

## Supporting Information

### 1,8-Naphthalimide-Based Nonfullerene Acceptors for Wide Optical Band Gap Polymer Solar Cells with an Ultrathin Active Layer Thickness of 35 nm

Jicheng Zhang,<sup>†</sup> Hongmei Xiao,<sup>†</sup> Xuejuan Zhang,<sup>†</sup> Yang Wu,<sup>‡</sup> Guangwu Li,<sup>†</sup> Cuihong  
Li,<sup>†,\*</sup> Xuebo Chen,<sup>†</sup> Wei Ma<sup>‡,\*</sup> and Zhishan Bo<sup>†,\*</sup>

<sup>†</sup> Beijing Key Laboratory of Energy Conversion and Storage Materials, College of  
Chemistry, Beijing Normal University, Beijing 100875, China

<sup>‡</sup> State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong  
University, Xi'an 710049, China

#### **Corresponding Author**

\*E-mail: licuihong@bnu.edu.cn; zsbo@bnu.edu.cn; msewma@mail.xjtu.edu.cn

### S1.1. Measurements and characterization

Unless otherwise noted, all reactions were performed under a nitrogen atmosphere and were monitored by thin layer chromatography (TLC) on silica gel plates.  $^1\text{H}$  and  $^{13}\text{C}$  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. Atomic force microscopy (AFM) measurements were conducted under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA using the tapping mode. The thickness of the blend films was measured by a Dektak 6 M surface profilometer. XRD experiments were performed with an X'Pert PRO MPD instrument. The electrochemical behaviour of the polymers was studied using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a three-electrode electrochemical cell in a 0.1 M  $\text{Bu}_4\text{NPF}_6$   $\text{CH}_3\text{CN}$  solution under an atmosphere of nitrogen with a scanning rate of 0.1 V/s. A glassy carbon working electrode, a Pt wire counter electrode and an  $\text{Ag}/\text{AgNO}_3$  (0.01 M in  $\text{CH}_3\text{CN}$ ) reference electrode were used. The ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple was used as the internal reference standard.

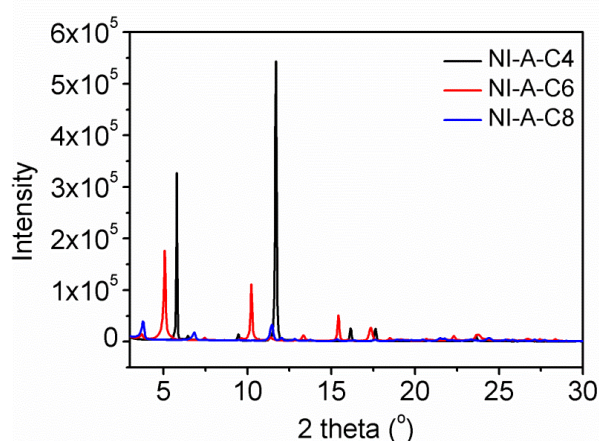
### S1.2. Polymer Solar Cells Fabrication and Characterization

PSCs were fabricated with the device configuration of ITO/PEDOT:PSS (35 nm)/**PCDTBT-C12:Acceptor**/LiF (0.7 nm)/Al (100 nm). The conductivity of ITO is 15  $\Omega$ . PEDOT:PSS (Baytron Al 4083 from H.C. Starck) was filtered with a 0.45  $\mu\text{m}$  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 50 s and was dried at 130  $^\circ\text{C}$  for 20 min on a hotplate. The thickness of the PEDOT:PSS layer was approximately 35 nm. A mixture of **PCDTBT-C12** and acceptor in 1,2-dichlorobenzene (DCB) was stirred at 90  $^\circ\text{C}$  overnight to ensure sufficient dissolution, and the blend solution was spin-coated onto the PEDOT:PSS layer to form the active layer. The concentrations of the blend of **PCDTBT-C12** and small molecules were all 25 mg/mL. To fabricate a thick active layer of **PCDTBT-C12:PC<sub>71</sub>BM**, a concentration of 25 mg/mL for the **PCDTBT-C12** and **PC<sub>71</sub>BM** blend was used. A dilute solution with a concentration of 10 mg/mL was

used for the **PCDTBT-C12**, and PC<sub>71</sub>BM blend was used to achieve a thin active layer. A top electrode of 0.7 nm LiF and 100 nm of aluminium were thermally evaporated at a pressure of 10<sup>-4</sup> Pa through a shadow mask. On one substrate, five cells with an effective area of 0.04 cm<sup>2</sup> each were fabricated. Current-voltage (I-V) and external quantum efficiency (EQE) measurements were conducted in air without encapsulation. The 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<sup>-2</sup>, and the white light intensity was calibrated with a standard single-crystal Si solar cell.

### **S1.3. Space-Charge Limited Current Measurement**

Hole-only devices with a structure of ITO/PEDOT:PSS (35 nm)/**PCDTBT-C12:Acceptor**/Au (100 nm) and electron-only devices with a configuration of FTO/**PCDTBT-C12:Acceptor**/Al (100 nm) were fabricated. FTO substrates were prepared by etching the commercial FTO substrates with HCl and Zn powders. The blend solution of **PCDTBT-C12** and acceptors in DCB was spin-coated onto the PEDOT:PSS layer to form the active layer, like PSC devices, and 100 nm of Au was thermally evaporated at a pressure of 10<sup>-4</sup> Pa through a shadow mask. For electron-only devices, the blend solution of **PCDTBT-C12** and acceptors in DCB was spin-coated on the clean FTO substrates to form an active layer. Al electrodes (100 nm) were vacuum-deposited on the polymer thin films. Dark *J-V* curves of the hole-only devices and electron-only devices were measured by the space-charge limited current (SCLC) method. The dark *J-V* curves of the devices were fitted using the Mott–Gurney equation:  $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$ , where *J* is the space-charge limited current,  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon_r$  is the permittivity of the active layer,  $\mu$  is the hole mobility or the electron mobility, and *L* is the thickness of the active layer.



**Figure S1.** XRD images of **NI-A-C4**, **NI-A-C6** and **NI-A-C8** films with a film thickness of 300 nm.

**Table S1.**  $M_n$ ,  $M_w$  and polydispersity indexes (PDI) of **PCDTBT-C12**.

Polymer	$M_n$ (kg/mol) <sup>a)</sup>	$M_w$ (kg/mol) <sup>a)</sup>	PDI
<b>PCDTBT-C12</b>	66.8	93.1	1.39

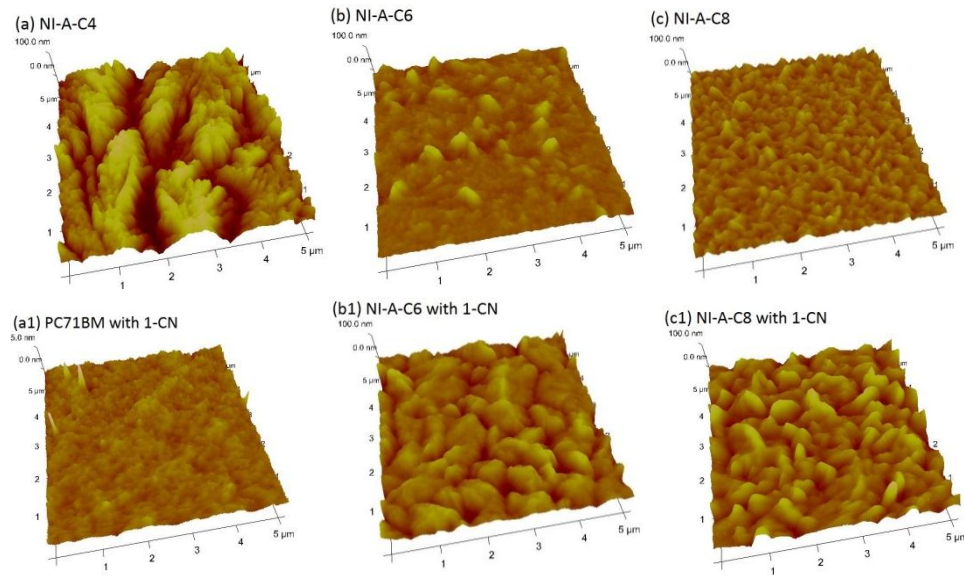
<sup>a</sup>  $M_n$ ,  $M_w$  and PDI of **PCDTBT-C12** were measured by gel permeation chromatography (GPC) at 80 °C using chlorobenzene as an eluent and narrowly distributed polystyrenes as the calibration standards.

**Table S2.** Summary of the photovoltaic properties of **PCDTBT-C12:PC<sub>71</sub>BM**-based optimized devices with different film thickness.

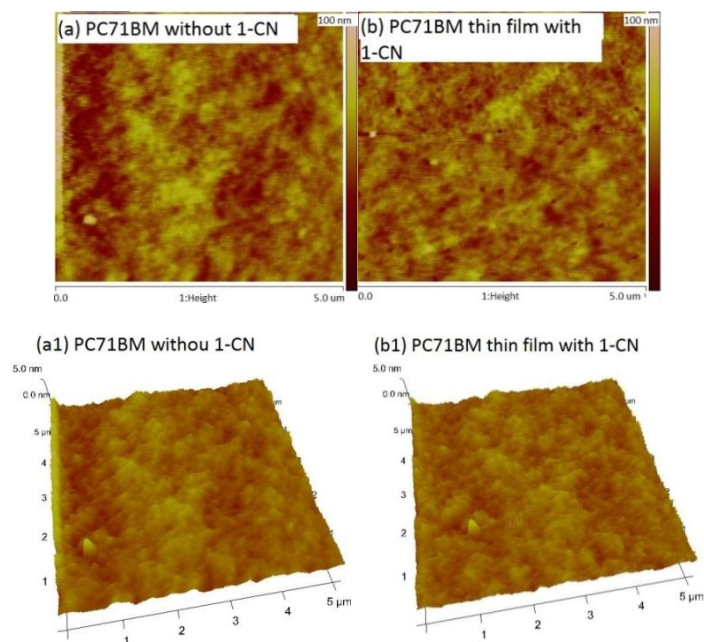
Active layer	RPM	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)	Thickness (nm)
	1100	0.85	7.48	0.41	2.62	144
	1600	0.86	8.39	0.47	3.39	121
<b>PCDTBT-C12:PC<sub>71</sub>BM</b>	2100	0.88	8.77	0.52	4.01	97
With 0.5% 1-CN	2600	0.89	8.65	0.53	4.08	75
	3100	0.88	8.36	0.55	4.04	72
	3600	0.88	8.28	0.55	4.00	69

**Table S3.** Summary of the  $\mu_e$  and  $\mu_h$  of the blend of **PCDTBT-C12:Acceptor** without and with 0.5% as the additive.

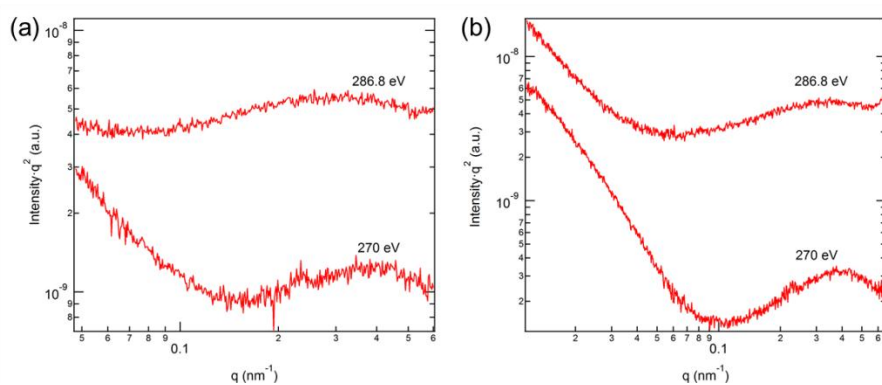
Devices	Thickness (nm)	Additive	$\mu_h$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$\mu_e$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )
<b>PCDTBT-C12:NI-A-C4</b>	37	no	$5.92 \times 10^{-7}$	$5.18 \times 10^{-7}$
<b>PCDTBT-C12:NI-A-C6</b>	32	no	$2.32 \times 10^{-7}$	$1.07 \times 10^{-8}$
	31	0.5% 1-CN	$2.15 \times 10^{-7}$	$3.05 \times 10^{-7}$
<b>PCDTBT-C12:NI-A-C8</b>	34	no	$1.26 \times 10^{-7}$	$6.45 \times 10^{-9}$
	32	0.5% 1-CN	$2.01 \times 10^{-7}$	$2.25 \times 10^{-8}$
<b>PCDTBT-C12:PCBM</b>	36	0.5% 1-CN	$7.57 \times 10^{-6}$	$3.78 \times 10^{-7}$
	74	0.5% 1-CN	$8.27 \times 10^{-6}$	$1.73 \times 10^{-6}$



**Figure S2.** Three-dimensional AFM images ( $5 \times 5 \mu\text{m}$ ) of **PCDTBT-C12:SMA** blend films without and with 0.5% 1-CN as the additive and **PCDTBT-C12:PC<sub>71</sub>BM** optimized blend films. The height scale bar of (a), (b), (b1), (c) and (c1) is 200 nm; the height scale bar of (a1) is 5 nm.



**Figure S3.** AFM height images and three-dimensional images ( $5 \times 5 \mu\text{m}$ ) of **PCDTBT-C12:PC<sub>71</sub>BM** blend films without 1-CN as the additive with a film thickness of 70 nm and **PCDTBT-C12:PC<sub>71</sub>BM** blend films with 1-CN as the additive with a film thickness of 30 nm. The height scale bar is 5 nm.



**Figure S4.** R-SoXS profiles in log scale for (a) **PCDTBT-C12:NI-A-C6** and (b) **PCDTBT-C12:NI-A-C8** blend films with the energy of 270 eV and 286.8 eV.