

Electronic Supplementary Information

Experimental details

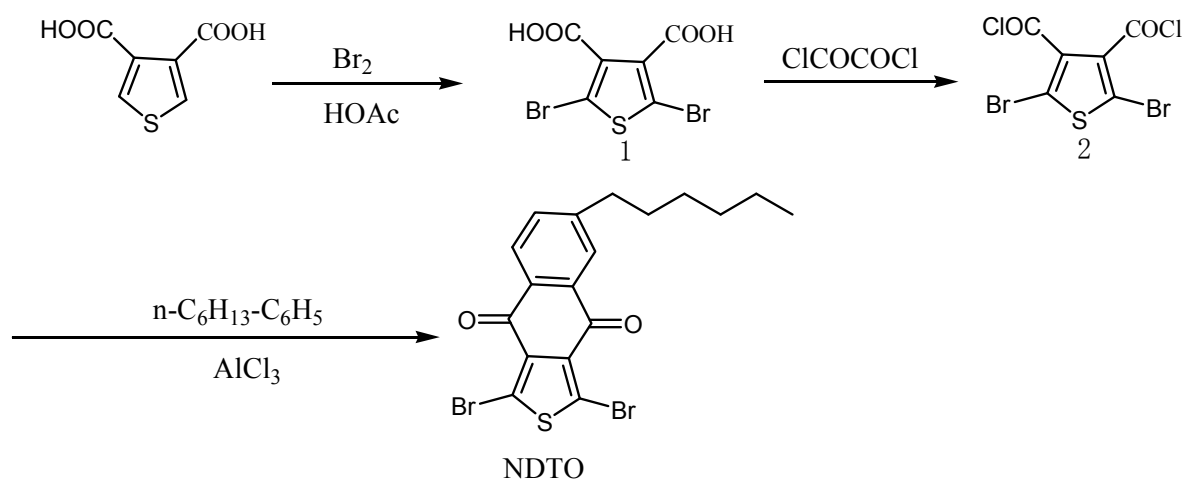
Measurements and Instruments. All new compounds were characterized by ^1H NMR spectroscopy performed on a Bruker DMX-400 spectrometer. For the ^1H NMR measurements, CDCl_3 was used as the solvent. Chemical shifts in the NMR spectra were reported in ppm relative to the singlet at 7.26 ppm for CDCl_3 . The molecular weight of the polymers was measured by gel permeation chromatography (GPC), and polystyrene was used as a standard. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. UV-vis absorption spectra were obtained on a Hitachi U-3010 spectrometer. Cyclic voltammetry was performed on a Zahner IM6e electrochemical workstation with a three-electrode system in a solution of 0.1 M Bu_4NPF_6 in acetonitrile at a scan rate of 100 mV/s. Glassy carbon disc coated with polymer film was used as the working electrode. The polymer films were coated on the glassy carbon electrode by dipping the electrode into the corresponding solutions and then drying. A Pt wire was used as the counter electrode, and Ag/Ag^+ was used as reference electrode.

Device Fabrication and Characterization of PSCs. PSCs were fabricated with ITO glass as a positive electrode, Ca/Al as a negative electrode and the blend film of the polymer/ PC_{70}BM between them as a photosensitive layer. The ITO glass was pre-cleaned and modified by a thin layer of PEDOT:PSS which was spin-cast from a

PEDOT:PSS aqueous solution (Clevious P VP AI 4083 H. C. Stark, Germany) on the ITO substrate, and the thickness of the PEDOT:PSS layer is about 30 nm. The photosensitive layer was prepared by spin-coating a blend solution of polymers and PC₇₀BM in o-dichlorobenzene on the ITO/PEDOT:PSS electrode. Then the Ca/Al cathode was deposited on the active layer by vacuum evaporation under 3×10^{-4} Pa. The effective area of one cell is 4 mm² and the thickness of the photosensitive layer is ca. 85 nm. The current-voltage (*J-V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit in drybox under inert atmosphere. A xenon lamp with AM 1.5 filter was used as the white light source, and the optical power at the sample was 100 mW/cm². The external quantum efficiency (EQE) was measured using a Stanford Research Systems model SR830 DSP lock-in amplifier coupled with a WDG3 monochromator and 500W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. All the measurements were performed under ambient atmosphere at room temperature.

Synthesis of Monomers.

4,4-bis(2-ethylhexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2',3'-*d*]silole^[16a] was synthesized according to the procedure in the literature, the synthetic route of the NTDO monomer was shown in **Scheme S1**.



Scheme S1 Synthetic route of the NTDO monomer.

2,5-Dibromothiophene-3,4-dicarboxylic Acid (1) Thiophene-3,4-dicarboxylic (5 g, 29.1 mmol) and glacial acetic acid (50 mL) were added to a 250 mL flask with a stirring bar. Bromine (9 mL, 0.174 mol) was added dropwise. The mixture was stirred overnight. Aqueous sodium bisulfate solution was added until the reddish color disappeared. The mixture was filtered and washed with 50 mL water, and a gray solid of 9.6 g (yield: 80%) was obtained. MS: $m/z=330$.

2,5-Dibromothiophene-3,4-dicarboxylic Acid Chloride (2) Oxalyl chloride (5.3 mL, 60.5 mmol) was slowly added to 2,5-Dibromothiophene-3,4-dicarboxylic Acid (5 g, 15.15 mmol) and DMF (1 drop) in toluene (100 mL). The mixture was heated to reflux for 1 h, then cooled to room temperature. The volatiles were removed in vacuum, and the product was used without further purification.

1,3-dibromo-6-hexylnaphtho[2,3-c]thiophene-4,9-dione (NDTO) A solution of 2,5-dibromothiophene-3,4-dicarboxylic acid chloride (2) (3.3 g, 9 mmol) in dichloromethane was slowly added to a suspension of aluminum chloride (5.3 g, 39.6 mmol) in dichloromethane (20 mL) at 0 °C. The mixture was allowed to stir at 0 °C

for 10 min. *n*-Hexylbenzene (2 mL, 10.8 mmol) was slowly added. The mixture was stirred for 30 min and then poured into ice. Dichloromethane (100 mL) was added, and the mixture was shaken vigorously. The layers were separated, and the aqueous layer was extracted with dichloromethane. The combined organic portions were washed with a saturated sodium bicarbonate solution and water and then dried over magnesium sulfate. The residue, which remained after the solvent was evaporated, was purified by flash chromatography on silica gel with ethyl acetate/hexane (1:10) to give 2.4 g (yield 58%) of the title compound. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.22~8.11 (d, 2H), 7.61 (s, 1H), 2.79 (s, 2H), 1.69~1.23 (m, 9H), 0.89 (s, 2H); ^{13}C NMR (100 MHz) δ (ppm): 178.1, 177.6, 146.1, 143.3, 134.1, 132.0, 130.6, 130.1, 129.2, 126.3, 37.1, 32.8, 32.2, 29.8, 23.7, 23.5, 15.3; MS: m/z =456.

Synthesis of PDTSNTDO: The polymerization was performed by Stille coupling reaction. In a 50 mL flask, NDTO (0.228 g, 0.5 mmol), and 4,4-bis(2-ethylhexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2',3'-*d*]silole (0.373 g, 0.5 mmol) were dissolved in toluene (16 mL), and flushed with argon for 10 min. Then, $\text{Pd}(\text{PPh}_3)_4$ (0.023 g, 0.020 mmol) was added into the flask, which was then flushed by argon for another 20 min. The solution was heated to reflux and stirred for 24 h under inert atmosphere. Then, the reactant was cooled to room temperature, and the polymer was precipitated by addition of 50 mL of methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol and hexane. The solid was dissolved in chloroform (150 mL) and passed through a column packed with alumina, Celite, and silica gel, the column was eluted with chloroform. The

combined polymer solution was concentrated and was poured into methanol. Subsequently, the precipitates were collected and dried under vacuum overnight to get PDTSNTDO 152 mg (yield 25%). ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.32 (d, 1H), 8.21 (s, 1H), 7.93 (d, 2H), 7.64 (d, 1H), 1.72~1.01 (m, 32H), 0.88~0.80 (m, 15 H). Anal. Calcd for $\text{C}_{53}\text{H}_{69}\text{N}_2\text{O}_2\text{S}_6$ (%): C, 69.86; H, 7.78; O, 4.2, S, 12.64. Found (%): C, 69.69; H, 7.79; O, 4.22, S, 12.67.

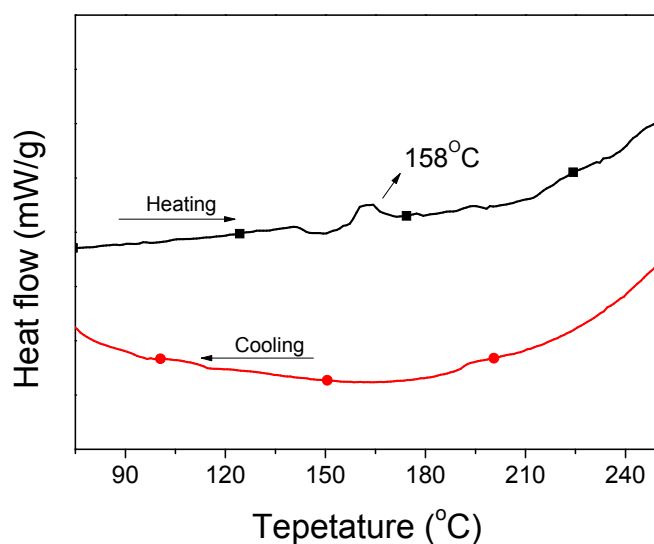


Figure S 1 The differential scanning calorimetry (DSC) of PDTSNTDO