

Supporting Information

1,8-Naphthalimide based small molecular acceptor for polymer solar cells with high open circuit voltage

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1.1 Measurements and characterization

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere and monitored by thin layer chromatography (TLC) on silica gel plates. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer. UV-visible absorption spectra were measured on a PerkinElmer UV-vis spectrometer model Lambda 750. Elemental analyses were carried out on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on TA2100 and Perkin-Elmer Diamond differential scanning calorimetry (DSC) instrument, respectively, under an atmosphere of nitrogen at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Atomic force microscopy (AFM) measurements were carried out under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA using the tapping mode. Transmission electron microscopy (TEM) experiments were performed on H600 TEM Instrument. The thickness of blend films was measured by a Dektak 6 M surface profilometer. XRD experiments were carried out by RAPID IP instrument. The electrochemical behavior of polymers was studied using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a three-electrode electrochemical cell in a $0.1\text{ M Bu}_4\text{NPF}_6$ CH_3CN solution under an atmosphere of nitrogen with a scanning rate of 0.1 V/S . A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO_3 (0.01 M in CH_3CN) reference electrode were used.

1.2 Polymer Solar Cells Fabrication and Characterization

PSCs were fabricated with the device configuration of ITO/PEDOT:PSS (30 nm)/PCDTBT-C12:NI-T-NI/LiF (0.7 nm)/Al (100 nm). The conductivity of ITO is 20 Ω . PEDOT:PSS (Baytron Al 4083 from H.C. Starck) was filtered with a 0.45 μ m polyvinylidene difluoride (PVDF) film before use. A PEDOT:PSS thin layer was spin-coated on top of the cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 $^{\circ}$ C for 20 min on a hotplate. The thickness of the PEDOT:PSS layer is about 30 nm. A mixture of PCDTBT-C12 and NI-T-NI in 1,2-dichlorobenzene (DCB) was stirred at 90 $^{\circ}$ C overnight to ensure sufficient dissolution and then the blend solution was spin-coated onto PEDOT:PSS layer to form active layer. Thermal annealing was carried out after the spin-coating process on a hotplate. A top electrode of 0.6 nm LiF and 100 nm of aluminum was thermally evaporated at a pressure of 10^{-4} Pa through a shadow mask. On one substrate five cells with an effective area of 0.04 cm^2 for each were fabricated. Current-voltage (I-V) and external quantum efficiency (EQE) measurements were conducted in air without encapsulation. I-V characteristics were recorded at room temperature using an Agilent B2902A Source Meter under the illumination of an AM1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mW cm^{-2} and the white light intensity was calibrated with a standard single-crystal Si solar cell. To investigate the stability of devices based on PCDTBT-C12:NI-T-NI, devices with a PCDTBT-C12:NI-T-NI weight ratio of 1:4 were fabricated and annealed at 90 $^{\circ}$ C for 3 min. These devices were stored in the glove box without encapsulation and periodically tested for 7 days to investigate the photovoltaic performance.

1.3 Field-Effect Devices Fabrication

Hole-only devices with a structure of ITO/PEDOT:PSS (30 nm)/PCDTBT-C12:NI-T-NI/Au (100 nm) and electron-only devices with a configuration of FTO/PCDTBT-C12:NI-T-NI/Al (100 nm) were fabricated. FTO substrates were prepared by etching the commercial FTO substrates with HCl and Zn powders. For hole-only devices, the blend solution of PCDTBT-C12 and NI-T-NI in 1,2-dichlorobenzene (DCB) was spin-

coated onto PEDOT:PSS layer to form active layer like PSC devices, and 100 nm of Au was thermally evaporated at a pressure of 10^{-4} Pa through a shadow mask. For electron-only devices, the blend solution of PCDTBT-C12 and NI-T-NI in 1,2-dichlorobenzene (DCB) were spin-coated on the clean FTO substrates to form active layer. Al electrodes (100 nm) were vacuum deposited on polymer thin films. Dark J-V curves of the hole-only devices and the electron-only devices were measured by the space-charge limited current (SCLC) method.

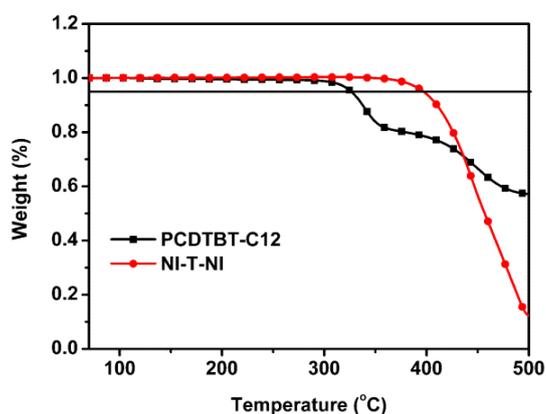


Figure. S1 TGA curves of PCDTBT-C12 and NI-T-NI under an atmosphere of nitrogen.

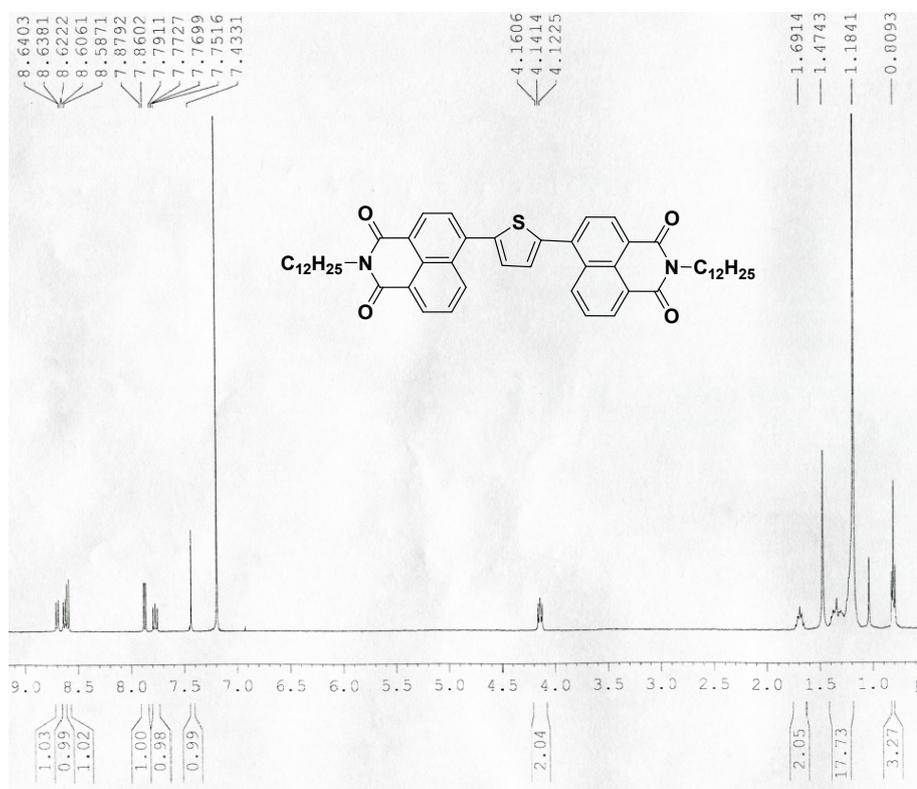


Figure. S2 ^1H NMR spectrum of NI-T-NI (measured in CDCl_3).

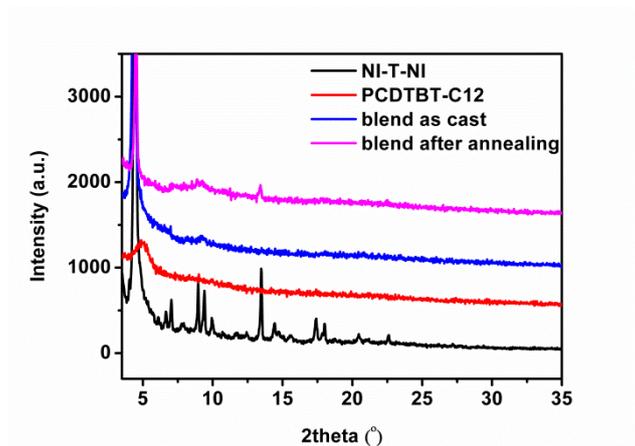


Figure. S5 XRD images of PCDTBT-C12, NI-T-NI and PCDTBT-C12:NI-T-NI blend films with a weight ratio of 1:4 before and after thermal annealing

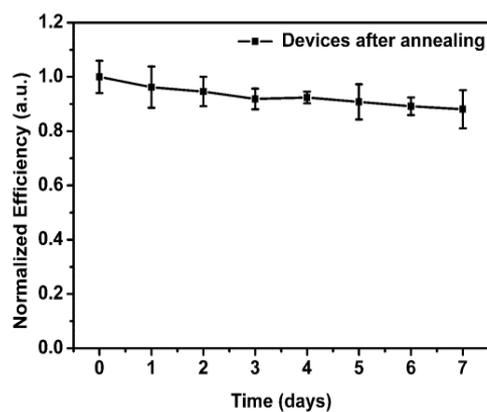


Figure. S6 Normalized efficiency plotted versus storage time for polymer solar cells based on PCDTBT-C12:NI-T-NI. Measurements were tested on five devices, and the error bars were plus or minus 1 standard deviation from the mean.

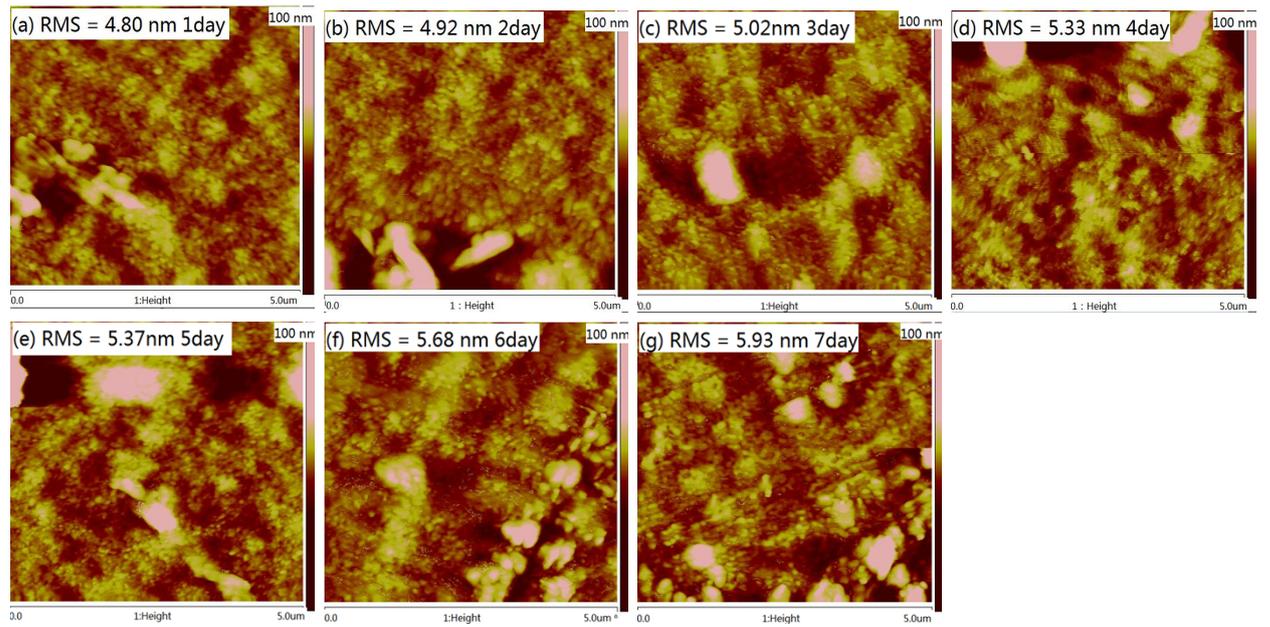


Figure. S7 AFM height images ($5 \mu\text{m} \times 5 \mu\text{m}$) of devices based on PCDTBT-C12:NI-T-**NI** under different storage time.