Supporting Information

High-efficiency Non-fullerene Polymer Solar Cell Fabricated by Simple Process Using New Conjugated Terpolymers

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Experimental

Materials

All starting reagents were purchased from Tokyo Chemical Industry, Sigma-Aldrich, and Acros Organics. The reagent-grade solvents used in this study were freshly dried using standard methods. ITIC, monomers 1–3, and copolymer, P1 was synthesized according to literature.^{1–4}

General synthetic procedure for the terpolymers

Monomer 1 (0.2 mmol), monomer 2 (0.15 to 0.05 mmol), and monomer 3 (0.05 to 0.15 mmol) were dissolved in dry toluene (10 mL) and DMF (1 mL) and then degassed with nitrogen for 10 min. Subsequently, a catalyst, tris(dibenzylideneacetone)dipalladium(0) (9.2 mg, 10.0 μ mol), and tri(*o*-tolyl)phosphine (12.2 mg, 40.0 μ mol) were added to the mother solution before heating to 100 °C for a specific time under nitrogen atmosphere. The solution was cooled to room temperature and poured into 300 mL of methanol to obtain polymer precipitates. The crude product was purified by Soxhlet extraction with acetone, hexane, and chloroform, successively. The chloroform fraction was evaporated and the polymer solution was reprecipitated using methanol, filtered, and dried to obtain the target polymer.

Synthesis of P2

P2 was synthesized with monomer 1 (0.181 g, 0.2 mmol), monomer 2 (0.045 g, 0.15 mmol), and monomer 3 (0.015 g, 0.05 mmol) by following the general procedure. The reaction time was 24 h, and the final product, a red powder, was obtained in 84% yield. (M_n = 24.9 kDa, PDI = 2.69). Elemental Anal. calcd for C₂₃₈H₂₆₈O₈S₂₉: C, 68.28; H, 6.45; O, 3.06; S, 22.21. Found: C, 68.21; H, 6.40; O, 3.08; S, 22.17.

Synthesis of P3

P3 was synthesized with monomer **1** (0.181 g, 0.2 mmol), monomer **2** (0.03 g, 0.10 mmol), and monomer **3** (0.077 g, 0.10 mmol) by following the general procedure. The reaction time was 24 h, and the final product, a purple powder, was obtained in 83% yield. ($M_n = 24.4 \text{ kDa}$, PDI = 3.52). Elemental Anal. calcd for C₁₀₆H₁₂₀O₄S₁₃: C, 67.91; H, 6.45; O, 3.41; S, 22.23. Found: C, 67.88; H, 6.41; O, 3.35; S, 22.25.

Synthesis of P4

P4 was synthesized with monomer 1 (0.181, 0.2 mmol), monomer 2 (0.015 g, 0.05 mmol), and monomer 3 (0.115 g, 0.15 mmol) by following the general procedure. The reaction time was 9 h, and the final product, a dark purple powder, was obtained in 86% yield. ($M_n = 22.9$ kDa, PDI = 2.84). Elemental Anal. calcd for C₁₈₈H₂₁₂O₄S₅: C, 67.66; H, 6.40; O, 3.84; S, 22.10. Found: C, 67.57; H, 6.39; O, 3.88; S, 22.07.

Synthesis of P5

P5 was synthesized with monomer **1** (0.181, 0.2 mmol) and monomer **3** (0.123 g, 0.16 mmol) by following the general synthetic procedure described as above. The reaction time was 8 h, and the final product, a dark blue powder, was obtained in 72 % yield. ($M_n = 20.5$ kDa, PDI = 4.13).

Instrumentation

¹H NMR spectra were acquired using a Varian Mercury Bruker 500 MHz spectrometer. Elemental analyses were performed using an EA1112 elemental analyzer to determine the C, H, N, and S contents. The absorption spectra were recorded on a UV-Vis absorption spectrophotometer (HP 8453, photodiode array). Cyclic voltammetry (CV) experiments were performed using an eDAQ EA161 potentiostat with Ag/AgCl and Pt wire (0.5 mm in diameter) as the reference and counter electrodes, respectively. The working electrodes were obtained by coating the prepared polymer films onto Pt plates. The electrolyte solution

consisted of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) in dry acetonitrile. The morphology of each polymer film surface was analyzed by atomic force microscopy (AFM; Advanced Scanning Probe Microscope, XE-100, PSIA). The internal morphologies of the blend films were investigated by transmission electron microscopy (TEM; Tecnai G2 F30, FEI Inc.) at an accelerating voltage of 300 kV. Grazing-incidence wide-angle X-ray diffraction (GIWAXD) measurements were carried out at the PLS-II 9A ultra-small-angle Xray scattering beamline at the Pohang Accelerator Laboratory (energy = 11.04 keV, wavelength (λ) = 1.126 Å, 2 Θ = 0–20°). The parameters q_{xy} and q_z represent the components of the scattering vectors parallel and perpendicular to the film surface, respectively.

Fabrication of non-fullerene polymer solar cells

Bulk heterojunction (BHJ) polymer solar cells (PSCs) were fabricated with an inverted device configuration (indium tin oxide (ITO)/ZnO(30 nm)/polymer:ITIC (85–95 nm)/MoO₃(10 nm)/Ag(100 nm)). A thin layer of ZnO was fabricated on the surface of ITO-patterned glass, which was treated with UV-ozone for 20 min. After annealing the ZnO layer thermally at 200 °C for 1 h, the active layer was prepared on top of the ZnO layer by spin-coating different compositions of the blended solution of polymer:ITIC in chlorobenzene with or without 1,8-diiodooctane (DIO) as the solvent additive. In addition, the active layer of PSC was annealed at different temperature ranges when necessary. The electrode was then thermally evaporated to form a 10 nm MoO₃ layer and a 100 nm Ag layer (area of photoactive region = 0.04 cm^2).

The current density-voltage (J–V) characteristics under illumination of AM 1.5G (100 mW cm⁻²) supplied by a solar simulator (Oriel, 1000 W) were investigated using a Keithley 2400 source meter. The required light intensity was adjusted using AM 1.5 filters (Oriel) and neutral density filters. The incident light intensity used to irradiate the PSC was measured with a calibrated broadband optical power meter (Spectra Physics, Model 404).

Space charge-limited current method for measuring charge carrier mobility

In order to investigate the hole and electron charge transport properties in the blend film, a multilayer device was fabricated and SCLC experiments were conducted.⁵ The configuration of the hole-only device (HOD) was ITO/poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT: PSS)/active layer (thickness = 110 ± 5 nm)/Au, while that of the electron-only device (EOD) was ITO/ZnO/active layer/LiF/Al.

The active layers of HOD and EOD were fabricated under the same conditions as those adopted for the fabrication of the PSC that exhibited optimum performance. Au or LiF/Al was deposited on the active layer in the vacuum state. The hole and electron carrier mobilities were determined using the modified Mott-Gurney equation, $J = (9/8)\varepsilon_0\varepsilon_r\mu(V^2/L^3)$, where J is the current density, μ is the mobility, V is the applied voltage, and the device thickness, L, is defined. In this equation, ε_0 and ε_r refer to the vacuum and relative permittivities, respectively.

In-situ Raman Spectroscopy

A home-built Raman spectrometer was used to record the Raman spectra of the polymers. With the information of the beam size, the energy density of the actinic light sources was determined to be 50 Sun condition ($1 \text{ Sun} = 1 \text{ kW m}^{-2}$) at the sample position. To monitor the degradation behavior, the polymer films were exposed under ambient conditions (40% humidity, 21 °C). In contrast, when the Raman spectra was measured, the polymer films were in Ar purging condition to prevent the polymer from further degradation owing to the probe beam. The wavelengths of the actinic light source and probe were 532 nm (GLK 32150TS, LASOS) and 473 nm (BLK73100TS, LASOS), respectively. The intensity of the probe beam was ~10 mW at the light source and the light exposure time was 1 s.



Figure S1. Design strategy for the terpolymer synthesized in this study.



Figure S2. UV-Vis absorption spectra of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, and (e) **P5** in diluted chlorobenzene solutions. The spectral change was monitored at different temperatures. (f) Photographs of **P1–P5** solutions at 20 and 100 °C.



Figure S3. (a) *J-V* curves and (b) EQE spectra of the **P3**:ITIC-based PSC. (i) As-cast blend film without 1,8-diiodooctane (DIO), (ii) thermally annealed blend film without DIO ($T_{annealing} = 140 \text{ °C}$), and (iii) thermally annealed blend film with 0.25% DIO ($T_{annealing} = 140 \text{ °C}$).

P3 :ITIC ratio (wt%)	Additive	Annealing Temp. (°C)	V _{oc} (V)	$J_{\rm sc}$ (mA cm ⁻²)	FF (%)	PCE (%)
1.5:1	-	-	0.95	16.32	60.85	9.43
1.2:1	-	-	0.94	16.97	61.70	9.84
1:1	-	-	0.94	17.18	63.52	10.26
1:1.2	-	-	0.93	17.01	62.96	9.96
1:1.5	-	-	0.92	17.07	61.44	9.65
1:1	-	120	0.92	16.84	63.36	9.82
1:1	-	130	0.92	17.19	64.91	10.27
1:1	-	140	0.91	17.49	66.53	10.59
1:1	-	160	0.89	15.12	51.63	6.95
1:1	0.25% DIO	140	0.92	17.22	69.56	11.02
1:1	0.5% DIO	140	0.91	17.15	67.77	10.58
1:1	1.0% DIO	140	0.92	16.65	68.10	10.43
1:1	0.25% DPE	140	0.91	16.90	65.01	10.00

Table S1. Device parameters of **P3**:ITIC-based polymer solar cells (PSCs) prepared using chlorobenzene solutions and fabricated under various process conditions.

*DIO: 1,8-diiodooctane and DPE: diphenyl ether

Р	Additive	Annealing Temp. (°C)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
Р2		-	0.95	15.76	59.76	8.95
	-	140	0.94	16.09	63.28	9.57
	0.25% DPE	140	0.93	16.25	63.66	9.62
P3	-	-	0.94	17.18	63.52	10.26
	-	140	0.91	17.49	66.53	10.59
	0.25% DIO	140	0.92	17.22	69.56	11.02
P4	-	-	0.90	17.19	61.77	9.56
	-	140	0.89	15.93	67.63	9.59
	0.25% DIO	140	0.87	16.52	62.07	8.92

Table S2. Device parameters of terpolymer:ITIC (1:1)-based PSCs prepared usingchlorobenzene solutions and fabricated under various process conditions.



Figure S4. Space charge-limited J-V characteristics of all the blend films under dark conditions for hole-only and electron-only devices of **P1**–**P5** blend films with ITIC. The active layer was made of the as-cast blend film without DIO.

Table S3. Measured electron and hole mobilities of space charge-limited current (SCLC) devices. The active layers were made with as-cast blend films of the five polymers and ITIC.

Active layer	$\mu_{\rm h}({\rm cm}^2{ m V}^{-1}{ m s}^{-1})$	$\mu_{\rm e} ({\rm cm}^2{ m V}^{-1}{ m s}^{-1})$	$\mu_{\rm h}/\mu_{\rm e}$
P1:ITIC	2.19×10^{-5}	1.65×10^{-6}	13.27
P2:ITIC	2.72×10^{-5}	3.49×10^{-6}	7.79
P3:ITIC	5.25×10^{-5}	1.56×10^{-5}	3.37
P4:ITIC	8.01×10^{-5}	1.21×10^{-5}	6.62
P5:ITIC	8.71 × 10 ⁻⁵	$1.79 imes 10^{-5}$	4.84



Figure S5. 2D Grazing incidence wide-angle X-ray diffraction (GIWAXD) patterns of the as-cast neat films of polymers (a). (f) Out-of-plane and (g) in-plane X-ray diffraction profiles of the as-cast neat films of the five polymers.

Polymer	$q_{ m xy} \ ({ m \AA}^{-1})$	d ₍₁₀₀₎ -spacing (Å)	FWHM (Å ⁻¹)
P1	0.2923	21.49	0.1424
P2	0.2936	21.39	0.1285
Р3	0.2926	21.47	0.1185
P4	0.2882	21.79	0.1144
P5	0.2972	21.14	0.1039

Table S5. Peak assignments for the (100) diffraction peak in the in-plane X-ray diffraction (XRD) profiles of the as-cast neat films of **P1–P5**.



Figure S6. 2D GIWAXD line-cuts of the blend films of **P1–P5** with ITIC (a). (b) Out-of-plane and (c) in-plane profiles of the blend films.

Blend film	$q_{xy} \ (m \AA^{-1})$	d ₍₁₀₀₎ -spacing (Å)	FWHM (Å ⁻¹)
P1:ITIC	0.3296	19.06	0.1237
P2:ITIC	0.3203	19.61	0.1342
P3:ITIC	0.3208	19.58	0.1359
P4:ITIC	0.3081	20.39	0.1260
P5:ITIC	0.3139	20.01	0.0878

Table S6. Peak assignments for the (100) diffraction peaks in the in-plane X-ray diffraction profiles of **P1–P5** blend films with ITIC.



Figure S7. Evaluation of the PSC performance stability measured under ambient conditions for up to 1056 h. The active layers in the PSCs were composed of as-cast blend films without DIO.



Figure S8. Evaluation of the PSC performance stability measured under ambient conditions for up to 1056 h. The active layers in the PSCs were composed of a thermally annealed blend film with DIO.



Figure S9. AFM height (a,c), phase (b,d) images (5 x 5 μ m), and surface profiles (e,f) of ascast **P3**:ITIC blend film (a,b,e) **P3**:ITIC blend films annealed at 140 °C with DIO (c,d,f). The films were aged under ambient conditions for up to 1056 h.



Figure S10. Evaluation of the PSC performance stability measured under continuous illumination for 1 h (AM 1.5, 100 mW cm⁻²). The active layers in the PSCs were composed of as-cast blend films without DIO.

Reference

(1) M. J. Cho, J. Seo, K. H. Kim, D. H. Choi, P. N. Prasad, *Macromol. Rapid Commun.* 2012, **33**, 146.

(2) J.-H. Kim, J. B. Park, F. Xu, D. Kim, J. Kwak, A. C. Grimsdaled, D. –H. Hwang, *Energy Environ. Sci.* 2014, 7, 4118.

(3) G. E. Park, S. Choi, S. Y. Park, D. H. Lee, M. J. Cho, D. H. Choi, *Adv. Energy Mater.*, 2017, 7, 1700566.

(4) W. Zhao, D. Qian, S. Zhang, S. Li, O. Inganäs, F. Gao, J. Hou, *Adv. Mater.* 2016, 28, 4734.

(5) Y. Shirota, H. Kageyama, Chem. Rev., 2007, 107, 953.