Supporting Information

Impact of Incorporating Nitrogen Atoms in Naphthalenediimide-Based Polymer Acceptors on the Charge Generation, Device Performance, and Stability of All-Polymer Solar Cells

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- **Materials and Synthesis**

  All chemicals were purchased from Tokyo Chemical Industry (TCI), Kanto Chemical Co. Inc., Wako Pure Chemical Industries, and Sigma Aldrich, and used as received unless otherwise stated. The polymer donor PBDB-T ($M_n = 62$ kg mol$^{-1}$ and $D = 1.9$) was purchased from 1-Materials. The monomers (4,7-bis(5-(trimethylstannyl)thiophen-2-yl)[1,2,5]thiadiazole (BTT), 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)[1,2,5]thiadiazolo[3,4-c]pyridine (PTT), and 4,7-bis(5-(tributylstannyl)thiazol-2-yl)benzo[c][1,2,5]thiadiazole (BTTz)) were synthesized following our previous report.$^1$ All the $P_A$S were polymerized by Stille coupling reaction between 4,9-dibromo-2,7-bis(2-decyldodecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (NDI2DT-Br$_2$) and benzothiadiazole (BT)-based derivative monomers (BTT, PTT, and BTTz, respectively) using chlorobenzene solvent and palladium(0)/copper(I) co-catalyst.

  **General procedure for polymerization:** NDI2DT-Br$_2$, BT-based derivative monomers, tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$), tri(o-tolyl)phosphine (P(o-tol)$_3$), and CuI were added to a 2-necked 30mL flask equipped with a magnetic bar. The flask was vacuumed for 5 min and then back filled with N$_2$ for three cycles. Subsequently, dry chlorobenzene (5 mL) was injected and the reaction mixture was stirred and heated at 120 $^\circ$C for 48 h in N$_2$. After cooling to room temperature, the reaction mixtures were precipitated into methanol (200 mL) with hydrochloric acid (1N, 10 mL) and washed by Soxhlet extraction using methanol, acetone, hexane, dichloromethane, and chlorobenzene. The polymer obtained from the chlorobenzene fraction was collected and dried under vacuum overnight.

  $P$(NDI2DT-BTT) polymers: The target polymer was obtained by Stille coupling reaction using NDI2DT-Br$_2$ (0.164 g, 0.150 mmol), BTT (0.094 g, 0.150 mmol), Pd$_2$(dba)$_3$ (0.005 g, 0.005
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mmol), P(o-tol)_3 (0.006 g, 0.02 mmol), and CuI (0.002 g, 0.01 mmol). Yield: 78%, SEC: number-average molecular weight (M_n) = 68.1 kg mol⁻¹; polydispersity (D) = 3.3. ^1^H NMR (CDCl₃, 300 MHz, ppm, 50 °C): δ = 8.89–8.78 (br), 7.15–7.10 (br), 4.15–4.03 (br), 1.95–1.35 (br), 1.45–0.95 (br), 0.90–0.75 (br).

P(NDI2DT-PTT) polymers: The target polymer was obtained by Stille coupling reaction using NDI2DT-Br₂ (0.164 g, 0.150 mmol), PTT (0.0940 g, 0.150 mmol), Pd₂(db₃a)₃ (0.005 g, 0.005 mmol), P(o-tol)_3 (0.006 g, 0.02 mmol), and CuI (0.002 g, 0.01 mmol). Yield: 75%. SEC: M_n = 61.4 kg mol⁻¹; D = 2.3. ^1^H NMR (CDCl₃, 300 MHz, ppm, 50 °C): δ = 7.69–7.50 (br), 7.10–6.80 (br), 4.26–4.02 (br), 1.90–1.31 (br), 1.21–0.91 (br), 0.88–0.75 (br).

P(NDI2DT-BTTz) polymers: The target polymer was obtained polymerized by Stille coupling reaction using NDI2DT-Br₂ (0.164 g, 0.150 mmol), BTTz (0.132 g, 0.150 mmol), Pd₂(db₃a)₃ (0.005 g, 0.005 mmol), P(o-tol)_3 (0.006 g, 0.02 mmol), and CuI (0.002 g, 0.01 mmol). Yield: 77%. SEC: M_n = 51.8 kg mol⁻¹; D = 2.6. ^1^H NMR (CDCl₃, 300 MHz, ppm, 50 °C): δ = 8.61–8.35 (br), 8.30–8.20 (br), 4.25–4.00 (br), 1.99–1.75 (br), 1.71–1.05 (br), 0.89–0.70 (br).

• Characterization

The ^1^H NMR spectra were obtained from a JEOL model AL300 (300 MHz) using CDCl₃ as a solvent. The M_n and D were determined by size exclusion chromatography (SEC) with o-dichlorobenzene (40 °C) as the eluent against polystyrene standards (JASCO GULLIVER 1500). The CV measurements were carried out in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) at a potential scan rate of 0.1 V s⁻¹. Redox potentials were internally calibrated using the ferrocene/ferrocenium (Fc/Fc⁺) redox couple (-4.8 eV). UV-vis spectra were obtained on a UV-1800 spectrophotometer (Shimadzu S-3).
Scientific Instruments). Differential scanning calorimetry (DSC) was performed on a TA Instruments Discovery DSC 25 at a heating rate of 10 °C min⁻¹ under nitrogen gas flow with scans from 25 °C to 360 °C. Photoluminescence spectra were measured on a Horiba LabRAM HR-800 spectrometer. Atomic force microscopy (Nanoman, Veeco) was used to investigate the morphology of the BHJ layer. The film thicknesses were measured by a surface profiler (Dektak-8, VEECO). Grazing incidence X-ray scattering (GIXS) measurements were performed at beamline 3C in the Pohang Accelerator Laboratory (South Korea). GIXS samples were prepared on Si wafers under the same fabrication conditions used for the optimized devices.

**Fabrication of All-Polymer Solar Cells (All-PSCs)**

The ITO glass substrates were cleaned by sonication in acetone, deionized water, and isopropyl alcohol, and dried in an oven at 80 °C for 30 min. Normal type all-PSC devices were fabricated with the structure of ITO/PEDOT:PSS/active layer/PNDIT-F3N-Br/Ag. PEDOT:PSS (40 nm) as a hole transport layer was spun on a cleaned ITO glass substrate at the rotation speed of 3000 rpm, and was dried at 150 °C for 20 min in ambient condition. The substrate was then transferred to a nitrogen glove box. The active layer solutions were prepared by dissolving PBDB-T:P₈ into chlorobenzene and heated at 80 °C overnight. The polymer concentration in the solution was 13 mg mL⁻¹ with a blend ratio of 1.5:1.0 (w/w). The active layer was then spin coated on the PEDOT:PSS layer. The resulting thicknesses of the active layers were 90–100 nm. The PNDIT-F3N-Br solution was subsequently spin coated onto the BHJ blend film at the rotation speed of 2000 rpm, producing ~ 5 nm thick layer. Then, 120 nm silver was thermally deposited on the top of the PNDIT-F3N-Br through a shadow mask in a
vacuum chamber with the high pressure below \(5 \times 10^{-6}\) Torr. The active area of the fabricated device was 0.164 cm\(^2\). The current density–voltage (\(J-V\)) curves of the devices were measured using a Keithley 2400 SMU and solar simulator (K201 LAB55, McScience), irradiating at 100 mW cm\(^{-2}\) with a 150 W Xe short-arc lamp filtered by an air mass 1.5 G filter, which satisfies the Class AAA, ASTM Standards. Light intensity was calibrated with a Si reference cell (McScience, K801S-K302). EQEs were characterized using a K3100 IQX (McScience Inc.). The devices were illuminated by monochromatic light from a xenon arc lamp (300 W) with an optical chopper (MC 2000 Thorlabs) and a monochromator (Newport). The calculated short-circuit current density (\(J_{SC}\)) values were obtained from integrating the EQE data, which show good agreement with the measured \(J_{SC}\) (within 3% mismatch).

**Space-Charge-Limited Current (SCLC) Measurements**

Hole and electron mobilities of P(NDI2DT-BTT), P(NDI2DT-PTT), and P(NDI2DT-BTTz) blend films were measured by the SCLC method using device structures of ITO/PEDOT:PSS/polymer blends/Au (hole only) and ITO/ZnO/polymer blends/LiF/Al (electron-only). The blend films were prepared as described in the device fabrication section above. A range of 0-8 V was used for the current-voltage measurements. Mobilities were calculated using the Mott-Gurney equation:

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J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu V^2 / L^3,
\]

in which \(\varepsilon_0\) is the permittivity of vacuum, \(\varepsilon_r\) is the relative dielectric constant of the active layer, \(\mu\) is the charge carrier mobility, \(V\) is the potential across the device (\(V = V_{applied} - V_{bi} - V_r\), where \(V_{bi}\) is the built-in potential and \(V_r\) is the voltage drop caused by the resistance), and \(L\) is the thickness of the blend film.
**Charge Dissociation Probability \((P(E,T))\)**

We measured the photocurrent density \((J_{ph})\) against the effective applied voltage \((V_{eff})\) for each of the devices. The photocurrent is defined as \(J_{ph} = J_L - J_D\), where \(J_L\) and \(J_D\) are the current densities under illumination and in the dark, respectively. \(V_{eff}\) is equal to \(V_0 = V_{appl}\), where \(V_0\) is the voltage when \(J_{ph} = 0\) and \(V_{appl}\) is the applied bias. The \(P(E,T)\) value under short-circuit conditions was calculated using the equation \(P(E,T) = J_{ph}/J_{ph,sat}\), where \(J_{ph,sat}\) is the saturation photocurrent density.
Figure S1. CV curves of P(NDI2DT-BTT), P(NDI2DT-PTT), and P(NDI2DT-BTTz).

Figure S2. Second cycle (a) heating and (b) cooling DSC curves of P(NDI2DT-BTT), P(NDI2DT-PTT), and P(NDI2DT-BTTz).
**Figure S3.** Frontier molecular orbitals distribution of the model compounds (a) P(NDI2DT-BTT), (b) P(NDI2DT-PTT), and (c) P(NDI2DT-BTTz).

**Figure S4.** Dihedral angle of the model compounds (a) P(NDI2DT-BTT), (b) P(NDI2DT-PTT), and (c) P(NDI2DT-BTTz).
**Figure S5.** AFM height images of (a) PBDB-T:P(NDI2DT-BTT), (b) PBDB-T:P(NDI2DT-PTT), and (c) PBDB-T:P(NDI2DT-BTTz) blend films.

**Figure S6.** 2D-GIXS images of (a) as-cast pristine films of P(NDI2DT-BTT), P(NDI2DT-PTT), and P(NDI2DT-BTTz). Line cuts of GIXS images: (b) in-plane and (c) out-of-plane.
REFERENCES