Supporting Information

Impact of Isomeric Structures on Transistor Performances in Naphthodithiophene Semiconducting Polymers

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Experimental Section.

1. Synthesis

Naphtho[2,3-*b*:6,7-*b′*]dithiophene (NDT1), naphtho[2,3-*b*:7,6-*b′*]dithiophene (NDT2), and naphtho[2,1-*b*:6,5-*b′*]dithiophene (NDT4), were synthesized according to the reported procedure, respectively.[1] 5,5'-dibromo-4,4'-dialkyl-2,2'-bithiophene (**5**) with R = $C_{16}H_{33}$[2] and $C_{20}H_{41}$[3] were synthesized through different procedures. The synthesis of poly(2,7-bis(3-alkylthiophene-2-yl)naphtho[1,2-*b*:5,6-*b′*]dithiophene) (PNDT3BT-*l*) were reported elsewhere.[4] All chemicals and solvents are of reagent grade unless otherwise indicated. THF was distilled from sodium benzophenone ketyl prior to use. Nuclear magnetic resonance (NMR) spectra were obtained in deuterated chloroform with TMS as internal reference; chemical shifts (δ) are reported in parts per million. EI-MS spectra were obtained on a Shimadzu QP-5050A spectrometer using an electron impact ionization procedure (70 eV). Molecular weights were determined by gel permeation chromatography (GPC) with a TOSOH HLC-8121GPC/HT at 140 °C using *o*-dichlorobenzene as a solvent and calibrated with polystyrene standards.

2,7-Bis(trimethylstannyl)naphtho[2,3-*b*:6,7-*b′*]dithiophene (1). To a solution of naphtho[2,3-*b*:6,7-*b′*]dithiophene (NDT1) (0.50 g, 2.08 mmol) in 50 mL of THF, 1.6 M solution of *n*-butyllithium in hexane (4 mL, 6.36 mmol) was added dropwise at –78 °C. The solution was stirred at –78 °C for 30 minutes and subsequently at room temperature for 30 minutes under N_2 atmosphere. After cooling to –78 °C, trimethyltin chloride (1.66 g, 8.34 mmol) was added in one portion. The solution was warmed to room temperature, and 50 mL of water and 50 mL

of dichloromethane were added. The organic layer was washed twice with 50 mL of brine and dried over magnesium sulfate. After removing the solvent, the residue was recrystallized from acetone to give 0.52 g of **1** as yellow crystals (yield = 44%). ^{1}H-NMR ($CDCl_3$, δ ppm): 0.46 (s, 18H, $Sn(CH_3)$) 7.49 (s, 2H, ArH) 7.8.35 (s, 2H, ArH) 8.48 (s, 2H, ArH). ^{13}C NMR ($CDCl_3$, δ): –8.3, 119.9, 120.1, 128.8, 131.6, 140.3, 141.3, 143.8. EI-MS (70 eV): *m*/*z*=566 (M^+). Anal. Calcd for $C_{20}H_{24}S_2Sn_2$: C, 42.44; H. 4.27%. Found: C, 42.55; H, 3.97%.

2,7-Bis(trimethylstannyl)naphtho[2,3-*b*:7,6-*b′*]dithiophene (2). This compound was synthesized as described for **1** to give 0.50 g of **2** as white crystals (yield = 43%). ^{1}H-NMR ($CDCl_3$, δ ppm): 0.46 (s, 18H, $Sn(CH_3)$) 7.49 (s, 2H, ArH) 8.41 (s, 2H, ArH) 8.42 (s, 2H, ArH). ^{13}C NMR ($CDCl_3$, δ): –8.3, 118.9, 121.1, 128.5, 129.0, 131.5, 140.0, 141.7, 143.6. EI-MS (70 eV): *m*/*z*=566 (M^+). Anal. Calcd for $C_{20}H_{24}S_2Sn_2$: C, 42.44; H. 4.27%. Found: C, 42.49; H, 4.15%.

2,7-Bis(trimethylstannyl)naphtho[2,1-*b*:6,5-*b′*]dithiophene (4). This compound was synthesized as described for **1** to give 0.88 g of **4** as white crystals (yield = 75%). ^{1}H-NMR ($CDCl_3$, δ ppm): 0.49 (s, 18H, $Sn(CH_3)$) 8.06 (d, 2H, *J*=8.6 Hz, ArH) 8.11 (s, 2H, ArH) 8.30 (d, 2H, *J*=8.6 Hz, ArH). ^{13}C NMR ($CDCl_3$, δ): –8.2, 120.1, 120.5, 126.0, 130.1, 137.9, 140.0, 141.5. EI-MS (70 eV): *m*/*z*=566 (M^+). Anal. Calcd for $C_{20}H_{24}S_2Sn_2$: C, 42.44; H. 4.27%. Found: C, 42.59; H, 4.09%.

General procedures for poly(2,7-bis(3-alkylthiophene-2-yl)naphthodithiophene) (PNDT*m*BT-*l*s). A solution of **1**, **2**, or **4** (170 mg, 0.30 mmol), **5** (0.30 mmol), tris(dibenzylideneacetone)dipalladium (0)-chloroform adduct ($Pd_2(dba)_3$·$CHCl_3$) (6 mg, 0.006 mmol), tri-*o*-tolylphosphine (P(*o*-Tol)$_3$) (7.2 mg, 0.024 mmol) in 20 mL of anhydrous chlorobenzene was refluxed for 3 days under N_2 atmosphere. After cooling to 50 °C the reaction solution was poured into 200 mL of methanol containing 5 mL of hydrochloric acid and stirred for 5 hours. Then the precipitated solid was subjected to sequential Soxhlet extraction with methanol, hexane and chloroform to remove low molecular weight fractions. The residue was extracted with chlorobenzene, and then precipitated in 200 mL of methanol to yield red solids (yield = 70~80%).

2. Measurements and calculation.

UV-Vis absorption spectra were measured using a Shimadzu UV-3100 spectrometer. Thermal analyses were carried out with differential scanning calorimetry (DSC) on a SHIMADZU DSC-60 at 10 °C/min for both heating and cooling processes. Ionization potential (IP) was determined from the onset of photoelectron spectra measured by using a RIKEN KEIKI CO., LTD photoelectron spectrometer MODEL AC-2 in air. MO calculations were carried out with the DFT/TD-DFT method using Gaussian 03 program package; Frisch, M. J. e. a. G., revision C.02; Gaussian, Inc., Wallingford, CT, 2004. Dynamic force-mode atomic force microscopy (AFM) study was carried out by a SII Nanotechnology, Inc. scanning probe microsope Nanocute system. Out-of-plane and in-plane grazing incidence X-ray diffractions of thin films deposited on hexamethyldisilazane (HMDS) treated Si/SiO_2 substrates were obtained using a Rigaku Ultima IV or a Rigaku SmartLab, respectively.

3. OFET fabrication and characterization.

OFET devices were fabricated in a "top-contact" configuration on heavily doped *n*+-Si (100) wafers with 200-nm-thick thermally grown SiO_2 (C_i = 17.3 nF cm^{-2}). The Si/SiO_2 substrates were carefully cleaned according to the literature procedure[5] and then treated with hexamethyldisilazane (HMDS) or a 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (FDTS) to form a self-assembled monolayer (SAM), in which the silicon wafers were exposed to HMDS or FDTS vapor in a closed desiccator. Polymer layers were then spin-coated from warm (~80 °C) 3 g/L dichlorobenzene solution with 2500 rpm for 45 sec, subsequently annealed at 150 °C for 30 min under nitrogen. On top of the polymer thin films, Au drain and source electrodes (thickness 80 nm) were deposited in vacuum through a shadow mask, where the drain-source channel length (L) and width (W) are 50 μm and ca. 1.5 mm, respectively. Current-voltage characteristics of the OFET devices were measured at room temperature in air with a Keithly 4200-SCS semiconductor characterization system. Field-effect mobilities were calculated in the saturation regime (V_{DS} = –60 V) of the I_{DS} using the following equation,

$$I_{DS} = (WC_i/2L)\,\mu\,(V_G - V_{th})^2$$

where C_i is the capacitance of the SiO_2 dielectric, I_{DS} is the source-drain current, and V_{DS}, V_G and V_{th} are the source-drain, gate and threshold voltages, respectively. Current on/off ratios (I_{on}/I_{off}) were determined from the minimum current at around V_G = 0–20 V (I_{off}) and the current at V_G = –80 V (I_{on}). The mobility data were collected more than 10 different devices.

References.

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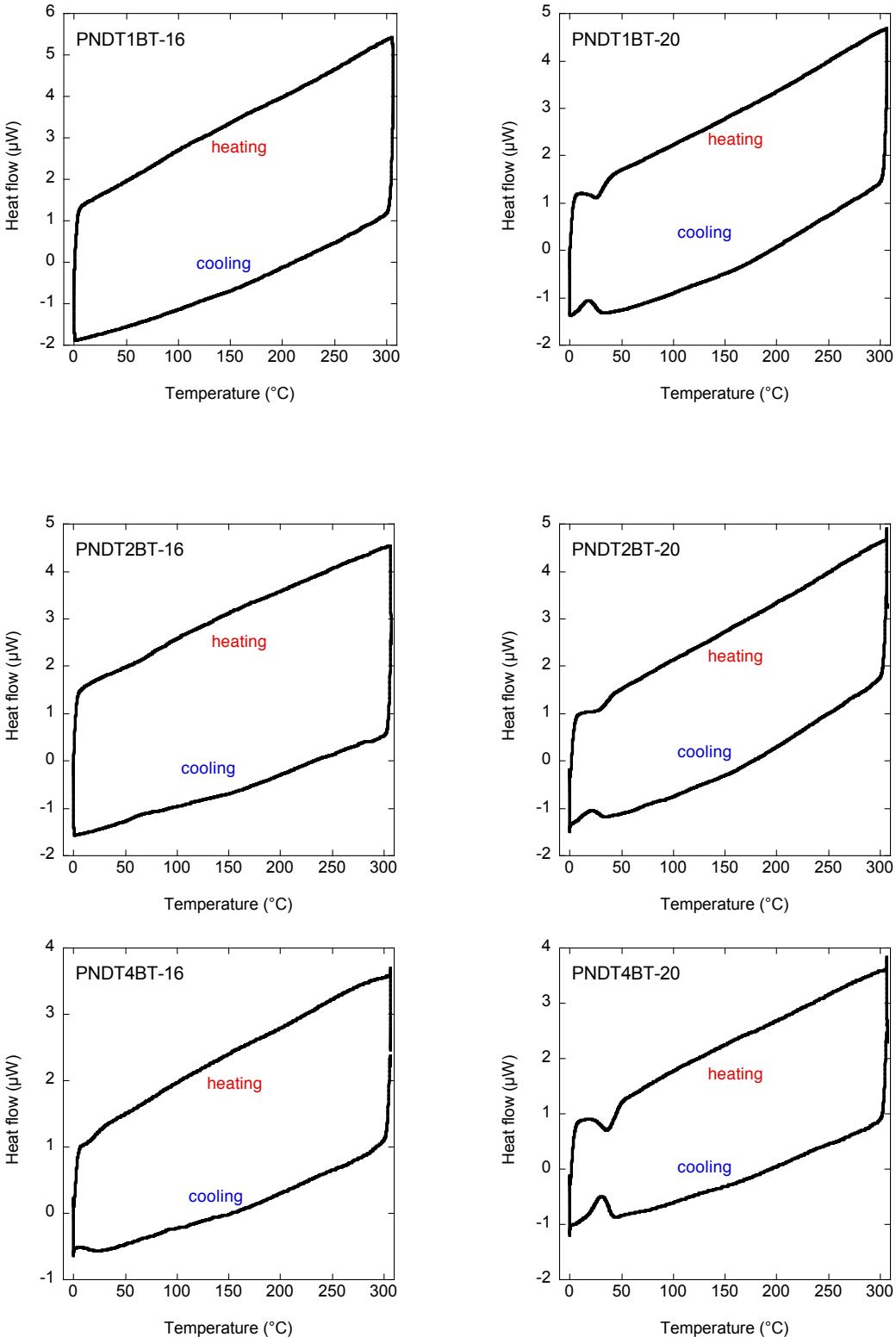

Figure S1. DSC curves of the polymers.

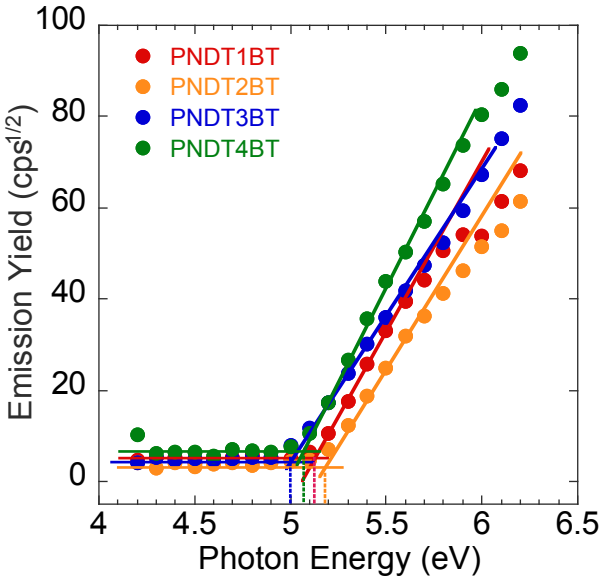

Figure S2. Photoelectron spectra of the polymers with the C16 side chain.

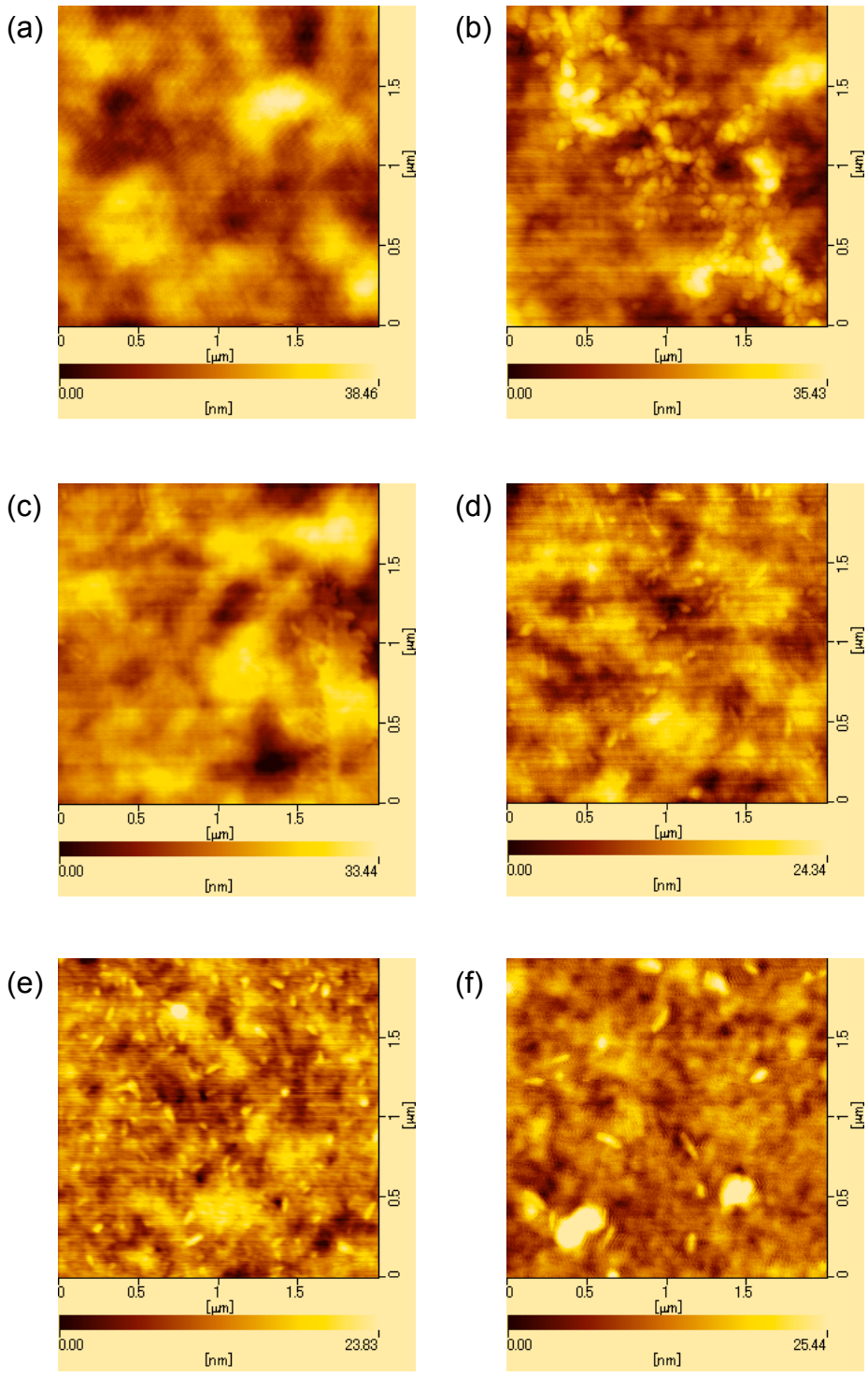

Figure S3. Topographic AFM images of polymer thin films after annealing at 150 °C on the HMDS-modified Si/SiO_2 surface; (a) PNDT1BT-16, (b) PNDT1BT-20, (c) PNDT2BT-16, (d) PNDT2BT-20, (e) PNDT4BT-16, (f) PNDT4BT-20 (see ref 41 for PNDT3BTs).