Supporting Information

Chloride-promoted Pd-catalyzed direct C-H arylation in highly efficient

phosphine-free synthesis of π -conjugated polymers

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Experimental Section

Chemicals

3,4-Ethylenedioxythiophene (TCI), 1,2,4,5-tetrafluorobenzene (Aldrich), pentafluorobenzene (TCI), bromobenzene (Kanto), chlorobenzene (Kanto), 2,7-dibromo-9,9-dioctylfluorene (TCI), 5,5'-dibromo-3,3'-dihexyl-2,2'-bithiophene (TCI), pivalic acid (TCI), 1-adamantanecarboxylic acid (TCI), K₂CO₃ (Kanto), 1 M tetra-*n*-butylammonium fluoride THF solution (Wako), tetra-*n*-butylammonium halide (chloride: TCI, bromide: TCI, iodide: TCI), palladium acetate (Wako), tris(dibenzylideneacetone) dipalladium(0) chloroform adduct (Aldrich), palladium chloride (Wako), palladium trifluoroacetate (Wako), di-*tert*-butyl(methyl)phosphonium tetrafluoroborate (Aldrich), tricyclihexylphosphonium tetrafluoroborate

(TCI), and dry N,N-dimethylacetoamide (Wako) were used as received.

Direct Arylation Polycondensation of EDOT with 2,7-Dibromo-9,9-dioctylfluorene

A procedure for the direct arylation polycondensation of EDOT with 2,7-dibromo-9,9-dioctylfluorene is as follows. A mixture of EDOT (43 mg, 0.30 mmol), 2,7-dibromo-9,9-dioctylfluorene (164 mg, 0.30 mmol), 1-adamantanecarboxylic acid (16 mg, 30 mol%), K₂CO₃ (125 mg, 0.90 mmol) and palladium chloride (0.46 mg, 1.0 mol%) was stirred in dry N,N-dimethylacetoamide (1.0 mL) for 120 min at 120°C under argon. The reaction mixture was diluted by toluene, rapidly cooled to room temperature, and then filtered to remove insoluble salts. The filtrate was pored into a large amount of methanol. The resulting polymer was collected by filtration, and then washed with a large amount of methanol. The polymer was dried under vacuum to give as an orange powder. The measurements of the polymer were performed without further treatment. The yield was estimated by the weight of the polymer, which was insoluble in methanol. Molecular weight (M_n) and polydispersity (M_w/M_n) of the polymer were estimated by size exclusion chromatography (SEC, polystyrene standard). **PEDOTF8**: reddish yellow powder. ¹H NMR (300 MHz, CDCl₃): δ 7.9-7.6 (Ar-H, br), 6.31 (end group of EDOT), 4.45 (O(CH₂)₂O, br), 2.05 (CH₂(CH₂)₆CH₃, br), 1.25-0.77 (CH₂(CH₂)₆CH₃, br).¹³C NMR (75.45 MHz, CDCl₃): δ 151.4, 139.5, 138.6, 131.7, 125.0, 120.3, 119.7, 116.1 64.6, 55.2, 40.4, 31.8, 30.0, 29.2₄, 29.2₁, 23.8, 22.6, 14.1. Anal. Calcd. for (C₃₅H₄₄O₂S)_n: C, 79.50; H, 8.39. Found: C, 79.28; H, 8.32.

Direct Arylation of EDOT with Bromobenzene

A mixture of EDOT (43 mg, 0.30 mmol), bromobenzene (104 mg, 0.66 mmol), 1-adamantanecarboxylic acid (16 mg, 30 mol%), K₂CO₃ (125 mg, 0.90 mmol) and palladium chloride (0.46 mg, 1.0 mol%) was

stirred in dry *N*,*N*-dimethylacetoamide (1.0 mL) for 120 min at 120°C under argon. The reaction mixture was diluted by diethylether, rapidly cooled to room temperature, and then filtered to remove insoluble salts. After reaction, a large amount of water was added to the reaction mixture, and then it was extracted with diethylether (5 times). The separated organic phases were dried over MgSO₄, evaporated and dried under reduced pressure. The further purification was performed using silica gel chromatography (hexane). A yellow solid was obtained. **2**: ¹H NMR (300 MHz, CDCl₃): δ 7.75 (*Ar-H*, d, *J* = 7.5, 4H), 7.37 (*Ar-H*, t, *J* = 14.1, *J* = 8.1, 4H), 7.23 (*Ar-H*, d, *J* = 6.3, 4H), 4.34 (O(CH₂)₂O, s, 4H). ¹³C NMR (75.45 MHz, CDCl₃): δ 138.5, 132.9, 128.6, 126.6, 126.0, 115.3, 64.5.

Synthesis of PEDOTBT6

A procedure for the direct arylation polycondensation of EDOT with 2,7-dibromo-9,9-dioctylfluorene is as follows. A mixture of EDOT (43 mg, 0.30 mmol), 5,5'-dibromo-3,3'-dihexyl-2,2'-bithiophene (149 mg, 0.30 mmol), 1-adamantanecarboxylic acid (16 mg, 30 mol%), K₂CO₃ (125 mg, 0.90 mmol) and palladium (1.0 mol%) was stirred in dry *N*,*N*-dimethylacetoamide (1.0 mL) for 120 min at 120°C under argon. The reaction mixture was diluted by toluene, rapidly cooled to room temperature, and then filtered to remove insoluble salts. The filtrate was pored into a large amount of methanol. The resulting polymer was collected by filtration, and then washed with a large amount of methanol. The polymer was dried under vacuum to give as an orange powder. The measurements of the polymer were performed without further treatment. The yield was estimated by the weight of the polymer, which was insoluble in methanol. Molecular weight (M_n) and polydispersity (M_w/M_n) of the polymer was estimated by size exclusion chromatography (SEC,

polystyrene standard). **PEDOTBT6**: reddish yellow powder. ¹H NMR (300 MHz, CDCl₃): δ 7.2-7.0 (*Ar-H*, br), 6.21 (end group of EDOT), 4.38 (O(CH₂)₂O, br), 2.53 (CH₂(CH₂)₄CH₃, br), 1.27 (CH₂(CH₂)₄CH₃, br), 0.87 (CH₂(CH₂)₄CH₃, br).¹³C NMR (75.45 MHz, CDCl₃): δ 142.6, 137.6, 134.1, 127.3, 124.4, 109.6, 65.0, 31.7, 30.6, 29.1, 29.0, 22.6, 14.1.

Direct Arylation Polycondensation of 1,2,4,5-Tetrafluorobenzene with 2,7-Dibromo-9,9-dioctylfluorene

procedure arylation polycondensation of 1,2,4,5-tetrafluorobenzene for the direct with А 2,7-dibromo-9,9-dioctylfluorene is as follows. A mixture of 1,2,4,5-tetrafluorobenzene (45 mg, 0.30 mmol), 2,7-dibromo-9,9-dioctylfluorene (164 mg, 0.30 mmol), 1-adamantanecarboxylic acid (16 mg, 30 mol%), K₂CO₃ (125 mg, 0.90 mmol), and PdCl₂ (0.56 mg, 1.0 mol%) was stirred in dry N,N-dimethylacetoamide (0.30 mL) for 10 h at 100°C under argon. The reaction mixture was diluted by toluene, rapidly cooled to room temperature, and then filtered to remove insoluble salts. The Filtrate was pored into a large amount of methanol. The resulting polymer was collected by filtration, and then washed with a large amount of methanol. The polymer was dried under vacuum to give as an orange powder. The measurements of polymer were performed without further treatment. The yield was estimated by the weight of the polymer, which was insoluble in methanol. Molecular weight (M_n) and polydispersity (M_w/M_n) of the polymer was estimated by size exclusion chromatography (SEC, polystyrene standard). **PpTP-F8**: white powder. ¹H NMR (300 MHz, CDCl₃): δ 8.0-7.8 (Ar-H, br), 7.7-7.5 (Ar-H, br), 2.05 (CH₂(CH₂)₆CH₃, br), 1.4-0.5 (CH₂(CH₂)₆CH₃, br).¹³C NMR (75.45 MHz, CDCl₃): δ 151.4, 145.9 (d), 141.2, 129.1, 126.5, 125.0, 120.2, 119.9 (m), 55.5, 40.1, 31.8, 29.9, 29.2, 23.8, 22.6, 14.1. ¹⁹F NMR (254.05 MHz, CDCl₃): δ -145.3

Direct Arylation of Pentafluorobenzene with Monohalobenzene

A procedure for the direct arylation polycondensation of pentafluorobenzene with monohalobenzene is as follows. A mixture of pentafluorobenzene, **1**, (74 mg, 0.44 mmol), monohalobenzene, **2**, (0.40 mmol), 1-adamantanecarboxylic acid (20 mg, 30 mol%), K₂CO₃ (136 mg, 1.20 mmol) and PdCl₂ (0.75 mg, 1.0 mol%) was stirred in dry *N*,*N*-dimethylacetoamide (0.40 mL) for 6 h at 100°C under argon. After reaction, a large amount of water was added to the reaction mixture, and then the mixture was extracted with diethyl ether (3 times). The separated organic phase was dried over MgSO₄, evaporated and dried under reduced pressure. A white crystal was obtained. **3**: ¹H NMR (300 MHz, CDCl₃): δ 7.50-7.45 (*Ar-H*, m, 3H), 7.44-7.38 (*Ar-H*, m, 2H). ¹³C NMR (75.45 MHz, CDCl₃): δ 130.1, 129.2, 128.7, 126.3. ¹⁹F NMR (254.05 MHz, CDCl₃): δ -144.2 (m, 2F), -156.7 (m, 1F), -163.3 (m, 2F).

Measurements

Liquid-state ¹H and ¹³C NMR spectra were recorded on a JEOL EX-300 spectrometer. Liquid-state ¹⁹F NMR spectrum was recorded on a JEOL EX-270 spectrometer. GPC analyses were performed by a Toso GPC system (HLC-8220), using tetrahydrofuran as the eluent after calibration with polystyrene standards. 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. Cyclic voltammetry (CV) measurements were performed

by ALS 611. A three electrode system equipped with the platinum electrode, platinum counter electrode and Ag/AgCl as a reference electrode was used in an electrolytic solution of DMAc containing 0.1 M tetraethylammonium tetrafluoroborate.

Table S1. Results of Direct Arylation Polycondensation of 3,4-Ethylenedioxythiophene with

2,7-Dibromo-9,9-doctylfluorene

Entry	[Pd]	Ligand	Yield (%) ^[a]	$M_{\rm n}^{[b]}$	$M_{ m w}/M_{ m n}^{[b]}$
1	$Pd(OAc)_2$	-	82	6600	2.47
2	$Pd(OAc)_2$	Cy ₃ PHBF ₄	33	3000	1.75
3	PdCl ₂	-	97	40000	2.83
4	Pd(CF ₃ COO) ₂	-	trace	1400	1.15
5	Pd ₂ (dba) ₃ -CHCl ₃	-	11	2000	1.29

Conditions: **EDOT** (0.30 mmol), **F8** (0.30 mmol), [Pd] (1.0 mol%), Cy₃PHBF₄ (0.0 or 2.0 mol%), 1AdCOOH (30 mol%), K₂CO₃ (3.0 mmol), DMAc (1.0 mL), 120 °C, 15 min, under argon. ^[a] Insoluble in

methanol. ^[b] Estimated by SEC measurements (eluent: THF, standard: polystyrene).



Figure S1. ¹H NMR spectrum of PEDOTF8 in CDCl₃. #: CHCl₃. /: H₂O. \$: TMS.

Entry	[Pd]	Additive	Yield (%)
1	$Pd(OAc)_2$	-	64
2	PdCl ₂	-	97
3	$Pd(OAc)_2$	ⁿ Bu ₄ NCl	93

Table S2. Direct arylation of EDOT by Various Pd Catalyst

Conditions: EDOT (0.30 mmol), 1a (0.63 mmol), [Pd] (1.0 mol%), "Bu₄NCl (0.0 or 2.0 mol%), 1AdCOOH

(30 mol%), K₂CO₃ (3.0 mmol), DMAc (1.0 mL), 120 °C, 10 min, under argon. ^[a] 15 min.



Figure S2. Cyclic volammograms of palladium under polycondensation conditions. (red line) $PdCl_2$, (blue line) $Pd(OAc)_2$, (purple dotted line) $Pd(OAc)_2 + {}^nBu_4NCl$ before heating, (purple solid line) $Pd(OAc)_2 + {}^nBu_4NCl$ after heating. Conditions: In 0.1 M Et₄NBF₄/DMAc; Pt counter electrode, Pt working electrode, Ag/AgCl reference electrode; scan rate, 0.1 V/sec; Fe/Fe⁺ = 0.41 V. * Back ground.



Figure S3. UV-vis absorption spectra of various palladium in DMAc. (red line) $PdCl_2$, (blue line) $Pd(OAc)_2$, (purple dotted line) $Pd(OAc)_2 + {}^nBu_4NCl$ before heating, (purple solid line) $Pd(OAc)_2 + {}^nBu_4NCl$ after

heating.

Table S3. Direct arylation of EDOT with F8

Entry	Conditions	Yield (%) ^[a]	$M_{\rm n}^{[b]}$	$M_{\rm w}/M_{\rm n}^{\rm [b]}$
1	without 1AdCOOH	0	-	-
2	without 1AdCOOH and K ₂ CO ₃	0	-	-
3	with 2.0 mol% of AgNO ₃	78	8600	2.13
4	with 30.0 mol% of AgNO ₃	8	1000	2.07
5	with 100.0 mol% of AgNO ₃	0	-	-

^[a] Insoluble in methanol. ^[b] Estimated by SEC measurements (eluent: THF, standard: polystyrene). Conditions: **EDOT** (0.30 mmol), **F8** (0.30 mmol), PdCl₂ (1.0 mol%), 1AdCOOH (30 mol%), K₂CO₃ (3.0

mmol), DMAc (1.0 mL), 120 °C, 2 h, under argon.



Scheme S1. Plausible mechanism of chloride-promoted direct arylation.

The plausible mechanism is the concerted metalation-deprotonation (CMD) ¹⁴ proposed for the Pd-catalyzed direct arylation (Scheme S1). The direct arylation polycondensation of **EDOT** with **F8** in the lack of carboxylate additives did not give the polymer (Table S3, entries 1 and 2). These results support the CMD mechanism. To clear the effect of chloride, the polycondensation with 1.0 mol% of PdCl₂ was carried out in the presence of AgNO₃ as a chloride scavenger. The polycondensation with 2.0 mol% of AgNO₃ gave the low molecular weight polymer ($M_n = 8600$, $M_w/M_n = 2.13$) in 78% yield (entry 3). The chloride scavenger decreased the reaction efficiency. Moreover, the excess amount of AgNO₃ did not give the polymeric products (entry 4 and 5). It is known that silver salt (AgCO₃ or AgNO₃ + K₂CO₃) plays an agent for the abstraction of halide ions from halopalladium species to generate reactive palladium species for some reactions ¹⁵. However, the excess chloride scavengers inhibited the direct arylation. These results suggested that the halide ion plays a good ligand for a cationic Pd(II) species and prevents the Pd catalyst from forming an inactive Pd species. Similar to the common phosphine ligands ¹⁶⁻¹⁸, the weak but moderately

donating nature of the chloride (or bromide) ligand would tune Pd(II) to the suitable cationic Pd character for moving from the intermediate **B** to **C** in the reaction (Scheme S1). On the other hand, the trifluoroacetate ion liberated from $Pd(CF_3COO)_2$ (Table S1, entry 4) and the nitrate ion from AgNO₃ (Table S3, entry 3-5) may not generate appropriate Pd(II) species for the C-H arylation because that these anions are non-donating ones.



Figure S4. ¹H NMR spectrum of PEDOTBT6 synthesized by PdCl₂-catalyzed direct arylation for 15 min.

#: CHCl₃. /: H₂O. \$: TMS.

Entry	[Pd]	Additive	Temp.	Time	Conc.	Yield	$M_{\rm n}^{[b]}$	$M_{\rm w}/M_{\rm n}^{\rm [b]}$
			(°C)	(h)	(M)	(%) ^[a]		
1	PdCl ₂	1AdCOOH	100	6	1.0	68	20200	6.16
2	$Pd(OAc)_2$	1AdCOOH	100	6, 24	1.0	0 ^[c]	-	-
3	Pd(CF ₃ COO) ₂	1AdCOOH	100	6, 24	1.0	0	-	-
4	PdCl ₂	-	100	6	1.0	0 ^[c]	-	-
5	$Pd(OAc)_2$	-	100	6	1.0	0 ^[c]	-	-
6	PdCl ₂	PivOH	100	6	1.0	76	11000	2.64
7	PdCl ₂	1AdCOOH	120	6	1.0	47 ^[d]	12000	3.27
8	PdCl ₂	1AdCOOH	80	6	1.0	0 ^[c]	-	-
9	PdCl ₂	1AdCOOH	100	10	1.0	86	21000	6.77
10	PdCl ₂	1AdCOOH	100	6	0.5	0 ^[c]	-	-
11	PdCl ₂	1AdCOOH	100	6	1.0 ^[e]	0 ^[c]	-	-
12	PdCl ₂	1AdCOOH	100	6	$1.0^{[f]}$	12	3500	1.53
13	PdCl ₂	1AdCOOH	100	18	$1.0^{[f]}$	79	13000	2.75

Table S4. Results of Direct Arylation Polycondensation of pTP with F8

^[a] Insoluble in methanol. ^[b] Estimated by SEC measurements (eluent: THF, standard: polystyrene). ^[c]

Suspended solution was observed after precipitation into methanol. ^[d] Insoluble products were obtained. ^[e]

toluene. ^[f] DMAc/toluene (1:1).



Figure S5. ¹H NMR spectrum of **PpPT-F8** in CDCl₃. #: CHCl₃. !: H₂O. \$: TMS.



Figure S6. ¹⁹F NMR spectrum of **PpPT-F8** in CDCl₃. #: hexafluorobenzene.

Entry	Aryl Halide	[Pd]	^t Bu ₂ MePHBF ₄	1AdCOOH	Yield (%) ^[a]
1	Br	PdCl ₂	-	2.0 eq	90
2		PdCl ₂	-	-	trace
3	1 a	$Pd(OAc)_2$	2.0 mol%	2.0 eq	91
4	CI	PdCl ₂	-	2.0 eq	71
	1b				

Table S5. Results of Direct Arylation of **3** with **2**

^[a] Isolated yield.



Figure S7. Summary of the Direct Arylation Polycondensation of EDOT with F8. The value shown in figure is polydispersity (M_w/M_n) .

The values of Figure 1a

Pd(OAc)2						
temp.	Mn	Mw/Mn	Yield	Mn	Mw/Mn	Yield
80	1800	1.39	20	4400	1.87	43
100	4600	2	73	23000	3.16	88
120	6600	2.47	82	40000	2.83	96

The values of Figure 1b

Pd(OAc)2						
time	Mn	Mw/Mn	Yield	Mn	Mw/Mn	Yield
2	-	-	-	7000	2.25	83
5	-	-	-	10500	2.1	86
15	6600	2.47	60	40000	2.83	96
30	38200	4	82	57600	6.82	97
60	47200	3.89	91	70600	4.26	96
120	47100	2.99	95	80000	4.09	97

The values of Figure 1c

{Pd}	additive		Mn	Yield	Mw∕Mn
PdCl2	-	1	40000	97	2.83
Pd(OAc)2	-	2	6600	82	2.47
Pd(OAc)2	nBu4NF	3	19700	93	4.81
Pd(OAc)2	nBu4NCl	4	18200	97	2.86
Pd(OAc)2	nBu4NBr	5	15400	94	2.57
Pd(OAc)2	nBu4NI	6	2600	76	1.5

The values of Figure 1d

	Pd(OAc)	2+nBu4NCl		PdCl2			
time	Mn	Mw/Mn	Yield	Mn	Mw/Mn	Yield	
2	-	-	-	7000	2.25	83	
5	7000	2.18	78	10500	2.1	86	
15	18200	2.86	97	40000	2.83	96	
30	45000	4.88	97	57600	6.82	97	
60	58500	3.23	93	70600	4.26	96	
120	70200	3.6	96	80000	4.09	97	