Supporting Information

Effects of the Terminal Structure, Purity, and Molecular Weight of an Amorphous Conjugated Polymer on Its Photovoltaic Characteristics

Junpei Kuwabara[†], Takeshi Yasuda[‡], Naoto Takase[†], Takaki Kanbara*[,†]

[†]Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8573, Japan.

[‡]Organic Thin-Film Solar Cells Group, Photovoltaic Materials Unit, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan

*E-mail kanbara@ims.tsukuba.ac.jp (T.K.)

Synthesis of the polymer used for evaluating purification methods.[1]

A mixture of $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol), 1-adamantanecarboxylic acid (27.1 mg, 0.15 mmol), K_2CO_3 (173 mg, 1.3 mmol), 2,7-dibromo-9,9-dioctylfluorene (274 mg, 0.50 mmol), 3,4-ethylenedioxythiophene (53.4 μL, 0.50 mmol) was stirred in anhydrous dimethylacetamide (1.67 mL) for 6 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred overnight at room temperature. The precipitate was separated by filtration and washed with 0.1 M HCl solution, distilled water, MeOH, and hexane. This preparation procedure was repeated three times. The crude roducts from four experiments were conbined and dissolved in $CHCl_3$. The solution was filtered to remove insoluble material. A reprecipitation from $CHCl_3$/MeOH gave PEDOTF as pale yellow solid (1.01 g, 95% yield). M_n = 40500, M_w/M_n = 3.94. Anal. Calcd. for $(C_{35}H_{44}O_2S)_n$: C, 79.50; H, 8.39, Found: C, 79.03; H, 8.53.

The synthesized polymer was used in evaluating purification methods for removal of Pd.

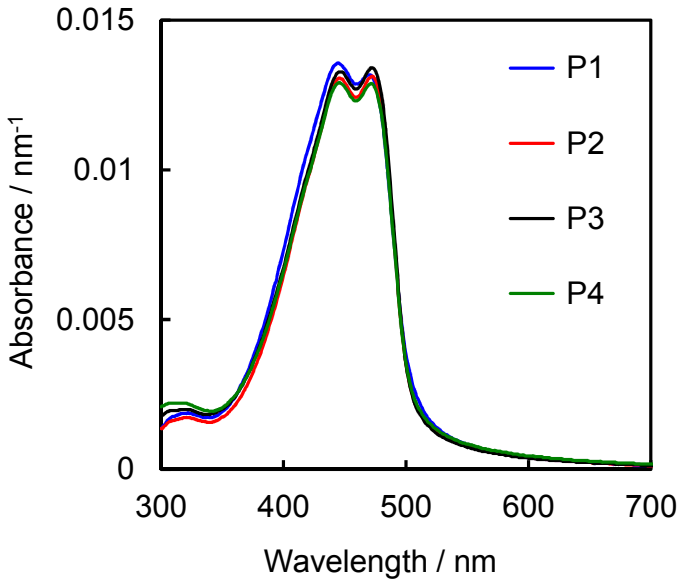

Figure S-1. UV-Vis absorption spectra of the polymers in the thin-film state.

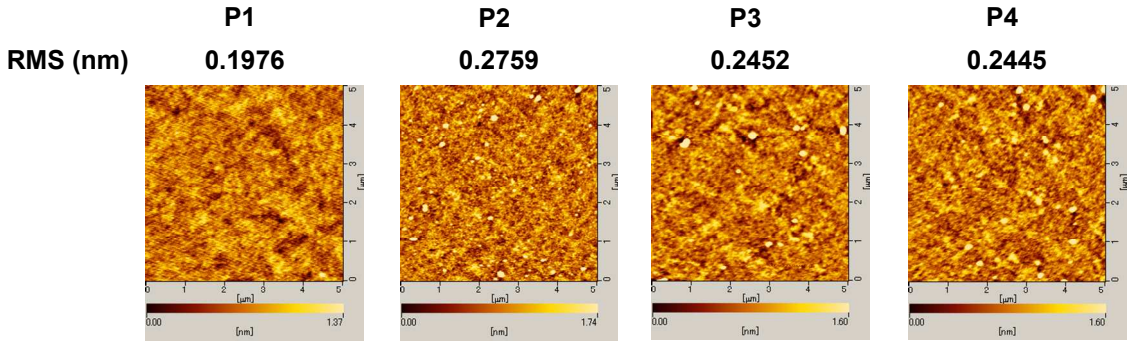

Figure S-2. AFM images (5 × 5 μm^2) of **P1-P4**.

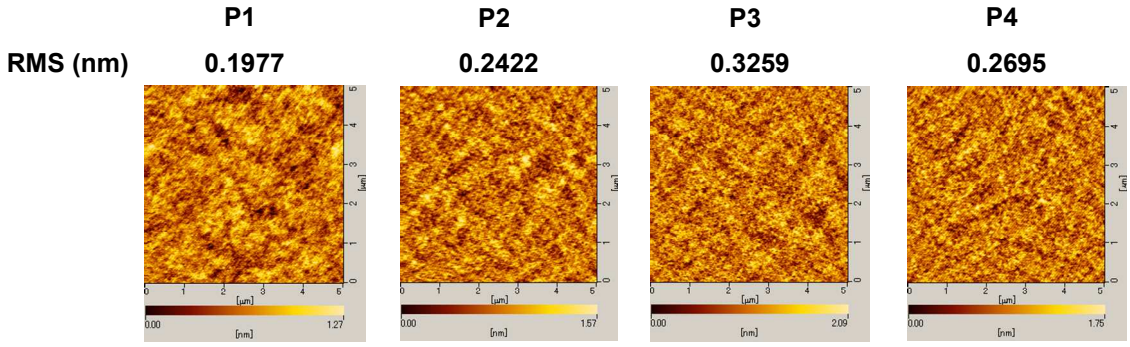

Figure S-3. AFM images (5 × 5 μm^2) of **P1-P4**:$PC_{71}BM$ (1:4).

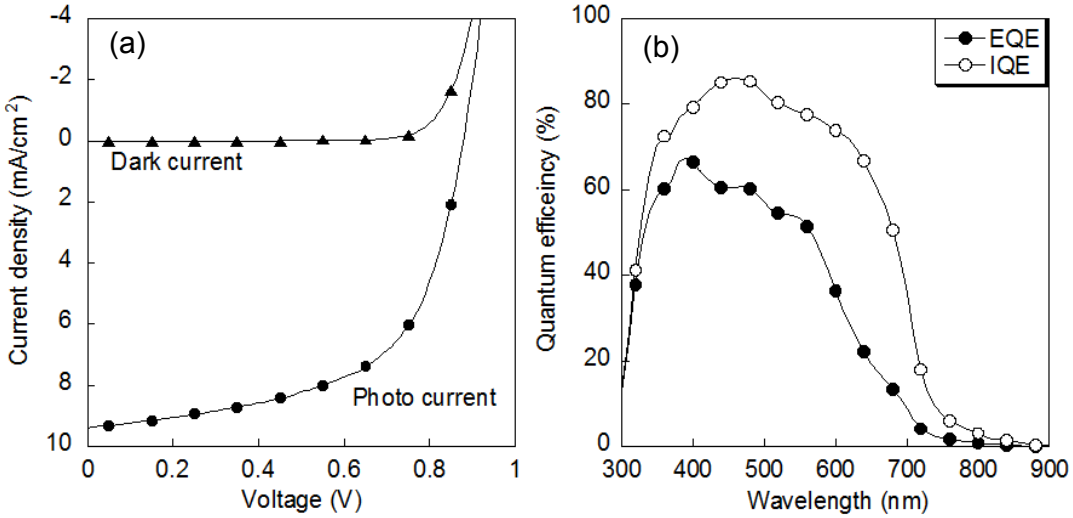

Figure S-4. Typical OPV characteristics for **P3** (a) Current density-voltage characteristics of **P3**:$PC_{71}BM$ (1:4) BHJ solar cells under AM1.5G illumination. (b) The external quantum efficiency (EQE) and the internal quantum efficiency (IQE) of the corresponding cells. Thickness = 105 nm, J_{sc} = 9.362 mA cm^{-2}, V_{oc} = 0.878 V, FF = 0.586, PCE = 4.819 %.

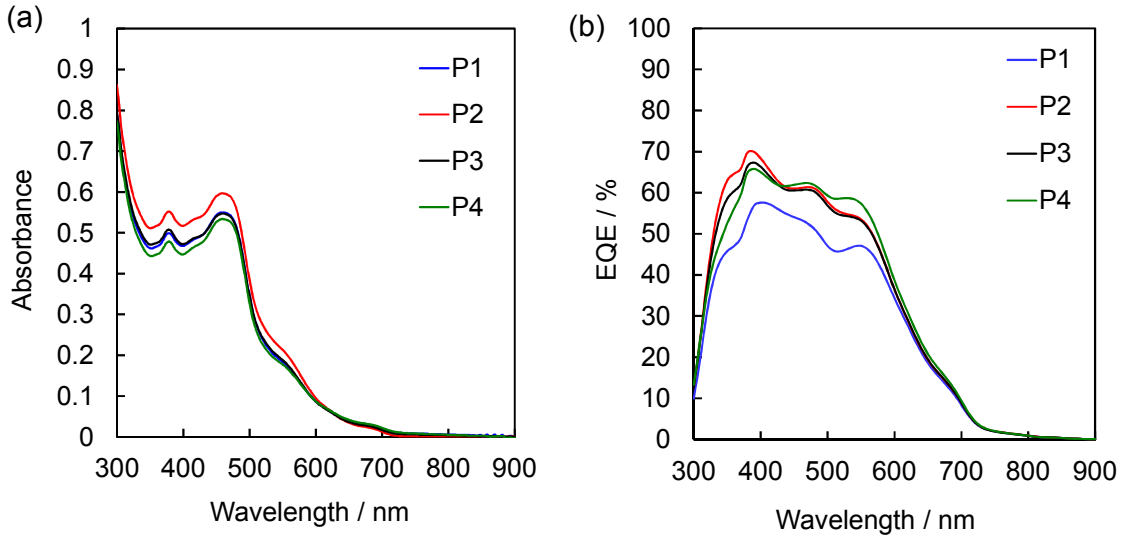

Figure S-5. (a) Absorption spectra of the BHJ layer. (b) The external quantum efficiency (EQE) of the cells with **P1**–**P4**.

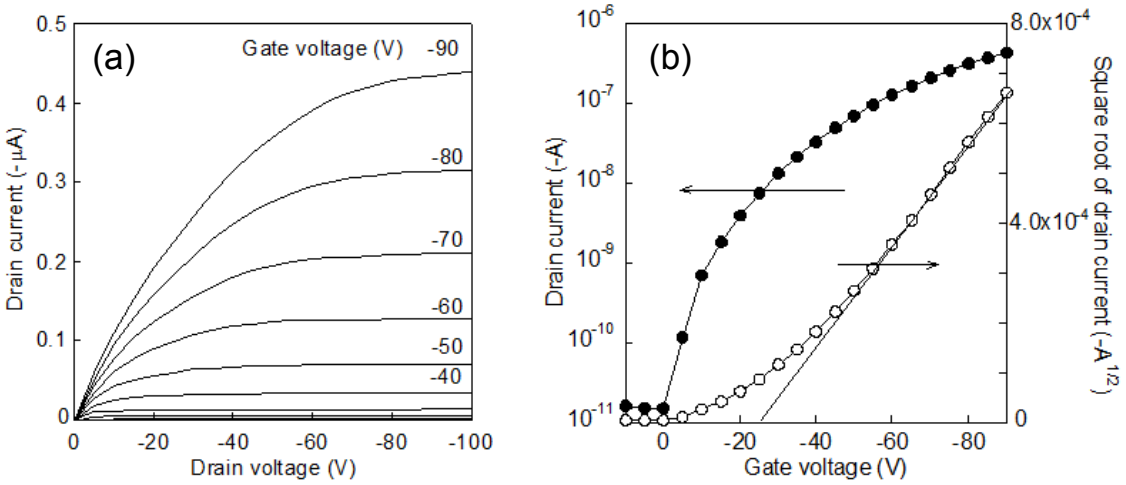

Figure S-6. Typical (a) output and (b) transfer characteristics (measured at drain voltage of −100 V) of the top-contact OFETs for **P3** films spin-coated from *o*-DCB solution and annealed for 10 min at 110 °C. $\mu_h = 1.30 \times 10^{-3}$ $cm^2V^{-1}s^{-1}$, on/off ratio = 2.93×10^4, V_{th} = -25.2 V.

Table S-1. Device characteristics of BHJ OPVs based on Polymer:$PC_{71}BM$ (1:4)

Polymer	**Thickness / nm**	J_{sc} / mAcm^{-2}	V_{oc} / V	***FF***	***PCE*** / %
P1	94	8.117	0.808	0.468	3.073
P1	94	7.801	0.792	0.449	2.778
P1	94	7.924	0.791	0.452	2.833
P1	96	8.853	0.743	0.415	2.739
Ave	95	8.2±0.5	0.78±0.03	0.45±0.02	2.9±0.1
P2	113	9.421	0.878	0.565	4.684
P2	113	9.622	0.874	0.558	4.700
P2	113	9.206	0.878	0.573	4.640
P2	113	9.343	0.873	0.566	4.624
Ave	113	9.4±0.2	0.876±0.003	0.566±0.006	4.66±0.04
P3	105	9.398	0.874	0.549	4.517
P3	105	9.362	0.878	0.586	4.819
P3	105	9.370	0.877	0.586	4.822
P3	105	9.332	0.896	0.574	4.796
P3	105	9.201	0.886	0.557	4.549
Ave	105	9.33±0.08	0.882±0.009	0.57±0.02	4.7±0.2
P4	98	9.695	0.856	0.570	4.739
P4	98	9.629	0.848	0.565	4.617
P4	98	9.403	0.846	0.551	4.384
P4	98	9.093	0.867	0.568	4.483
Ave	98	9.5±0.3	0.85±0.01	0.564±0.009	4.6±0.2

Table S-2. OPV characteristics of the devices with different polydispersity [a]

Polymer	M_n	M_w/M_n	**Thickness / nm**	J_{sc} **/ mA cm^{-2}**	V_{oc} **/ V**	***FF***	***PCE* / %**
P2	40300	2.17	113	9.4 ± 0.2	0.876 ± 0.003	0.566 ± 0.006	4.66 ± 0.04
P2′ [b]	54000	3.75	111	10.1 ± 0.2	0.85 ± 0.01	0.55 ± 0.02	4.7 ± 0.1

[a] The average values with standard deviations were calculated from the results of four or more OPV samples. OPV configuration: ITO/PEDOT:PSS (40 nm)/**P2 or P2′**:$PC_{71}BM$ (1:4)/LiF (1 nm)/Al (80 nm). [b] The amount of Br was determined to be less than 0.2 %. The amount of Pd residue was determined to be 184 ppm.

Reference

(1) Yamazaki, K.; Kuwabara, J.; Kanbara, T. Detailed Optimization of Polycondensation Reaction via Direct C–H Arylation of Ethylenedioxythiophene. *Macromol. Rapid Commun.* **2013**, *34*, 69.