

Supporting Information for

**Synthesis and Characterization of Regioregular  
Cyano-substituted Poly(*p*-phenylenevinylene)**

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## Measurement

Gel permeation chromatography (GPC) of regiorandom CN-PPV (**1**) was performed using a Shimadzu Prominence system equipped with a UV detector employing  $\text{CHCl}_3$  as the eluent at 40 °C. The polymer solution was filtered using a PTFE filter (pore size: 0.2  $\mu\text{m}$ ) before sample injection. For the regioregular sample (**3**), GPC was performed on a Waters Alliance GPC 2000 system with a differential refractive index detector with TSKgel GMH<sub>6</sub>-HT and GMH<sub>6</sub>-HTL columns and dichlorobenzene as the eluent at 140 °C. The polymer solution was filtered at 145 °C using a ceramic filter (pore size: 1.0  $\mu\text{m}$ ) before sample injection.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a JEOL Alpha FT-NMR spectrometer equipped with an OXFORD superconducting magnet system (500 MHz or 400 MHz). UV-vis and FT-IR spectra were recorded on JACSO V-650 and FT/IR-4100 spectrometers, respectively. Fluorescence spectra were recorded on a Hitachi F-4500, using an excitation at maximum absorption wavelength. GC-MS measurement was performed on Focus GC and Polaris Q (Thermo Fisher, United States). Photoelectron yield spectroscopy (PYS) was recorded on an AC-3 photoelectron spectroscopy in air (Riken Keiki Co., Ltd., Japan).

## Synthesis

All reagents were purchased from Wako (Japan), TCI (Japan), and Aldrich (United States) chemicals and used as received. 3,7-Dimethyloctylbromide was synthesized by following the procedure reported previously.<sup>2</sup>

### *2-Bromo-1-(3,7-dimethyl-octyloxy)-4-methoxy-benzene (4)*<sup>3, 4</sup>

$\text{Br}_2$  (4 mL, 79.6 mmol) was added dropwise to a stirred solution of 4-methoxyphenol (9.56 g, 76.9 mmol) in  $\text{CH}_2\text{Cl}_2$  (400 mL) accompanied with spontaneous liberation of HBr. After 3 h at room temperature, the solvent was removed under reduced pressure. The oily residue was solidified on standing in a freezer. The solid (16 g) was dissolved in MeCN (300 mL) and treated with  $\text{K}_2\text{CO}_3$  (19.0 g, 136 mmol) and 3,7-dimethyloctylbromide (20.3 g, 92.4 mmol). After refluxing for 9 h, the precipitate

was removed by filtration over a plug of Celite<sup>®</sup>. The filtrate was concentrated by evaporation, diluted with CHCl<sub>3</sub> (100 mL) and washed with 5 % aqueous NaOH and brine. The CHCl<sub>3</sub> layer was dried over MgSO<sub>4</sub>, filtrated and evaporated to yield brown oil. Vacuum distillation provided pale yellow liquid (23.7 g, 90%): b.p. 90 °C (2 mmHg)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.86-1.89 (m, 19H), 3.75 (s, 3H, -OCH<sub>3</sub>), 3.96-4.01 (m, 2H, -OCH<sub>2</sub>-), 6.78-6.85 (m, 2H, Ar-*H*), 7.11 (d, *J* = 2.9 Hz, 1H, Ar-*H*). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 153.95, 149.87, 118.76, 114.57, 113.67, 112.77, 68.50, 55.86, 39.19, 37.24, 36.15, 29.76, 27.95, 24.65, 22.69, 22.60, 19.69. GC-MS: *m/z* 344.0, 342.1 (M<sup>+</sup>), 204.0, 202.5 ([M-C<sub>10</sub>H<sub>21</sub>+H]<sup>+</sup>)

#### *4-Bromo-5-(3,7-dimethyl-octyloxy)-2-methoxy-benzaldehyde (5)*<sup>5</sup>

A solution of TiCl<sub>4</sub> (1.78 mL, 16.4 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (3.06 mL) was added to a stirred solution of compound **4** (2.35 g, 6.84 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (14.2 mL) at 0 °C under nitrogen, whereupon the colorless solution turned deep red. After 20 min, the reaction mixture was treated dropwise with a solution of dichloromethylmethylether (0.907 mL, 10.3 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (6.4 mL) over 30 min. The ice bath was removed and stirring was continued for 90 min before the reaction mixture was poured onto a mixture of ice (25 g) and conc. HCl (0.8 mL). The biphasic mixture was stirred for 14 h, during which time the green organic layer turned orange. The phases were separated and the aqueous layer was extracted with CHCl<sub>3</sub> (2 × 10 mL). The combined organic solutions were washed with water (3 × 20 mL), dried over MgSO<sub>4</sub>, filtrated, and evaporated to yield a brown solid. Purification by SiO<sub>2</sub> column chromatography using CHCl<sub>3</sub>/hexane (1:3) as eluent gave the pale yellow crystal (1.89 g, 74%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 0.83-1.89 (m, 19H), 3.90 (s, 3H, -OCH<sub>3</sub>), 4.01-4.07 (m, 2H, -OCH<sub>2</sub>-), 7.24 (s, 1H, Ar-*H*), 7.33 (s, 1H, Ar-*H*), 10.39 (s, 1H, -CHO). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 188.83, 156.02, 150.01, 124.10, 120.90, 117.50, 110.75, 68.21, 56.33, 39.17, 37.18, 35.91, 29.80, 27.95, 24.65, 22.69, 22.59, 19.68. GC-MS: *m/z* 370.0, 371.9 (M<sup>+</sup>), 230.1, 231.9 ([M-C<sub>10</sub>H<sub>21</sub>+H]<sup>+</sup>)

2-[4-Bromo-5-(3,7-dimethyl-octyloxy)-2-methoxy-phenyl]-5,5-dimethyl-[1,3]dioxane (**6**)<sup>6</sup>

Compound **5** (3.85 g, 10.3 mmol) was mixed with 2,2-dimethyl-1,3-propanediol (1.19 g, 11.3 mmol, 1.1 equiv.) and *p*-toluenesulfonic acid (10 mg, cat.) in toluene (30 mL) in a flask equipped with a Dean-Stark water separator and heated to reflux for 9 h. The cooled mixture was neutralized with two drops of triethylamine and washed with a saturated solution of NaHCO<sub>3</sub>. The water phase was extracted twice with CHCl<sub>3</sub> (2 x 50 mL), and the combined organic phase was dried over MgSO<sub>4</sub>, filtered, and evaporated to dryness. The toluene was removed in vacuo to give orange-yellow oil (4.44 g, 94%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.79-1.85 (m, 27H), 3.67 (d, *J* = 11.2 Hz, 2H), 3.75 (d, *J* = 11.2 Hz, 2H), 3.79 (s, 3H, -OCH<sub>3</sub>), 4.02-4.07 (m, 2H, -OCH<sub>2</sub>-), 5.69 (s, 1H, ArCHO-) 7.07 (s, 1H, Ar-*H*), 7.22 (s, 1H, Ar-*H*). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 150.73, 149.91, 126.66, 116.38, 113.02, 112.40, 96.47, 77.77, 68.28, 56.44, 39.17, 37.20, 36.15, 30.21, 29.72, 27.91, 24.63, 23.11, 22.68, 22.58, 21.81 19.68. GC-MS: *m/z* 458.1, 456.1 (M<sup>+</sup>), 316.2, 318.0 ([M-C<sub>10</sub>H<sub>21</sub>+H]<sup>+</sup>), 230.1, 232.3 ([M-C<sub>10</sub>H<sub>21</sub>-C<sub>5</sub>H<sub>10</sub>O+H]<sup>+</sup>)

[4-(5,5-Dimethyl-[1,3]dioxan-2-yl)-2-(3,7-dimethyl-octyloxy)-5-methoxy-phenyl]-methanol (**7**)<sup>7, 8</sup>

Compound **6** (3.56 g, 7.78 mmol) was dissolved in dry THF (25 mL) and cooled to -63 °C under nitrogen. *n*-BuLi (1.6 M in hexane, 5.34 mL, 1.1 equiv.) was added in one portion, and the reaction mixture was kept cooled with stirring for another 10 min to complete the reaction. Dry DMF (2.42 mL) was added in excess, and the cooling bath was removed. After 1 h at room temperature, water (10 mL) was added and the reaction mixture was stirred for 1.5 h. Amount of the solvents were reduced by evaporation. The remaining oil/water mixture was taken up in CHCl<sub>3</sub>, dried over MgSO<sub>4</sub>, filtered, and evaporated again. The remaining benzaldehyde derivative (3.4 g) was dissolved in THF (15 mL) and NaBH<sub>4</sub> (469 mg, 12.4 mmol) was added all at once with stirring at 0 °C. The mixture was stirred at room temperature for a further 4.5 h, then water (15 mL) was added, and the solvents were reduced by evaporation. The remaining mixture was extracted with four portions of CHCl<sub>3</sub>, washed with brine, dried over MgSO<sub>4</sub>, filtered, and evaporated again. The crude product was purified by SiO<sub>2</sub> column

chromatography using CH<sub>2</sub>Cl<sub>2</sub> and subsequently CH<sub>2</sub>Cl<sub>2</sub>/EtOH as the eluent. The oily residue was solidified under vacuum to give the product as yellow-brown solid (2.75 g, 87%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 0.79-1.85 (m, 27H), 2.37 (t, *J* = 6.7 Hz, 1H, -OH), 3.68 (d, *J* = 11.0 Hz, 2H), 3.75 (d, *J* = 11.0 Hz, 2H), 3.81 (s, 3H, -OCH<sub>3</sub>), 4.02-4.10 (m, 2H, -OCH<sub>2</sub>-), 4.66 (d, 2H, *J* = 6.1 Hz, ArCH<sub>2</sub>O-), 5.75 (s, 1H, ArCHO-) 6.86 (s, 1H), 7.17 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 150.82, 150.32, 130.64, 126.13, 111.79, 109.80, 96.73, 77.79, 77.20, 66.68, 62.02, 56.40, 39.16, 37.22, 36.35, 30.21, 29.92, 27.90, 24.65, 23.13, 22.66, 22.55, 21.84 19.64. GC-MS: *m/z* 408.2 (M<sup>+</sup>), 250.1 ([M-C<sub>10</sub>H<sub>21</sub>-OH]<sup>+</sup>)

#### 2-[4-Bromomethyl-5-(3,7-dimethyl-octyloxy)-2-methoxy-phenyl]-5,5-dimethyl-[1,3]dioxane (**8**)<sup>7</sup>

To a solution of alcohol **7** (2.7g, 6.61 mmol) in dry THF (30 mL), CBr<sub>4</sub> (2.62 g, 7.92 mmol, 1.2 equiv) and PPh<sub>3</sub> (2.07 g, 7.92 mmol, 1.2 equiv) were added at 0 °C. The resulting mixture was then stirred at 0 °C until the complete dissolution of the reagents (around 5 min) and for 5 h at room temperature. Additional CBr<sub>4</sub> (1.31 g, 0.6 equiv) and PPh<sub>3</sub> (1.03 g, 0.6 equiv) were added. After stirring for 3 h, the white precipitate was removed by filtration over a plug of Celite<sup>®</sup>. The filtrate was concentrated and subjected to a short layer of silica column using CHCl<sub>3</sub> as the eluent to remove most of the triphenylphosphine oxide. Careful chromatography on SiO<sub>2</sub> (hexane-CH<sub>2</sub>Cl<sub>2</sub> gradient) afforded the mixture of **8** and its deprotected compound. The mixture was reprotected using the same procedure as for the compound **6** to give pale yellow oil (1.50 g, 48%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 0.79-1.87 (m, 27H), 3.67 (d, *J* = 11.0 Hz, 2H), 3.75 (d, *J* = 11.0 Hz, 2H), 3.80 (s, 3H, -OCH<sub>3</sub>), 4.02-4.10 (m, 2H, -OCH<sub>2</sub>-), 4.53 (s, 2H, -CH<sub>2</sub>Br), 5.72 (s, 1H, ArCHO-), 6.86 (s, 1H, Ar-*H*), 7.17 (s, 1H, Ar-*H*). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 151.28, 150.19, 128.00, 127.31, 113.78, 110.91, 96.61, 77.83, 67.09, 56.42, 39.22, 37.25, 36.37, 30.27, 29.77, 28.86, 27.96, 24.69, 23.16, 22.71, 22.60, 21.89 19.72. GC-MS: *m/z* 470.1 472.0 (M<sup>+</sup>), 391.2 ([M-Br]<sup>+</sup>), 305.3 ([M-Br-C<sub>5</sub>H<sub>10</sub>O]<sup>+</sup>), 251.2 ([M-Br-C<sub>10</sub>H<sub>21</sub>+H]<sup>+</sup>), 167.3

*[2-(3,7-Dimethyl-octyloxy)-4-formyl-5-methoxy-phenyl]-acetonitrile (2)*<sup>9, 10</sup>

To a solution of **8** (1.50 g, 3.18 mmol) in 15 mL of acetonitrile, 522 mg (7.95 mmol, 2.5 equiv.) of KCN, 848 mg (3.18 mmol, 1.0 equiv.) of 18-crown-6 and 1.0 mL of water were added. The mixture was heated to reflux for 22 h. After cooling, the mixture was separated with aqueous solution of nickel nitrate and CHCl<sub>3</sub>. The organic phase was washed several times with water to remove 18-crown-6, dried over MgSO<sub>4</sub>, filtered, and evaporated. The oily residue (1.4 g) was taken up in CH<sub>2</sub>Cl<sub>2</sub> and water (150 mL each) and hydrolyzed with TFA (120 mL). The reaction mixture was stirred at room temperature for 7 h. Subsequently, the mixture was washed with water twice and with 5% solution of NaHCO<sub>3</sub> (200 mL each). The organic phase was dried over MgSO<sub>4</sub>, filtered, and evaporated. The crude product was purified by flash chromatography on SiO<sub>2</sub> (hexane/CH<sub>2</sub>Cl<sub>2</sub> = 1:1) to give yellow oil (587 mg, 56%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  0.86-1.87 (m, 19H), 3.76 (s, 2H, -CH<sub>2</sub>CN) 3.94 (s, 3H, -OCH<sub>3</sub>), 4.00-4.05 (m, 2H, -OCH<sub>2</sub>-), 7.09 (s, 1H, Ar-H), 7.31 (s, 1H, Ar-H), 10.43 (s, 1H, -CHO). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  189.02, 156.30, 150.14, 126.84, 124.61, 117.17, 113.04, 109.20, 67.18, 56.30, 39.17, 37.18, 35.99, 29.88, 27.94, 24.63, 22.67, 22.56, 19.63, 19.30. IR (KBr, cm<sup>-1</sup>): 2956-2870 (alkyl side chains, s), 2255 (Csp<sub>3</sub>-C $\equiv$ N, w), 1684 (C=O, s), 1616 (aromatic ring, w), 1498 (aromatic ring, s), 1465 (aromatic ring, m), 1419 (aromatic ring, s), 1394 (C=O, m), 1330 (CH, w), 1276 (C-O-C, m), 1214 (C-O-C or C=O, s), 1155 (aromatic ring, w), 1110 (aromatic ring, w), 1029 (C-O-C, s), 876 (C=O, w) 736 ((CH<sub>2</sub>)<sub>n</sub>, w). GC-MS: m/z 331.0 (M<sup>+</sup>), 191.1 ([M-C<sub>10</sub>H<sub>21</sub>- C<sub>5</sub>H<sub>10</sub>O+H]<sup>+</sup>). Anal. Calcd. for C<sub>20</sub>H<sub>29</sub>NO<sub>3</sub>; C, 72.47; H, 8.82; N, 4.23. Found: C, 72.31; H, 8.96; N, 3.96.

*Poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene-1-cyanovinylene] (Regioregular CN-PPV) (3)*<sup>11</sup>

At first, the reaction was done in a mixed solvent of THF and *t*-BuOH (1:1), which is a common condition to synthesize the regiorandom CN-PPV (**1**) and its derivatives.<sup>9, 12, 13</sup> However, this reaction condition gave insoluble product, probably due to the difficulty in controlling the molecular weight. After the investigation of the reaction conditions, the use of mixed solvent of THF/MeOH (6:1)<sup>14</sup> or

toluene/*t*-BuOH (10:1)<sup>11</sup> was found to be the optimal conditions to synthesize soluble regioregular products.

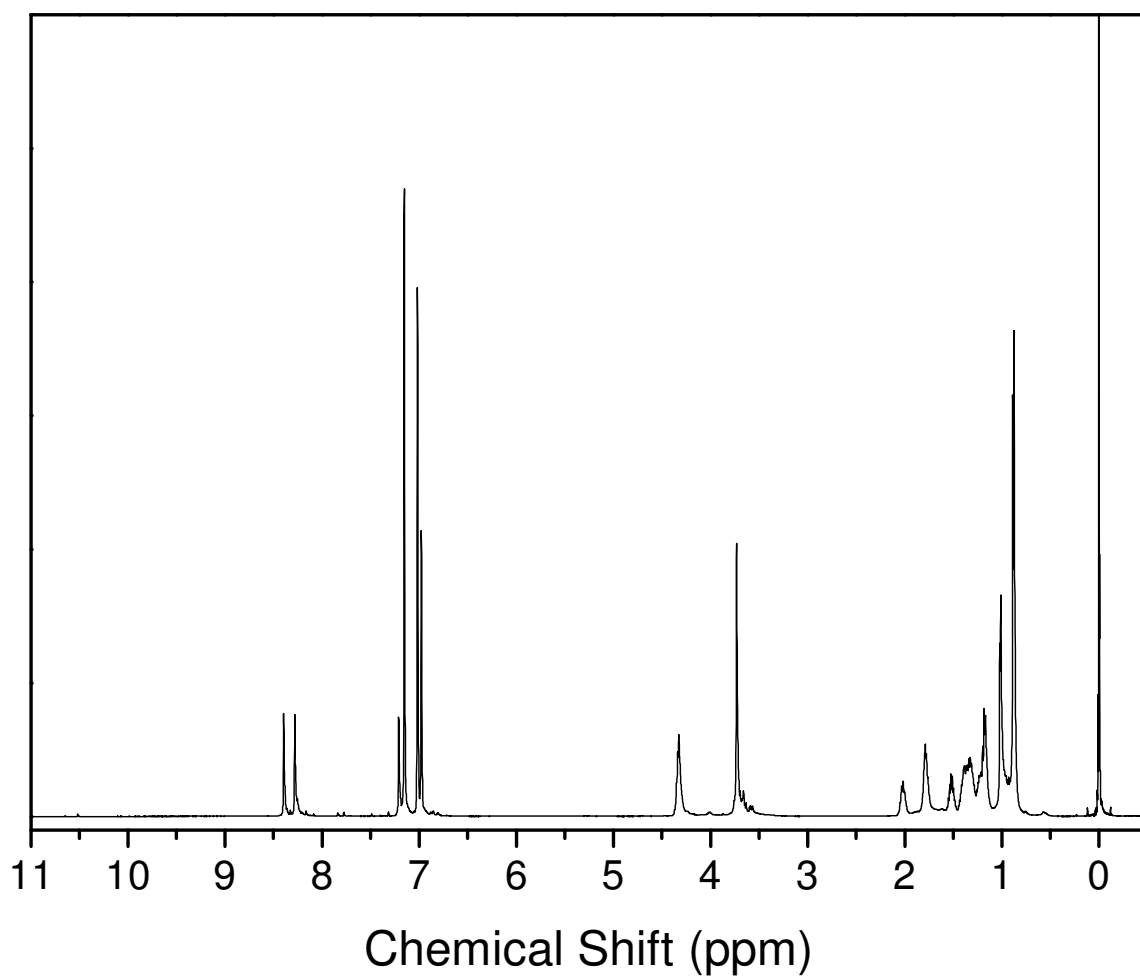
Monomer **2** (55.1 mg, 0.166 mmol) was dissolved in a mixture of 800  $\mu$ L toluene and 80  $\mu$ L *t*-BuOH under nitrogen. The temperature was raised to 100 °C while stirring, and 1 M solution of *t*-BuOK in *t*-BuOH (0.02 mL, 0.02 mmol) was added to the mixture. After 2 h, additional *t*-BuOK (0.035 mL, 0.035 mmol) was added. Reaction was continued for 18 h before cooling down to room temperature. The remaining mixture was diluted with 1 mL of toluene, poured into 100 mL of methanol (acidified with 0.1 mL of acetic acid), stirred and filtrated. The remaining bluish solid was washed with methanol, acetone, and 50 mL of CH<sub>2</sub>Cl<sub>2</sub>, and then dissolved in dichlorobenzene at 120 °C. The hot orange solution was filtered through glass-fiber filter (1  $\mu$ m), reprecipitated into hexane, and filtered again. The collected solid was dried in vacuo at 60 °C (19 mg, 36%).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl, 500 MHz 100 °C):  $\delta$  0.87-2.03 (m, 19H), 3.73 (s, 3H, -OCH<sub>3</sub>), 4.33 (m, 2H, -OCH<sub>2</sub>-), 7.21 (s, 1H, C=C-H), 8.28 (s, 1H, Ar-H), 8.39 (s, 1H, Ar-H). IR (KBr, cm<sup>-1</sup>): 2956 and 2922 and 2849 (alkyl, s), 2205 (Csp<sub>2</sub>-C $\equiv$ N, m), 1684 (Ar-CHO, w), 1652 and 1635 (C=C, w), 1616 (aromatic rings, w), 1506 (aromatic rings, m), 1464 (aromatic rings, s), 1414 (aromatic rings, m), 1384 (-CH<sub>3</sub>, m), 1345 (CH, w), 1307 (C=C, w), 1261 (Ar-O-CH<sub>2</sub>, w), 1220 (Ar-O-CH<sub>2</sub>, s), 1191 (aromatic rings, w), 1126 and 1080 (aromatic rings, m), 1039 (Ar-O-CH<sub>2</sub>, s), 925 (C=C, w), 853 and 800 (>C=CH-, s), 720 ((CH<sub>2</sub>)<sub>n</sub>, m). See Figure S1 for <sup>1</sup>H NMR spectrum.

*Poly[5-(3,7-dimethyloctyloxy)-2-methoxy-cyanoterephthalylidene]* (Regiorandom CN-PPV) (**1**)

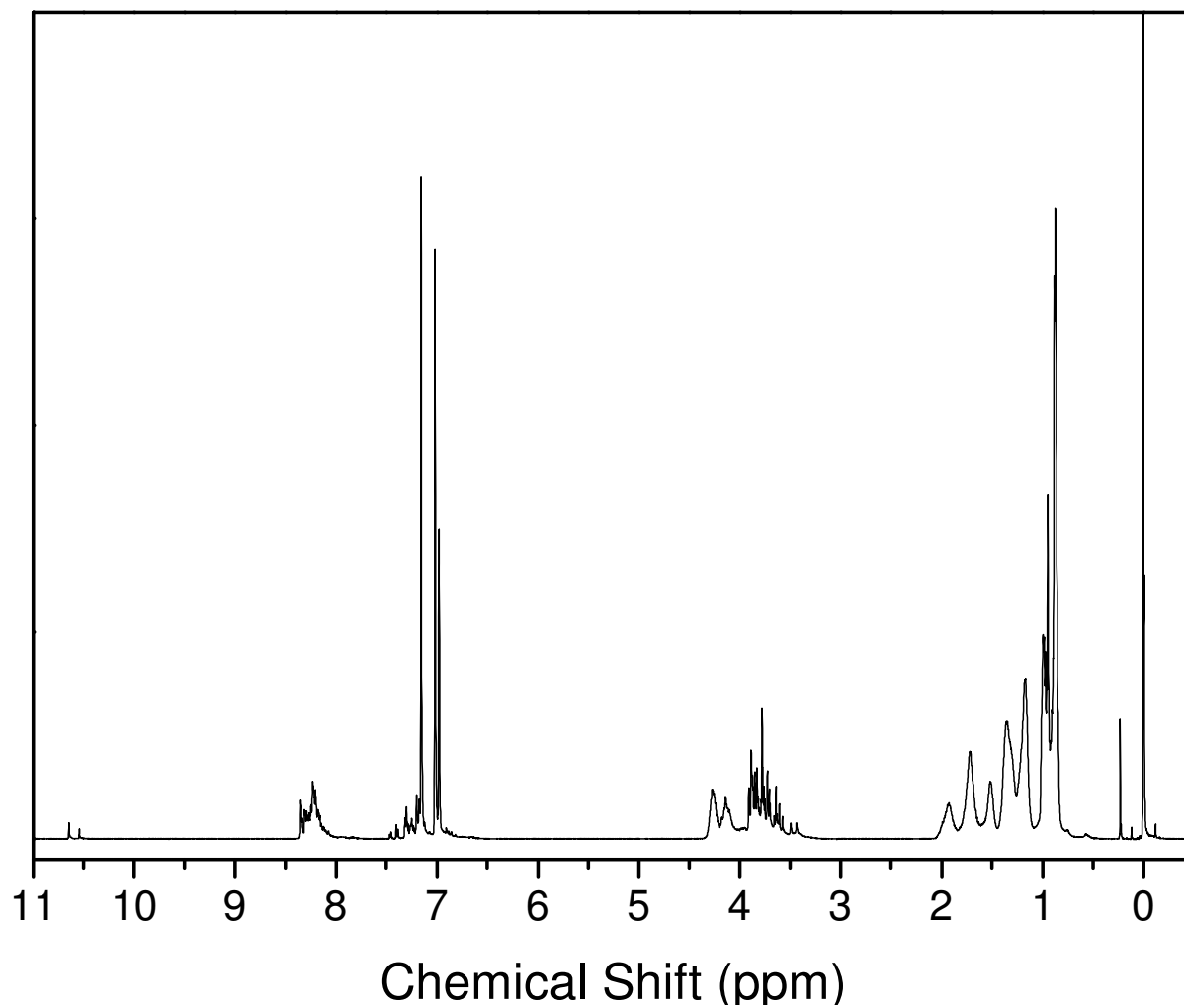
Poly[5-(3,7-dimethyloctyloxy)-2-methoxy-cyanoterephthalylidene] (152 mg) purchased from Aldrich was dissolved in CHCl<sub>3</sub> (3 mL) and precipitated using methanol (250 mL). The reddish solid was collected by filtration, washed well with methanol and hexane, and dried under vacuum (135 mg).

See Figure S2 for the <sup>1</sup>H NMR spectrum.

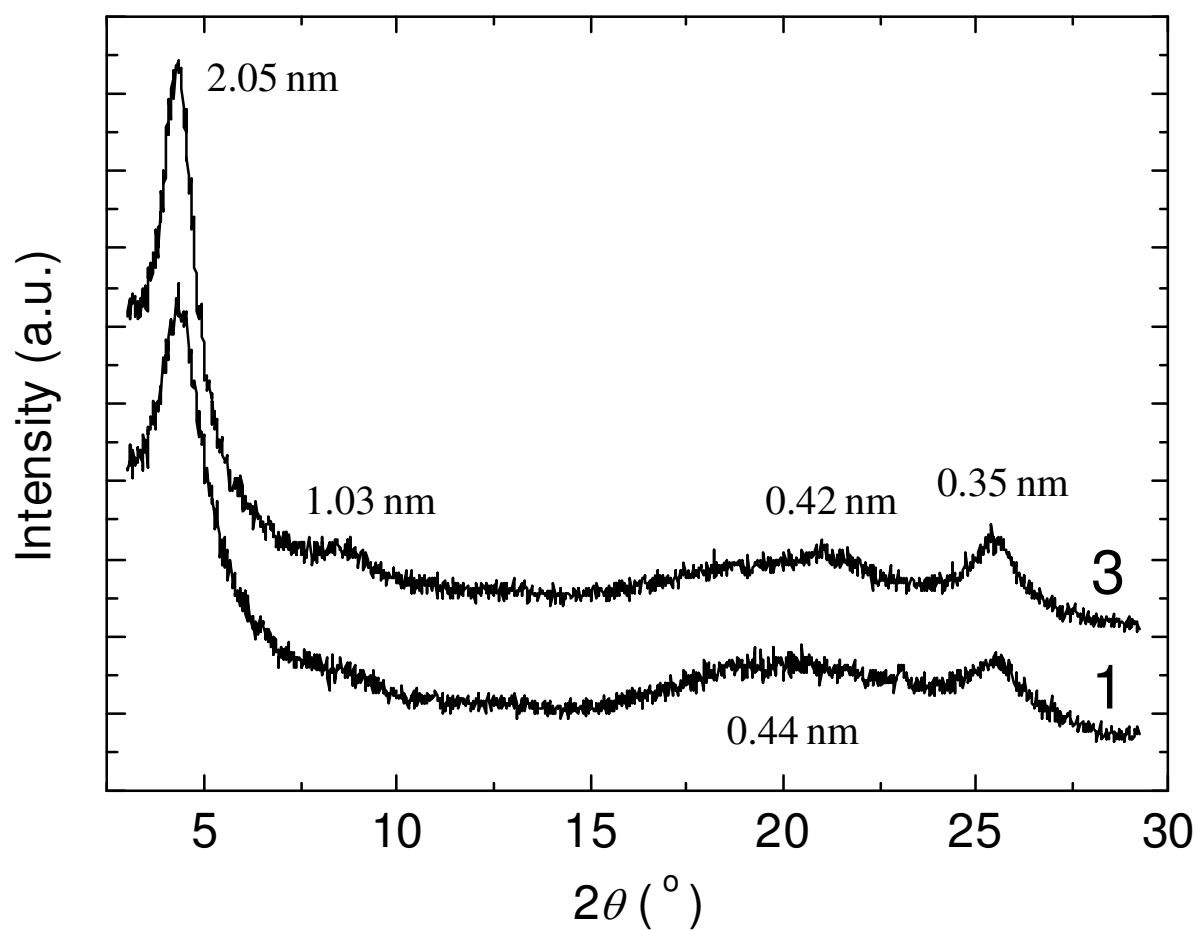


**Figure S1.**  $^1\text{H}$  NMR spectrum of regioregular CN-PPV (**3**) ( $\text{C}_6\text{D}_5\text{Cl}$ , 500 MHz 100  $^\circ\text{C}$ ).





**Figure S2.**  $^1\text{H}$  NMR spectrum of regiorandom CN-PPV (**1**) ( $\text{C}_6\text{D}_5\text{Cl}$ , 500 MHz, 100  $^\circ\text{C}$ ).



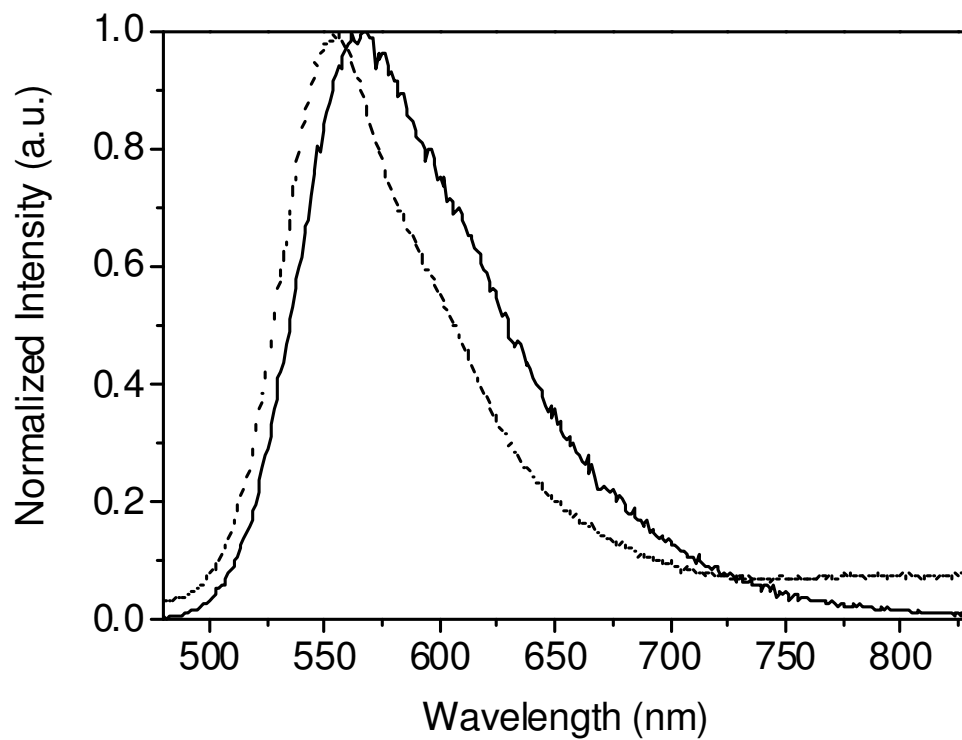
**Figure S3.** Powder X-ray diffraction patterns of regioregular **3** (upper) and regiorandom **1** (lower).

### **Film preparation by spin-coating**

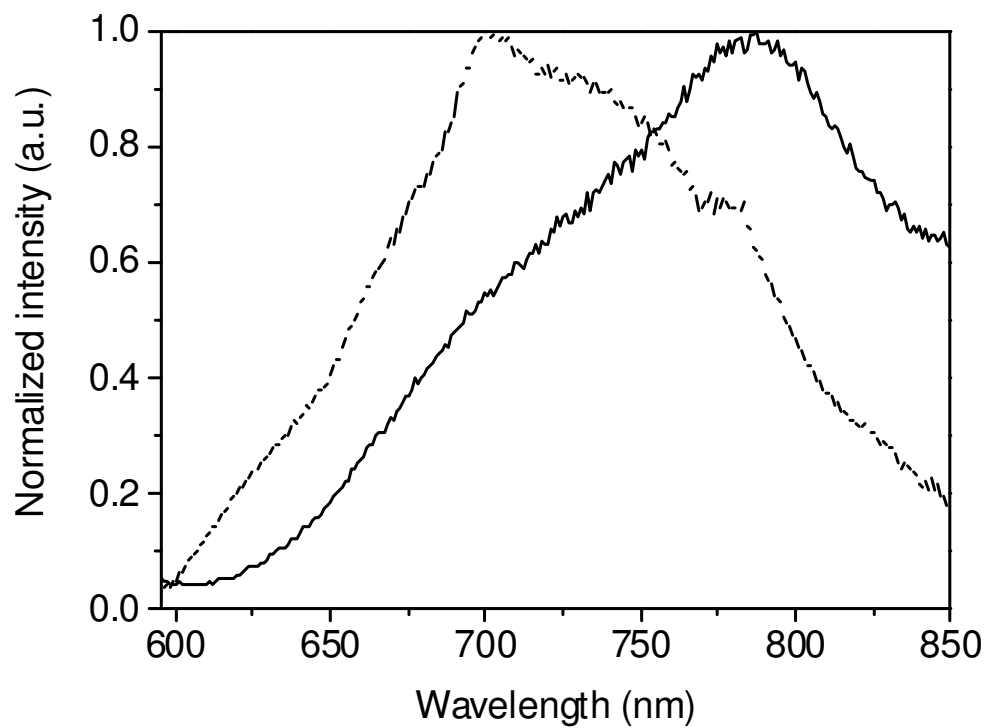
CN-PPV (**1** or **3**) was dissolved in chlorobenzene at 100 °C. The substrates and glass pipettes were heated to approximately 130 °C in an oven prior to the casting. Spinning was started immediately after the hot chlorobenzene solution (100 °C) was dropped on the hot substrate using the hot glass pipettes. Spinning ratio was between 800 and 2500 rpm. For UV-Vis and fluorescence measurements, glass substrates were used. For PYS and SCLC measurements, ITO substrates were used. Film thickness was measured by surface profilometry (Dektak 6M).

### **Cyclic voltammetry<sup>15</sup>**

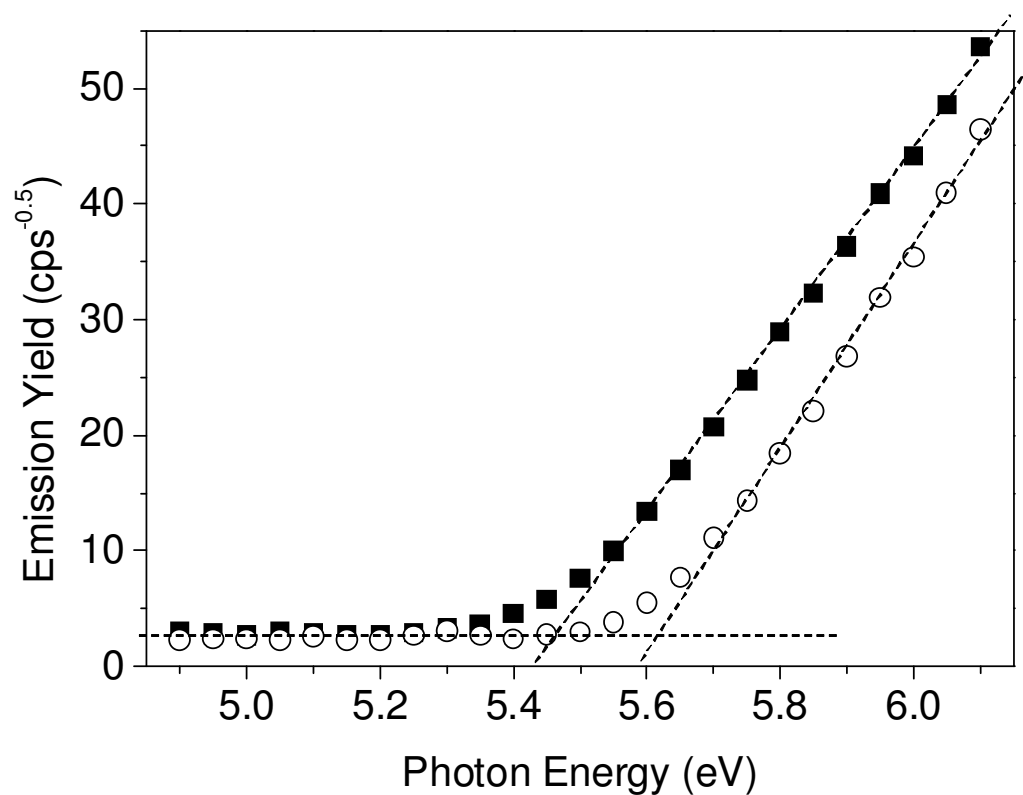
Cyclic voltammograms (CVs) were recorded on HSV-100 (Hokuto Denkou) potentiostat using Pt electrodes at a scan rate of 50 mV/s and an Ag/Ag<sup>+</sup> (0.10 M of AgNO<sub>3</sub> in acetonitrile) reference electrode in an anhydrous and nitrogen-saturated solution of 0.1 M of Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile. The oxidation half potential of ferrocene (+0.45 V vs. SCE) was used as a standard. HOMO and LUMO energy levels were determined from the oxidation and the reduction onsets of the third scan from CV data, respectively, taking into account the SCE level at -4.7 eV.<sup>1</sup>



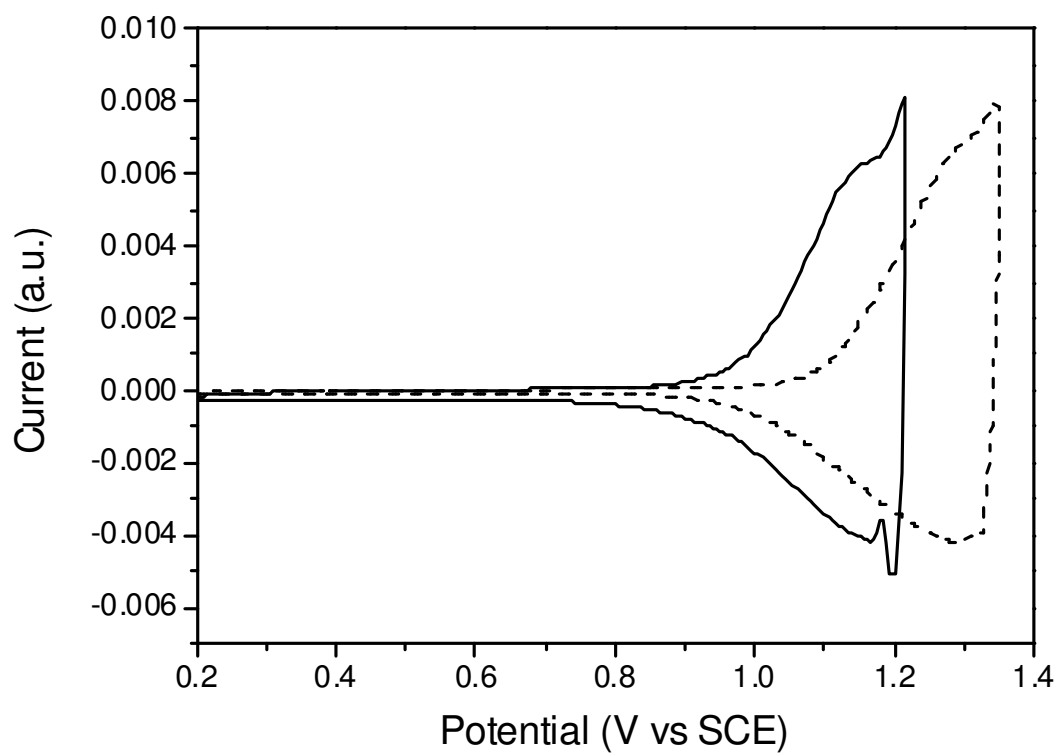
**Figure S4.** Fluorescence spectra of the solutions of regiorandom (dashed line) and regioregular (solid line) CN-PPVs in CHCl<sub>3</sub> excited at 455 nm. Emission maxima were at 556 nm for regiorandom **1** and 567 nm for regioregular **3**.



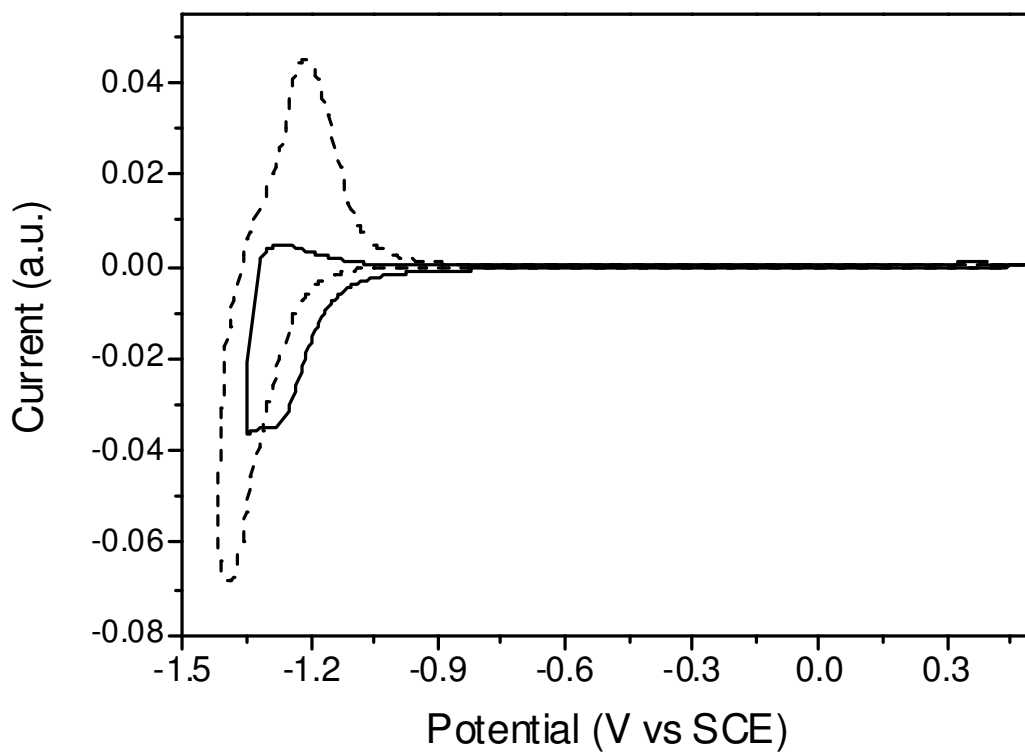
**Figure S5.** Fluorescence spectra of thin films of regiorandom (dashed line) and regioregular (solid line) CN-PPVs, excited at the absorption maxima. The film thickness was 170 nm and 75 nm for **1** and **3**, respectively. Emission maxima were at 701 and 787 nm for **1** and **3**, respectively.



**Figure S6.** Photoelectron yield spectra (PYS) of regiorandom (open circle) and regioregular (filled square) CN-PPVs films on ITO substrates. Ionization potentials are estimated from the onsets as 5.61 eV and 5.46 eV for regiorandom and regioregular CN-PPVs, respectively.



**Figure S7.** Cyclic voltammograms of regioregular (solid line) and regiorandom CN-PPV (dashed line) films on a Pt wire in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/MeCN at 50 mV s<sup>-1</sup>. HOMO levels are estimated from the onset potentials of oxidation peaks as -5.69 eV (regioregular **3**) and -5.81 eV (regiorandom **1**) assuming the SCE level at -4.7 eV.<sup>1</sup>



**Figure S8.** Cyclic voltammograms of regioregular (solid line) and regiorandom CN-PPV (dashed line) films on a Pt wire in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/MeCN at 50 mV s<sup>-1</sup>. LUMO levels are estimated from the onset potentials of reduction peaks as -3.54 eV (regioregular **3**) and -3.49 eV (regiorandom **1**), assuming the SCE level at -4.7 eV.<sup>1</sup>



## Mobility measurement by space-charge limited current (SCLC)

### Electron-only device

Electron mobility was estimated from the measurements on the current-voltage behavior of “electron-only” devices. In this type of samples a polymer layer is sandwiched between two electrodes of low work function materials. Ca electrode (work function 2.8 eV) was used for the electron injection.<sup>16, 17</sup> Since LUMO levels of CN-PPVs were determined as -3.5 eV by CV, an ohmic-contact should be achieved between Ca electrode and the polymer layer for the electron injection. For the counter electrode, ITO electrode coated with Cs<sub>2</sub>CO<sub>3</sub> was used. It has been reported that Cs<sub>2</sub>CO<sub>3</sub> makes strong dipole on the ITO, and thus the work function of this electrode becomes as small as c.a. 3.5 eV.<sup>18</sup> The low work functions of both electrodes relative to the HOMO levels of CN-PPVs ensure that hole injection is prohibited since there are energy offsets of approximately 2.0 eV existing at the interfaces. Therefore, the injected and transported carriers in the diode configuration adopted here should be only electrons.

### Experimental

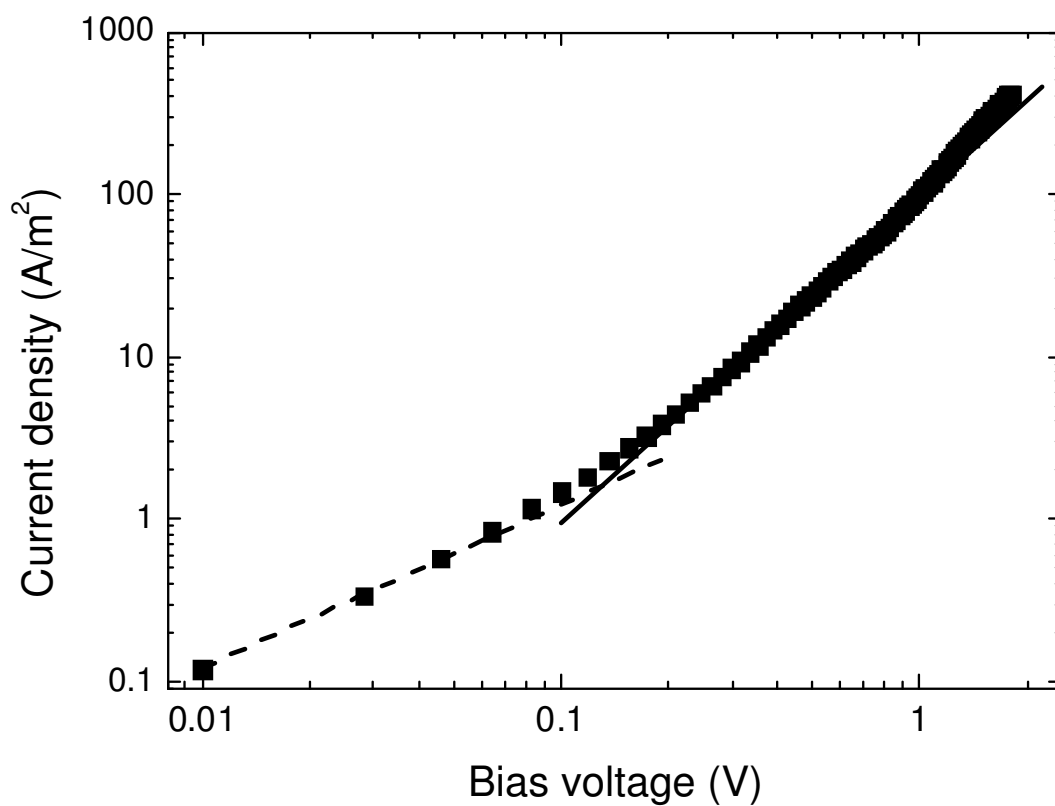
For the device fabrication, the ITO substrates first underwent routine cleaning procedures, including sonication in detergent followed by deionized water, acetone, and isopropyl alcohol, and finally treatment with UV-O<sub>3</sub>. After the cleaning, Cs<sub>2</sub>CO<sub>3</sub> dissolved in 2-ethoxyethanol (0.2 wt %) was spin-coated on the ITO at 2000 rpm. The ITO substrates and glass pipettes were heated to around 130 °C in an oven. The regiorandom CN-PPV was dissolved in chlorobenzene (14 mg/mL) and filtered through a PTFE filter (pore size: 200 nm) at 55 °C. The regioregular CN-PPV was dissolved in chlorobenzene (6 mg/mL) at above 100 °C. Spinning was started immediately after the hot solution (100 °C) was casted onto the hot substrates. Variation of the film thickness was from 50 to 150 nm. Onto the films, Ca was evaporated at the rate of 0.3~0.6 Å/s, followed by Al at 0.3~1.0 Å/s under vacuum (10<sup>-4</sup> Pa). The thicknesses of evaporated metals were 15 and 30 nm for Ca and Al, respectively. The active area of each device was 5 × 3 mm<sup>2</sup>. The prepared devices were transferred thorough N<sub>2</sub> atmosphere, and current-voltage behavior was measured with Keithley 6430 in vacuo (10<sup>-5</sup> Torr) at 19 °C.

## Analysis<sup>15</sup>

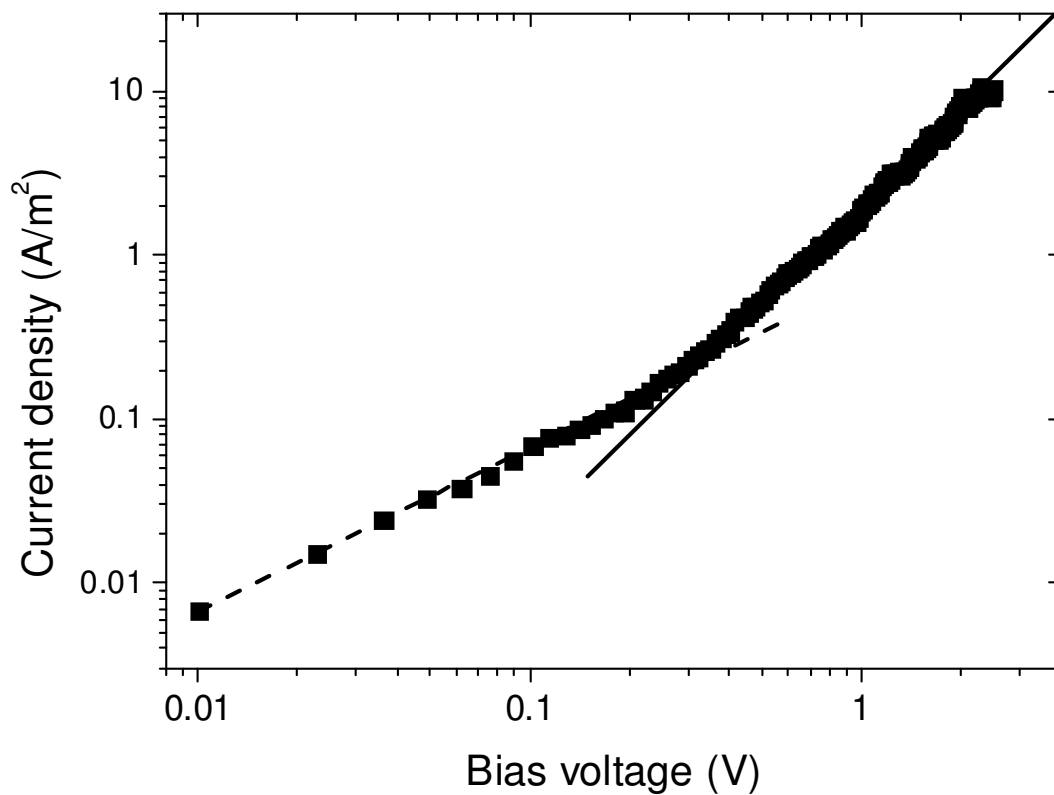
We used a simple SCLC model assuming field-independent mobility, which is expressed by the Child's law<sup>19</sup>:

$$J = \frac{9}{8} \epsilon \mu_e \frac{V^2}{d^3}$$

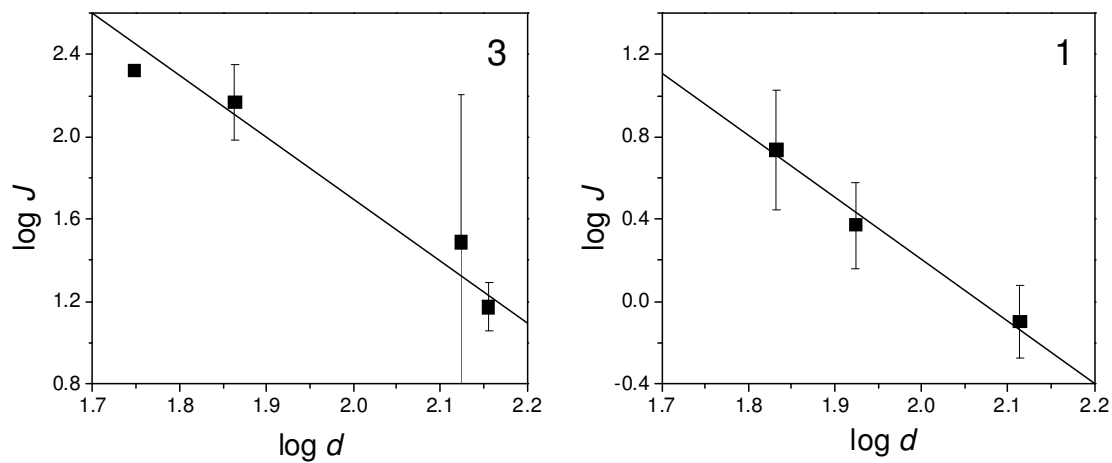
where  $J$  is the current density,  $\epsilon = \epsilon_0 \epsilon_r$  is the permittivity of the polymer,  $\mu_e$  is the electron mobility, and  $d$  is the film thickness. SCLC regions in double logarithm plots of the  $J$ - $V$  under dark were linearly fitted with a slope of 2, shown in Figures S9 and S10. The SCLC regions were between 0.2 and 2 V depending on the thickness of the films. Assuming  $\epsilon_r = 3$ , electron mobility  $\mu_e$  was calculated for each film by this fitting. Validity of the SCLC regions was confirmed by the thickness dependence of the current density at the same voltage (1.0 V) shown in Figure S11, where the slopes of the lines were fitted to -3. The plot shows that  $J$  is proportional to  $d^{-3}$  in the SCLC regions, indicating the validity of the measurements.



**Figure S9.**  $J$ - $V$  characteristics of electron-only device (ITO/ $\text{Cs}_2\text{CO}_3$ /Regioregular CN-PPV/Ca/Al) with thickness  $d = 73$  nm (filled squares). The dashed line with a slope of 1 was fitted to indicate the ohmic region. The solid line with a slope of 2 corresponds to the SCLC region.



**Figure S10.**  $J$ - $V$  characteristics of electron-only device (ITO/Cs<sub>2</sub>CO<sub>3</sub>/Regiorandom CN-PPV/Ca/Al) with thickness  $d = 83$  nm (filled squares). The dashed line with a slope of 1 was fitted to indicate the ohmic region. The solid line with a slope of 2 corresponds to the SCLC region.



**Figure S11.** Thickness dependence of the current density at the voltage of 1.0 V in the electron-only devices of CN-PPVs. (left: regioregular **3**; right: regiorandom **1**). The lines with the slope of -3 were fitted to indicate the dependence of  $J$  proportional to  $d^{-3}$ . The units for  $J$  and  $d$  are  $\text{A/m}^2$  and nm, respectively.

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