Supporting Information for
Synthesis of Conjugated Polymers via Direct C–H/C–Cl Coupling Reactions Using a Pd/Cu Binary Catalytic System

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Scheme S1. Direct arylation polycondensation under the conventional conditions.1
Scheme S2. Plausible reaction mechanism of the side reactions.$^2$
Figure S1. MALDI-TOF-MS spectra of P1 (Table 1, Entry 1-4).
Figure S2. $^1$H NMR spectrum of P1 (Table 1, Entry 3) (400 MHz, CDCl$_3$).

Figure S3. $^{19}$F NMR spectrum of P1 (Table 1, Entry 3) (376 MHz, CDCl$_3$). The spectrum was measured with hexafluorobenzene as an external standard (-162.9 ppm).
Figure S4. $^1$H NMR spectrum of 2,7-bis-(5-chlorothiophene-2-yl)-9,9-bis(2-ethylhexyl)fluorene (400 MHz, CDCl$_3$).

Figure S5. $^{13}$C-$^1$H and DEPT 135 NMR spectra of 2,7-bis-(5-chlorothiophene-2-yl)-9,9-bis(2-ethylhexyl)fluorene (150 MHz, CDCl$_3$).
Figure S6. MALDI-TOF-MS spectra of P2 (Table 2, Entry 1-4).
Figure S7. $^1$H NMR spectra of P2-6 (Table 2, Entry 6) and reference compounds (600 MHz, C$_2$D$_2$Cl$_4$, 373 K).

Figure S8. $^{19}$F NMR spectrum of P2-6 (564 MHz, C$_2$D$_2$Cl$_4$, 373 K).
Figure S9. $^{13}\text{C}\{^1\text{H}\}$ and DEPT 135 NMR spectra of P2-6 (150 MHz, C$_2$D$_2$Cl$_4$, 373 K).
Figure S10. Absorption and emission spectra of P2-3 and P2-6 in the solution and film state.

Figure S11. AFM images and root mean square roughness (RMS) of the thin films of P2-3 and P2-6.
Figure S12. (a) PL spectrum of thin film of P2-3 and EL spectrum of OLED with P2-3 at 11 V. (b) Current efficiency and EQE of the OLED. Configuration ITO/PEDOT:PSS(40 nm)/P2-3(48 nm)/TPBi(40 nm)/LiF(1 nm)/Al(100 nm)

Figure S13. (a) PL spectrum of thin film of P2-6 and EL spectrum of OLED with P2-6 at 8 V. (b) Current efficiency and EQE of the OLED. Configuration ITO/PEDOT:PSS(40 nm)/P2-6(48 nm)/TPBi(40 nm)/LiF(1 nm)/Al(100 nm)
Figure S14. (a) PL spectrum of thin film of P2-6 and EL spectrum of the improved OLED with P2-6 at 8 V. (b) Current efficiency and EQE of the OLED. Configuration ITO/PEDOT:PSS(40 nm)/PVK(26 nm)/P2-6(29 nm)/TPBi(30 nm)/LiF(1 nm)/Al(100 nm)

Table S1. Results of elemental analysis

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<tr>
<td>Calcd.</td>
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<td>P2-3 a</td>
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<td>P2-6 b</td>
<td>72.01</td>
<td>6.06</td>
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a The polymer from Entry 3 in Table 2. b The polymer from Entry 6 in Table 2.

Table S2. Physical properties of P2

<table>
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<th>Absorption maximum (nm)</th>
<th>Absorption edge (nm)</th>
<th>Energy level (eV)</th>
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<tr>
<td></td>
<td>Solution</td>
<td>Film</td>
</tr>
<tr>
<td>P2-3 a</td>
<td>409</td>
<td>408</td>
</tr>
<tr>
<td>P2-6 b</td>
<td>408</td>
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</table>

a The polymer from Entry 3 in Table 2. b The polymer from Entry 6 in Table 2.
Synthesis of 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene.\(^3\)

Potassium tert-butoxide (5.61 g, 50 mmol), 2,7-dibromofluorene (6.48 g, 20 mmol), and cyclopentylmethyl ether (200 mL) were added to a 500 mL Schlenk tube under a N\(_2\) atmosphere. The mixture was stirred for 15 min at room temperature. 1-Bromo-2-ethylhexane (7.11 mL, 2.2 mmol) was added to the mixture under N\(_2\) gas flow. The mixture was stirred at room temperature for 1 h, and at 60 °C overnight. After cooling to room temperature, water was added to the reaction mixture. The organic phase was separated, washed with water, and dried with Na\(_2\)SO\(_4\). Purification by column chromatography (silica gel, hexane) afforded 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene as a white solid (10.9 g, 99%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.52\) (d, \(J = 8.0\) Hz, 2H), 7.49-7.47 (m, 2H), 7.45 (dd, \(J = 8.0, 1.6\) Hz, 2H), 1.93 (m, 4H), 0.89-0.68 (m, 14H), 0.54 (m, 16H), 0.58-0.42 (m, 2H).

Synthesis of 2,7-bis(thiophene-2-yl)-9,9-bis-(2-ethylhexyl)fluorene\(^4,5\)

2,7-Dibromo-9,9-bis(2-ethylhexyl)fluorene (1.37 g, 2.5 mmol), 2-thiopheneboronic acid (1.40 g, 11 mmol), K\(_2\)CO\(_3\) (1.52 g, 11 mmol), and Pd(PPh\(_3\))\(_4\) (11.6 mg, 0.010 mmol) were added to a 200 mL Schlenk tube. After degassing and filling with N\(_2\), EtO(CH\(_2\))\(_2\)OH/H\(_2\)O (18 mL/2 mL) was added under N\(_2\) gas flow. After stirring at 100 °C for 4 h under a N\(_2\) atmosphere, water and CHCl\(_3\) were added. The organic phase was separated, washed with water, and dried with Na\(_2\)SO\(_4\). Purification by column chromatography (silica gel, hexane) afforded 2,7-bis(thiophene-2-yl)-9,9-bis-(2-ethylhexyl)fluorene as a colorless oil (1.31 g, 94%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.67\) (d, \(J = 8.4\) Hz, 2H), 7.60-7.58 (m, 4H), 7.34 (m, 2H), 7.28 (d, \(J = 5.0\) Hz, 2H), 7.10 (m, 2H), 2.05 (m, 4H), 0.95-0.47 (m, 30H).
Synthesis of 2,7-bis(5-chloro-thiophene-2-yl)-9,9-bis(2-ethylhexyl)fluorene

2,7-Bis(thiophene-2-yl)-9,9-bis(2-ethylhexyl)fluorene (545 mg, 1.0 mmol) and CH₂Cl₂ (2 mL) were added to a 25 mL Schlenk tube under a N₂ atmosphere. A mixture of N-chlorosuccinimide (294 mg, 2.2 mmol) and 2,4,6-trimethylaniline (14 μL, 0.10 mmol) in CH₂Cl₂ (2 mL) was added to solution of 2,7-bis(thiophene-2-yl)-9,9-bis(2-ethylhexyl)fluorene (545 mg, 1.0 mmol) in CH₂Cl₂ (2 mL) in a dropwise manner under light shielding condition. The mixture was stirred for 24 hours at room temperature. Purification by column chromatography (silica gel, hexane) afforded 2,7-bis(5-chloro-thiophene-2-yl)-9,9-bis(2-ethylhexyl)fluorene as a yellow solid (557 mg, 89 %).

Fabrication of OLED with an electron blocking layer

OLED with a poly(9-vinylcarbazole) (PVK) layer was fabricated in the following configuration: ITO/PEDOT:PSS/electron blocking PVK layer/light-emitting P2 layer/electron transporting (hole blocking) TPBi layer/LiF/Al. The patterned indium tin oxide (ITO) glass (conductivity: 10 Ω/square) was precleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet-ozone chamber. A thin layer (40 nm) of PEDOT:PSS was spin-coated onto the ITO at 3000 rpm and air-dried at 110 °C for 10 min on a hot plate. The substrate was then transferred to a N₂-filled glovebox where it was redried at 110 °C for 10 min on a hot plate. A chloroform solution of PVK (3 mg/1 mL) was subsequently spincoated onto the PEDOT:PSS surface to form electron blocking layer (26 nm), followed with a baking process for 10 min at 150 °C. A toluene solution of P2 (5 mg/1 mL) was subsequently spincoated onto the PVK surface to form the light-emitting layer (29 nm), followed with an annealing process for 10 min at 80 °C. TPBi (30 nm), LiF (1 nm), and Al (100 nm) were then deposited onto the active layer with conventional thermal evaporation at a chamber pressure lower than 5 × 10⁻⁴ Pa, which provided the devices with an active area of 2 × 2 mm².
References


