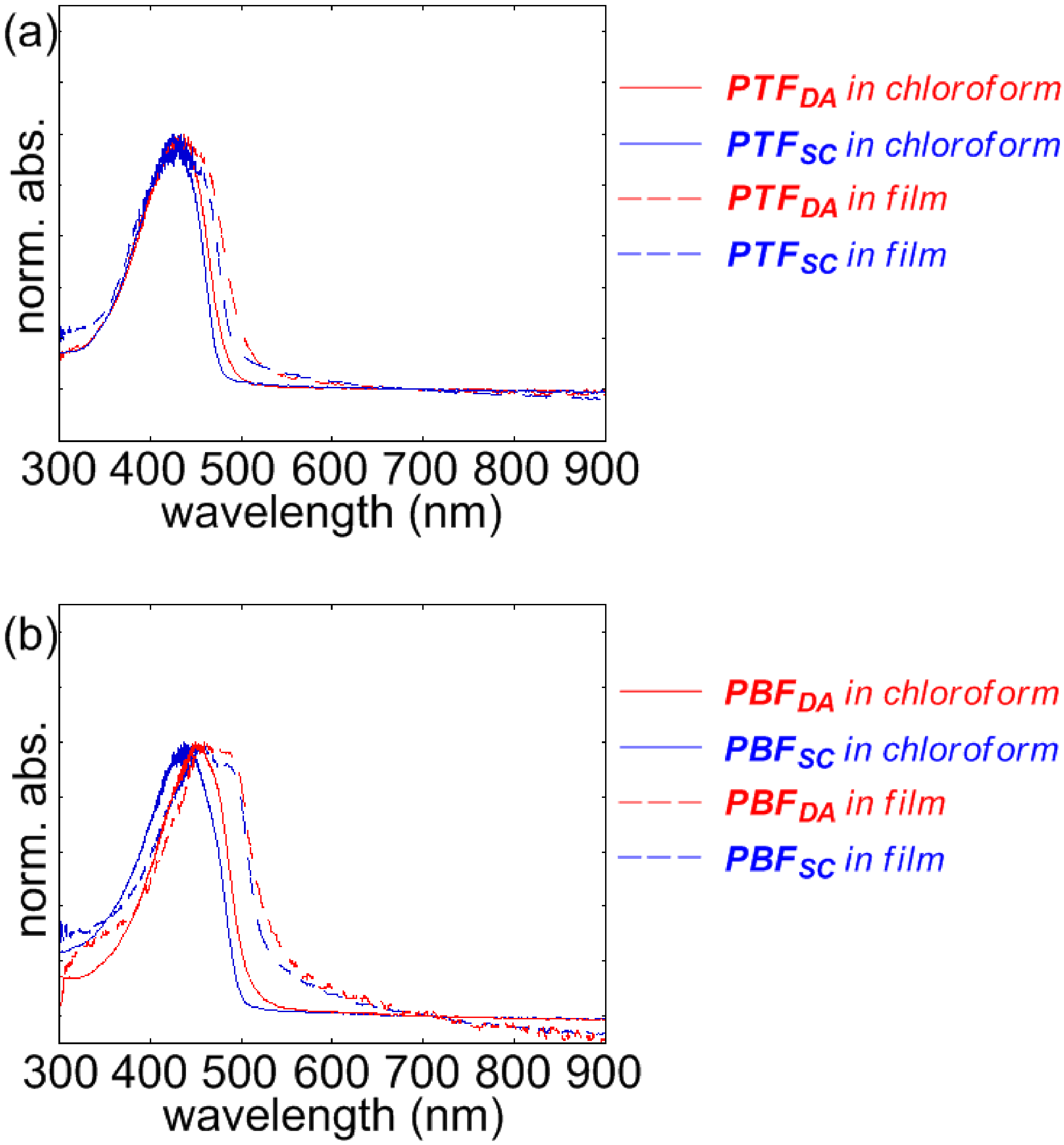


Figure S6. (a) UV-vis absorption spectra of **PTF$_{DA}$** (red line) and **PTF$_{SC}$** (blue line) in chloroform (solid line) and in film spin-coated from a toluene solution (dashed line). (b) UV-vis absorption spectra of **PBF$_{DA}$** (red line) and **PBF$_{SC}$** (blue line) in chloroform (solid line) and in film spin-coated from a toluene solution (dashed line), respectively.

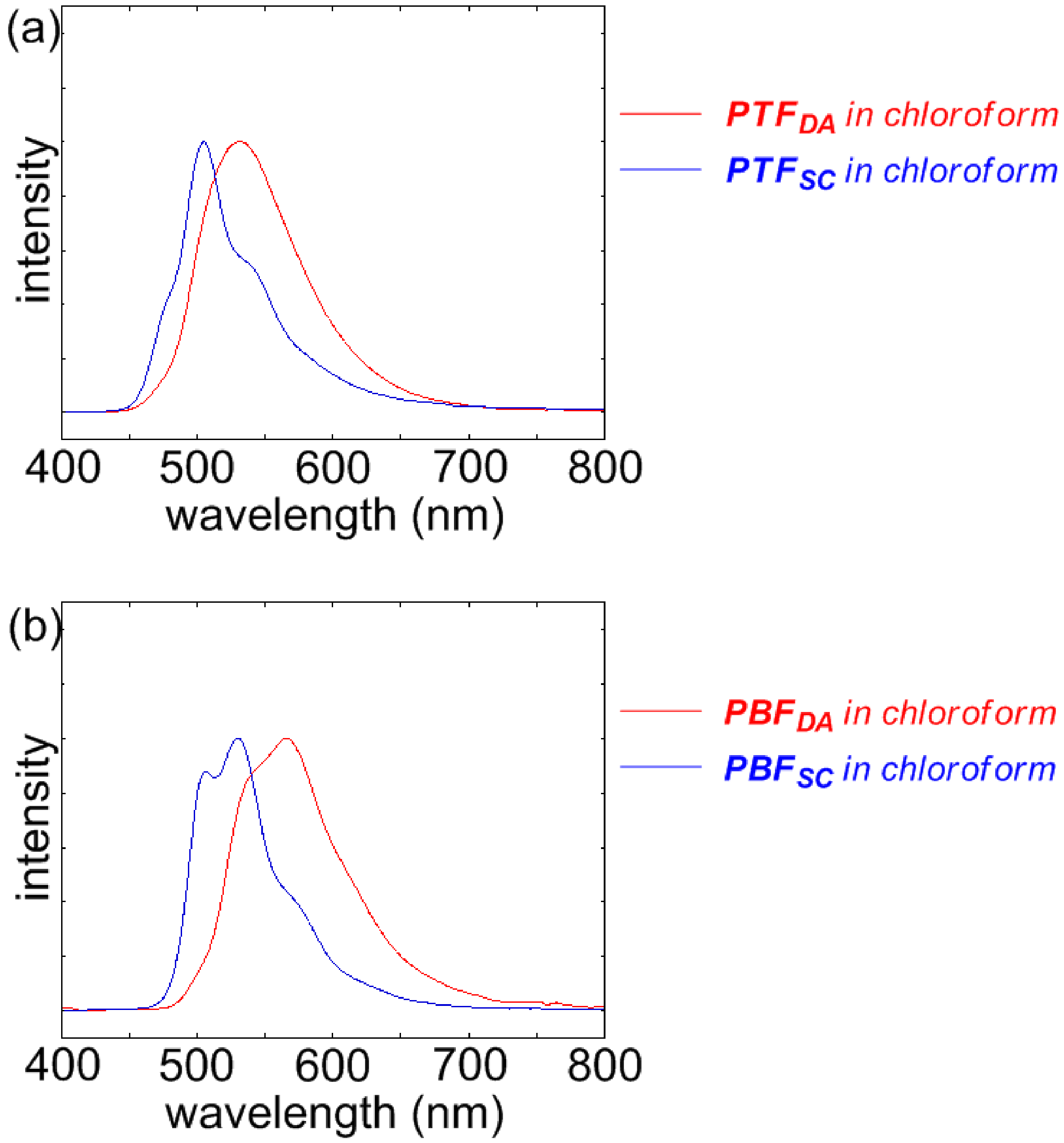


Figure S7. (a) Fluorescence spectra of **PTF**$_{\mathbf{DA}}$ (red line) and **PTF**$_{\mathbf{SC}}$ (blue line) in chloroform (solid line). (b) Fluorescence spectra of **PBF**$_{\mathbf{DA}}$ (red line) and **PBF**$_{\mathbf{SC}}$ (blue line) in chloroform (solid line).