Supporting Information for

Synthesis and Application of Poly(fluorene-*alt*-naphthalene diimide) as an n-type Polymer for All-polymer Solar Cells

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Characterization ^{1}H NMR (400 MHz) spectra were measured using a JEOL Alpha FT-NMR spectrometer equipped with an Oxford superconducting magnet system. Absorption spectra were measured using a SHIMADZU spectrophotometer MPC-3100. Cyclic voltammograms (CVs) were recorded on an HSV-100 (Hokuto Denkou) potentiostat. A Pt plate coated with a thin polymer film was used as the working electrode. A Pt wire and an Ag/Ag$^+$ (0.01 M of $AgNO_3$ in acetonitrile) electrode were used as the counter and the reference electrodes (calibrated vs. Fc/Fc+), respectively. AFM measurement was carried out using a Digital Instrumental Nanoscope 31 operated in the tapping mode.

Fabrication and characterization of polymer solar cells

PSCs were constructed in the conventional sandwich structure through several steps. ITO-coated glass substrates were cleaned by ultrasonication sequentially in detergent, water, acetone and 2-propanol. After drying the substrate, PEDOT:PSS (Baytron P) was spin-coated (4000 rpm for 30 s) on ITO. The film was dried at 150 °C under N_2 atmosphere for 5 min. After cooling the substrate, a blend solution of p-type materials and n-type materials was spin-coated. The substrate was annealed at 80 °C for 30 min inside a nitrogen-filled glove box to dry the solvent completely. Then, a Ca/Al (20 nm / 60 nm) electrode was evaporated onto the substrate under high vacuum (10^{-4}-10^{-5} Pa) in an evaporation chamber (ALS Technology, H-2807 vacuum evaporation system with E-100 load lock). The photovoltaic cells without protective encapsulation were subsequently tested in air under simulated air mass (AM) 1.5 solar irradiation (100 mW/cm^2, Peccell Technologies, PCE-L11). Light intensity was adjusted by using a standard silicon solar cell with an optical filter (Bunkou Keiki, BS520). The current-voltage characteristics of the photovoltaic cells were measured using a Keithley 2400 I-V measurement system. The external quantum efficiency (EQE) of the devices was measured on a Hypermonolight System (Bunkou Keiki, SM-250F).

The configuration of the shadow mask afforded eight independent devices on each substrate, and each device has an active layer of ~0.15 cm^2. To avoid the so-called “edge effect” and evaluate the PCEs of the photovoltaic devices accurately, the “effective” area of the PSCs was defined using a metal photomask (2 mm× 3 mm) during irradiation of the simulated solar light.

Synthesis of monomers and polymers

2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic acid diimide (**monomer 1**) was synthesized according to procedures in the literature [S1]. 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (**monomer 3**) and other chemicals were purchased from Alfa, Aldrich or Wako and used without further purification.

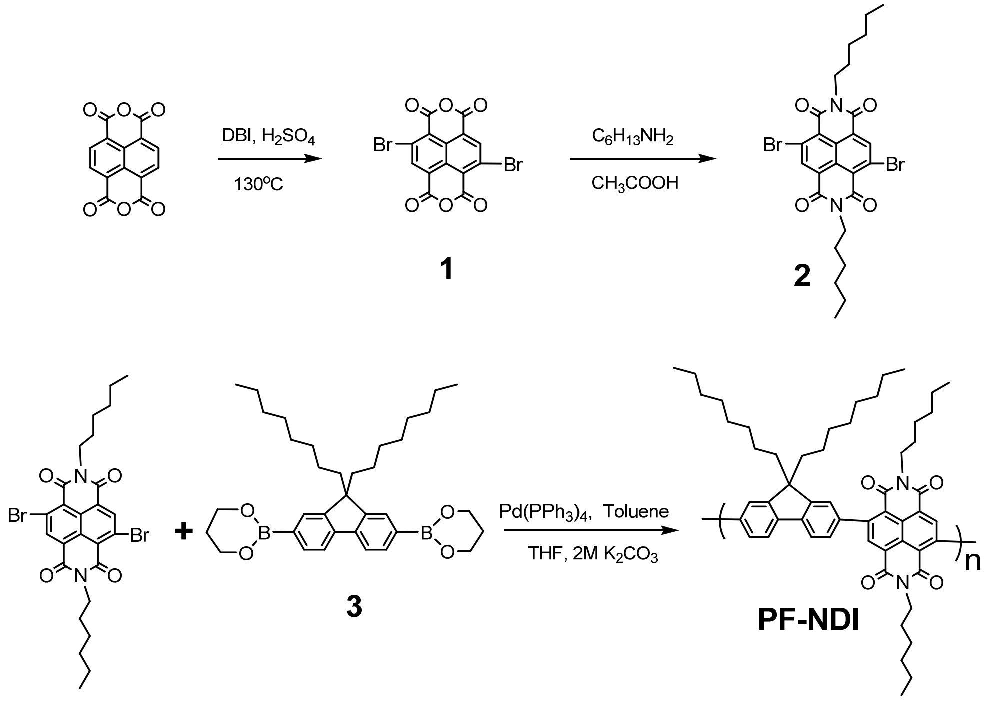
N,*N′*-Dihexyl-2,6-dibromo-1,4,5,8-naphthalene diimide (monomer 2)

Compound **1** (4.26 g, 10 mmol) and glacial acetic acid (100 mL) were added to a 200-mL double-neck round-bottom flask. Then, hexylamine (4.0 mL, 30 mmol) was added dropwise and the reaction mixture was heated at 130 °C overnight. After cooling to room temperature, the precipitate was isolated by filtration and purified by column chromatography (silica gel; eluent: chloroform/hexane, 1:1 v/v), and compound **2** was isolated as a slight yellow powder. Yield: 1.8 g (30%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) 9.00 (s, 2H), 4.19 (t, 4H), 1.76 (m, 4H), 1.5-1.3 (m, 12H), 0.90 (t, 6H).

Poly[9,9-dioctylfluorene-2,7-diyl-*alt-N,N′*-dihexyl-1,4,5,8-naphthalene diimide-2,6-diyl] (PF-NDI)

Monomer **2** (236.9 mg, 0.4 mmol) and monomer **3** (223.4 mg, 0.4 mmol) were dissolved in a mixture of THF (20 mL), toluene (5 mL) and 2 mol/L aqueous solution of K_2CO_3 (10 mL). The reaction container was purged with N_2 for 30 min to remove O_2. $Pd(PPh_3)_4$ (3%, 14 mg) was added and the mixture was heated under reflux for 48 hours. Phenylboronic acid (100 mg in 1 mL THF) was added and after 2 h, bromobenzene (1 mL) was introduced. The mixture was allowed to reflux for 2 h, cooled to room temperature and the polymer was precipitated by slowly adding the mixture into CH_3OH. The precipitates were collected by filtration, and then washed with MeOH and hexane. The solid was dissolved in $CHCl_3$ (150 mL) and passed through a column packed with alumina, Celite, and silica gel. The column was eluted with $CHCl_3$. The combined polymer solution was concentrated and was poured into MeOH. After which, the precipitates were collected and dried under vacuum overnight. Yield: 240 mg (73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm)

8.83 (s, 2H), 7.96 (m, 2H), 7.6-7.3 (m, 4H), 4.11 (br, 4H), 2.1-0.6 (m, 56H). M_n = 12.2 kg/mol; $M_w/M_n = 1.59$



Scheme S1: Synthesis routes of NDI-based monomer and the polymer.

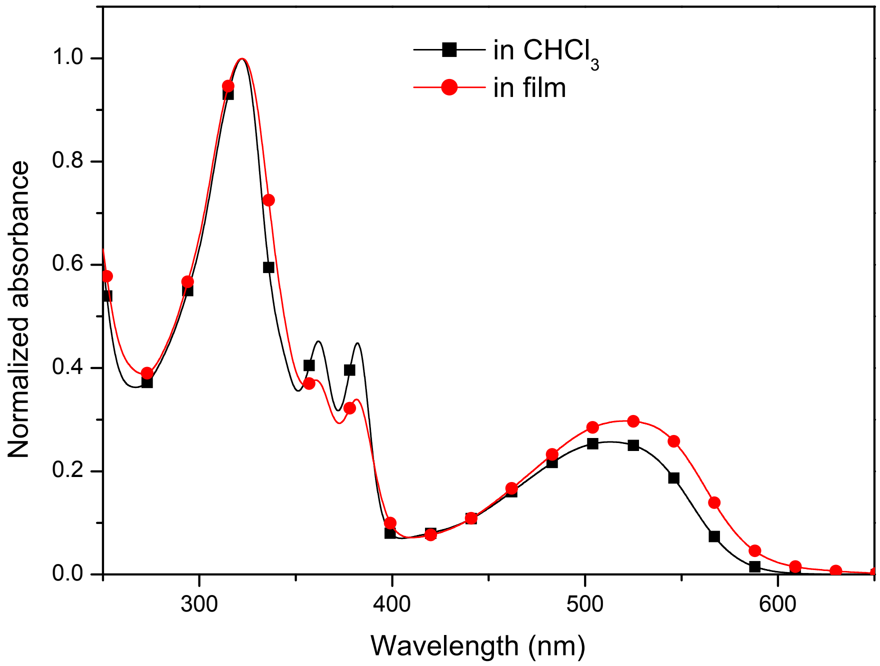


Figure S1. Normalized UV-vis absorption spectra of PF-NDI in $CHCl_3$ solution and in film on quartz plates.

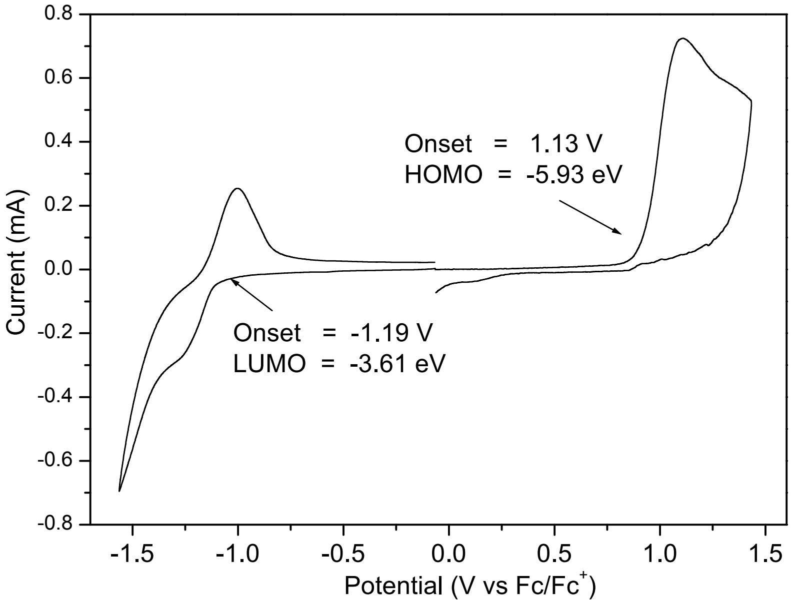


Figure S2. Cyclic voltammogram of PF-NDI film on a platinum plate in acetonitrile solution of 0.1 mol/L $[Bu_4N]PF_6$ (Bu = butyl) at scan rate of 50 mV/s.

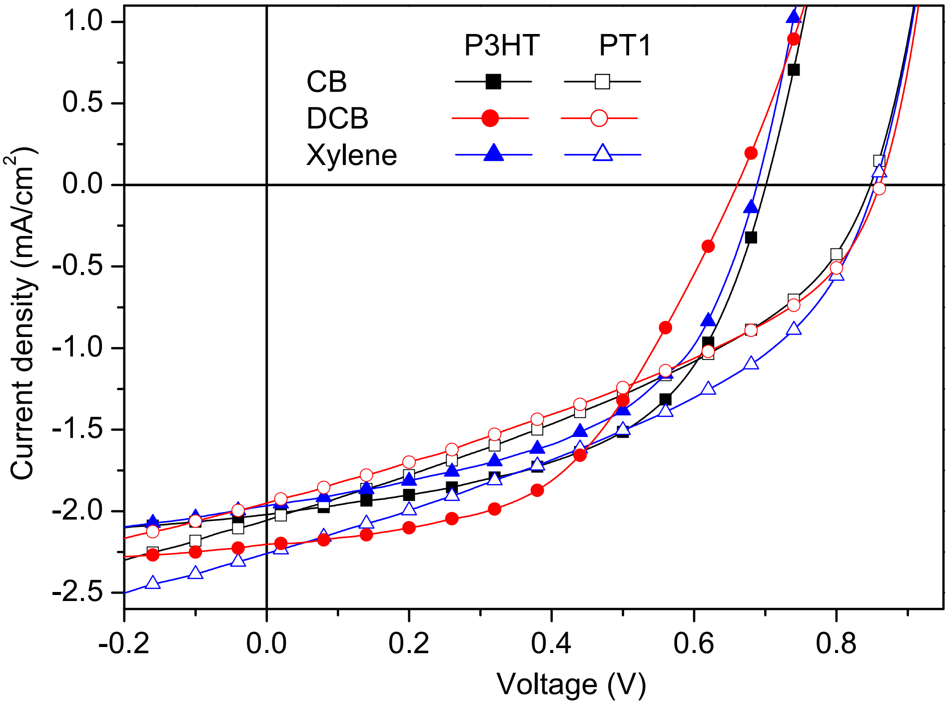


Figure S3. *J-V* curves under AM 1.5 illumination (100 mW/cm^2) for all-PSCs based on the combinations of P3HT:PF-NDI and PT1:PF-NDI which were spin-coating from different solvents.

Table S1. Device characteristics of All-PSCs fabricated from three solvents.

Active layer		V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE
Solvent	Donor				
CB	P3HT	0.70	2.02	0.54	0.76%
	PT1	0.84	2.06	0.38	0.65%
DCB	P3HT	0.66	2.20	0.50	0.73%
	PT1	0.86	1.95	0.38	0.64%
Xylene	P3HT	0.68	1.97	0.52	0.75%
	PT1	0.86	2.26	0.40	0.78%

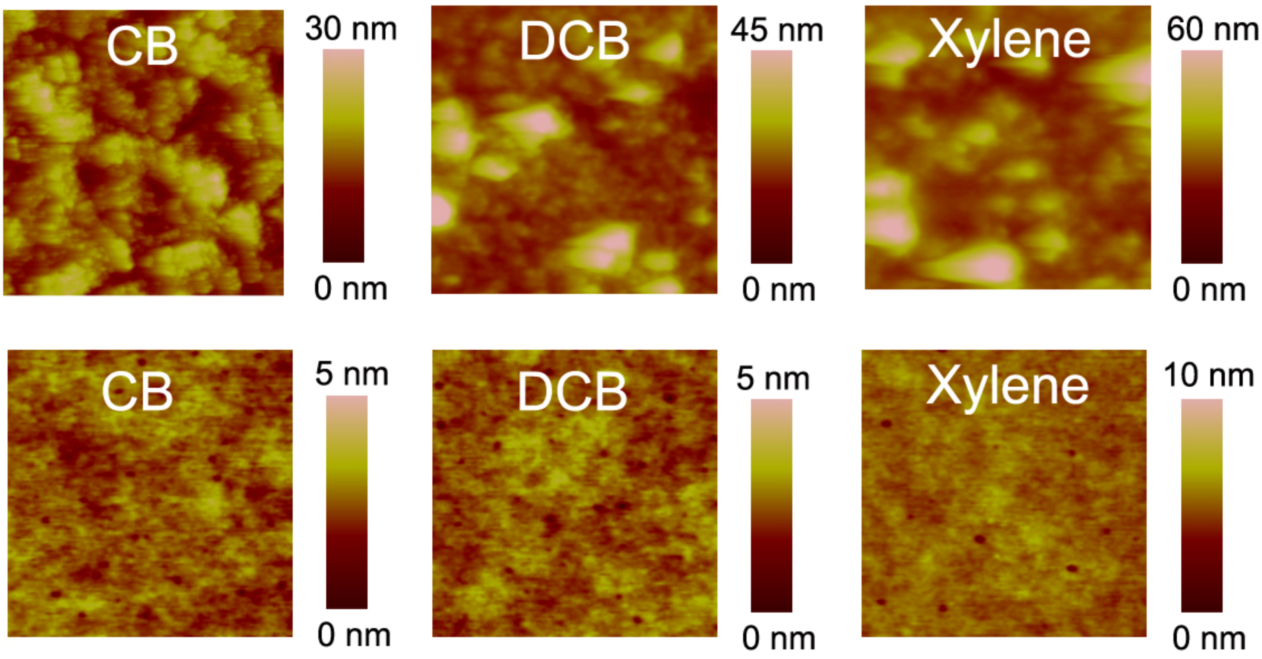


Figure S4. AFM height images of P3HT:PF-NDI (upper) and PT1:PF-NDI (lower) composite films, spin-coated from different solvents (image size: 2 μm × 2 μm).

S1 Z. H. Chen, Y. Zheng, A and Facchetti, *J. Am. Chem. Soc.* 2009, **131**, 8.