

Rylene Diimide and Dithienocyanovinylen Copolymers for Polymer Solar Cells*

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Abstract Two polymers containing (*E*)-2,3-bis(thiophen-2-yl)acrylonitrile (CNTVT) as a donor unit, perylene diimide (PDI) or naphthalene diimide (NDI) as an acceptor unit, are synthesized by the Stille coupling copolymerization, and used as the electron acceptors in the solution-processed organic solar cells (OSCs). Both polymers exhibit broad absorption in the region of 300–850 nm. The LUMO energy levels of the resulted polymers are *ca.* –3.93 eV and the HOMO energy levels are –5.97 and –5.83 eV. In the binary blend OSCs with PTB7-Th as a donor, PDI polymer yields the power conversion efficiency (PCE) of up to 1.74%, while NDI polymer yields PCE of up to 3.80%.

Keywords Perylene diimide; Naphthalene diimide; Polymer solar cell; Non-fullerene acceptor

INTRODUCTION

Organic solar cells (OSCs) based on the solution processed bulk heterojunction (BHJ) have been studied intensively in these years because of their advantages, including low cost, light weight, facile fabrication, and flexibility^[1–9]. Over the past decades, fullerene and its derivatives are well known as the electron acceptors because of their large electron affinity and high electron mobility. However, weak absorption, limited energy level variation and difficult purification of fullerene derivatives have hindered the development of such materials. In contrast, the non-fullerene acceptors have drawn increasing attention recently^[10–17], such as the conjugated polymers based on boron-nitrogen coordination bond^[18], which show broad absorption in the visible region and the tunable energy levels to achieve high short circuit current density (J_{sc}), high open circuit voltage (V_{oc}) and low cost. More importantly, the non-fullerene-based OSCs acceptors display excellent device performance. For instance, the power conversion efficiencies (PCEs) of single-junction OSCs based on fused-ring electron acceptors (FREAs) have reached 8%–11%^[11–13, 19–22], comparable to or even better than those based on fullerene acceptors.

Rylene diimide such as perylene diimide (PDI) and naphthalene diimide (NDI) were widely used as the

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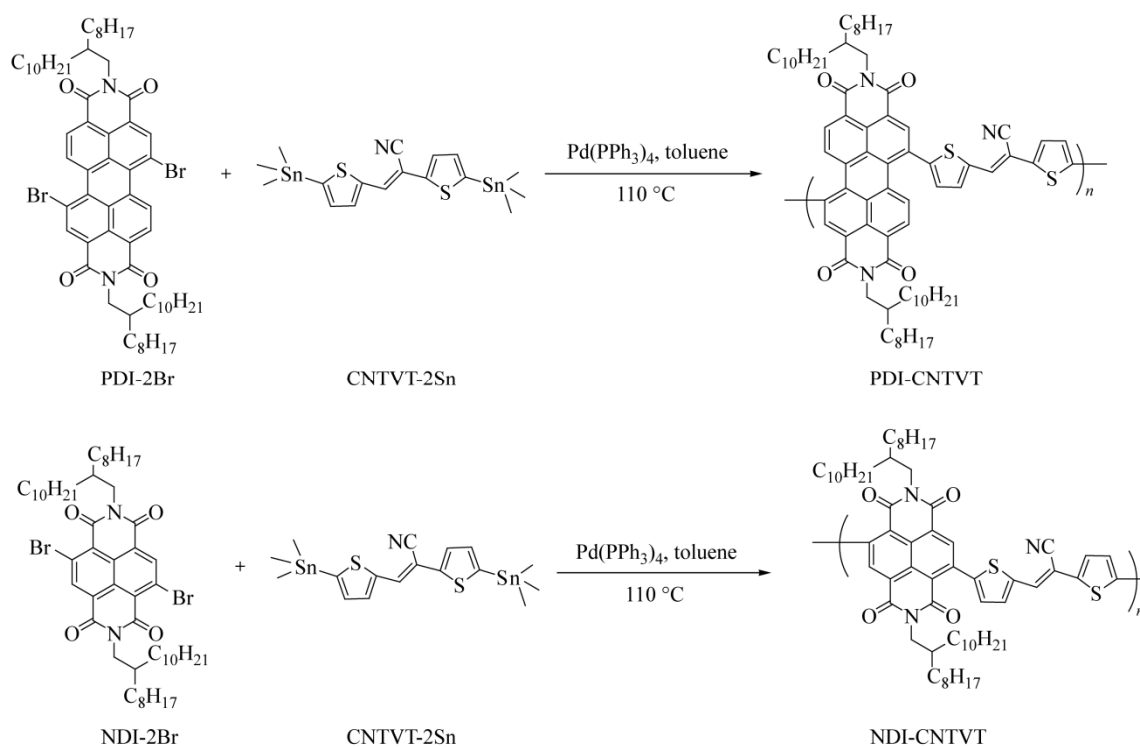
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non-fullerene acceptors in OSCs in the past decade due to their good electron mobility and chemical stability^[5, 23]. However, the planar cores of PDI and NDI tend to aggregate in blended films to form extra large crystalline domains and phase separation, which is unfavorable for the performance of OSCs. Therefore, twisted structures, such as dimers, trimers and tetramers, were proposed to decrease the planarity, self-aggregation, crystalline domains, and phase separation^[24–35].

In 2007, Zhan *et al.* reported the first PDI polymer that was used as the non-fullerene acceptor in OSCs^[36], since then many PDI and NDI polymers were reported^[37–43]. Kwon *et al.* incorporated a cyano group in the dithienovinylene (TVT) moiety to construct weak donating unit CNTVT used in organic field-effect transistors^[44]. Compared with TVT unit, CNTVT could lower both the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels, and keep planar molecular backbone. Here, we used CNTVT as a donor unit, PDI and NDI as the acceptor units to construct polymer acceptors for OSCs (Scheme 1). The effects of PDI and NDI units on absorption, energy level, charge transport, morphology and OSC performance were investigated.



Scheme 1 Synthetic routes to the polymers

EXPERIMENTAL

Synthesis

Unless stated otherwise, all the used solvents and chemical reagents were obtained commercially without further purification. Toluene was distilled from sodium benzophenone under nitrogen, PDI-2Br, NDI-2Br, CNTVT-2Sn were purchased from Suna Tech Inc.

PDI-CNTVT synthesis

PDI-2Br (0.15 mmol, 166.4 mg), CNTVT-2Sn (0.15 mmol, 81.4 mg) and Pd(PPh₃)₄ (0.009 mmol, 11 mg) were dissolved in anhydrous toluene (20 mL). The solution mixture was stirred at 110 °C for 72 h under argon atmosphere. After cooling to room temperature, the reaction mixture was poured into methanol (200 mL). The isolated crude product was then subjected to Soxhlet extraction with methanol, acetone, and hexane successively.

Finally, the product was extracted with chloroform, and the extract was concentrated before it was precipitated with methanol again, affording a dark solid (140 mg, 83.8%). GPC: $M_n = 22$ kDa, $M_w = 54$ kDa, $M_w/M_n = 2.4$. $^1\text{H-NMR}$ (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, δ): 8.70 (m, 2H), 8.38–8.19 (m, 4H), 7.61–7.25 (m, 5H), 4.11 (m, 4H), 2.01 (m, 2H), 1.22–0.84 (br, 76H).

NDI-CNTVT synthesis

NDI-2Br (0.15 mmol, 147.8 mg), CNTVT-2Sn (0.15 mmol, 81.4 mg) and $\text{Pd}(\text{PPh}_3)_4$ (0.009 mmol, 11 mg) were dissolved in anhydrous toluene (20 mL). The solution mixture was stirred at 110 °C for 72 h under argon atmosphere. After cooling to room temperature, the reaction mixture was poured into methanol (200 mL). The isolated crude product was then subjected to Soxhlet extraction with methanol, acetone, and hexane successively. Finally, the product was extracted with chloroform, and the extract was concentrated before it was precipitated with methanol again, affording a dark solid (138 mg, 85.4%). GPC: $M_n = 41$ kDa, $M_w = 84$ kDa, $M_w/M_n = 2.0$. $^1\text{H-NMR}$ (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, δ): 8.79 (s, 2H), 8.72–7.35 (m, 5H), 4.09 (m, 4H), 1.98 (m, 2H), 1.23–0.86 (br, 76H).

Characterization

The $^1\text{H-NMR}$ spectra were measured using a Bruker AVANCE 400 MHz spectrometer employing tetramethylsilane (TMS, $\delta = 0$) as an internal standard. The molecular weights and dispersity were measured by gel permeation chromatography (GPC) on Agilent PL-GPC220 at 120 °C using *o*-dichlorobenzene (DCB) as an eluent and polystyrene as the standard. UV-Vis absorption spectra of the solution (chloroform) and the thin film (on a quartz substrate) were recorded using a Jasco V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen in a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate ($0.1 \text{ mol}\cdot\text{L}^{-1}$) in acetonitrile using a potential scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ with a computer-controlled Zahner IM6e electrochemical workstation, a glassy-carbon working electrode coated with the copolymer films, a platinum-wire auxiliary electrode, and an Ag/AgCl electrode as a reference electrode. The potentials were referenced to a ferrocenium/ferrocene ($\text{FcP}_2^{+/0}$) couple using ferrocene as an internal standard. Thermogravimetric analysis (TGA) measurements were performed using a Shimadzu thermogravimetric analyzer (Model DTG-60) under flowing nitrogen gas at a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. The grazing incidence X-ray diffraction (GIXRD) data were obtained at beamline 1W1A of the Beijing Synchrotron Radiation Facility (BSRF) at a wavelength of 0.154 nm. 1W1A was a beamline based on a bending mirror and a Si (220) bent crystal monochromator was employed to monochromatize the beam. The size of the focus spot is about $0.7 \text{ mm} \times 0.4 \text{ mm}$ and the end station is equipped with a Huber 4-Circle diffractometers 424-511.1. A NaI scintillation detector was used for data collection. The nanoscale morphology of the blended films was observed using a Bruker multimode ScanAsyst atomic force microscope (AFM).

Fabrication and Characterization of the Photovoltaic Cells

Organic solar cells were fabricated with the structure, ITO/PEDOT:PSS/donor:acceptor/Ca/Al. Patterned indium tin oxide (ITO) glass (sheet resistance = $15 \Omega\cdot\text{sq}^{-1}$) was precleaned in an ultrasonic bath with acetone and isopropanol, and treated in an ultraviolet-ozone chamber (Jelight Company, USA) for 23 min. A thin layer (35 nm) of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron PVP AI 4083, Germany) was spin-coated onto the ITO glass, and then baked at 150 °C for 15 min. A donor:acceptor mixture in chloroform was spin-coated on the PEDOT:PSS layer to form a photosensitive layer. The calcium layer (*ca.* 20 nm) and the aluminum layer (*ca.* 80 nm) were then evaporated onto the surface of the photosensitive layer under vacuum (*ca.* 10^{-5} Pa) to form the negative electrode. The active area of the device was 4 mm^2 . The current density-voltage (J - V) curve was measured using a computer-controlled B2912A Precision Source/Measure Unit (Agilent Technologies). An XES-70S1 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, $70 \text{ mm} \times 70 \text{ mm}$ photobeam size) coupled with AM1.5G solar spectrum filters was used as the light source, and the optical power at the sample was $100 \text{ mW}\cdot\text{cm}^{-2}$. A $2 \text{ cm} \times 2 \text{ cm}$ monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. The incident photon to converted current efficiency (IPCE) spectrum was measured using a solar cell spectral response measurement system QE-R3011 (Enlitech

Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell. Hole-only or electron-only diodes were fabricated using the architectures ITO/PEDOT:PSS/active layer/Au for holes and Al/active layer/Al for electrons. The mobility was extracted by fitting the J - V curves using the Mott-Gurney relationship (space charge limited current, SCLC).

RESULTS AND DISCUSSION

Material Preparation and Characterization

Two polymers were synthesized *via* the Stille coupling reactions between PDI-2Br/NDI-2Br and CNTVT-2Sn in one pot (Scheme 1). Both compounds are readily soluble in common organic solvents, such as *o*-dichlorobenzene (DCB) and chloroform at room temperature. The molecular weights and dispersity of the polymers were measured by GPC (Table 1). The number average molecular weights (M_n) of PDI-CNTVT and NDI-CNTVT are 22 kDa and 41 kDa with the dispersity (M_w/M_n) of 2.4 and 2.0, respectively. Both polymers possess good thermal stability with decomposition temperatures (T_d , 5% weight loss) exceeding 280 °C (Fig. 1). PDI-CNTVT with lower molecular weight showed lower T_d , while NDI-CNTVT with higher molecular weight had higher T_d .

Table 1 Molecular weights and thermal stability of the polymers

Copolymer	M_n (kDa)	M_w (kDa)	M_w/M_n	T_d (°C)
PDI-CNTVT	22	54	2.4	284
NDI-CNTVT	41	84	2.0	401

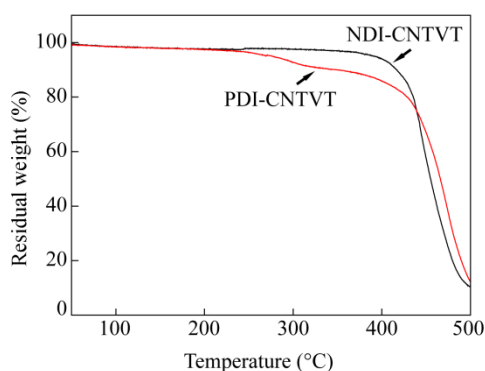


Fig. 1 TGA curves of the polymers

Absorption

Figure 2 shows the normalized optical absorption spectra of the polymers in solution and as a thin film. In a chloroform solution, both polymers exhibit broad absorption in the region of 300–850 nm (Table 2). The molar absorption coefficients of PDI-CNTVT and NDI-CNTVT are 4.3×10^4 and 8.1×10^4 mol⁻¹·L·cm⁻¹, respectively. The two absorption bands at *ca.* 400 and 600 nm are from CNTVT, PDI/NDI and intramolecular charge transfer (ICT) between the donor CNTVT and the acceptor PDI/NDI. The absorption of PDI-CNTVT and NDI-CNTVT films red shift 4 and 12 nm, 16 and 48 nm at *ca.* 400 and 600 nm relative to its solution, respectively. Compared with PDI-CNTVT, the stronger red shift of absorption of NDI-CNTVT film is attributed to the more planar backbone and stronger aggregation. The two polymers show narrow optical bandgaps of 1.63–1.68 eV, estimated from their absorption edges in the thin films (Table 2).

Electrochemistry

The electrochemical properties of the copolymers were investigated by cyclic voltammetry (CV) with the films on a glassy-carbon working electrode in an acetonitrile solution containing 0.1 mol·L⁻¹ Bu₄NPF₆ using a potential scan rate of 100 mV·s⁻¹. As shown in Fig. 3(a), both polymers exhibit two reversible or quasi-reversible reduction waves and one irreversible oxidation wave. The HOMO and LUMO levels of two compounds are estimated from the onset oxidation and reduction potentials, respectively, assuming the absolute energy level of

$\text{FeCp}_2^{+/0}$ to be 4.8 eV below vacuum (Table 2). The LUMO (−3.94 eV to −3.93 eV) energy levels of these molecules are similar, and PDI-CNTVT exhibits slightly up-shifted HOMO level (−5.83 eV) than NDI-CNTVT (−5.97 eV). Figure 3(b) shows the energy alignment for the polymers and PTB7-Th, the energy offset (> 0.3 eV) between PTB7-Th and the polymer acceptors are large enough to guarantee efficient exciton dissociation^[45].

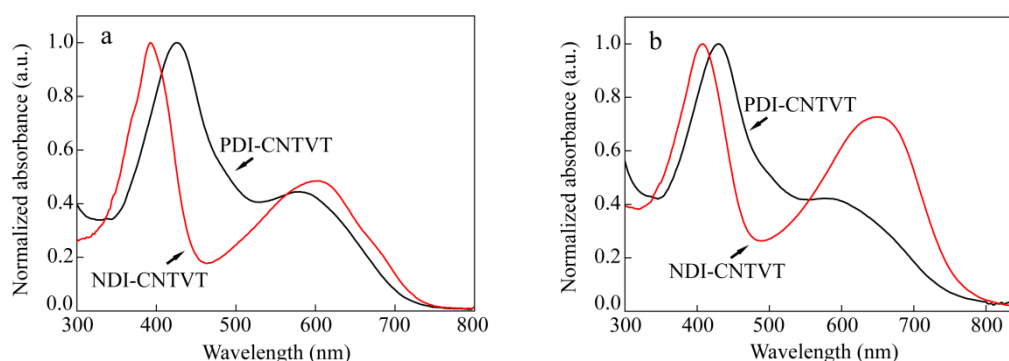


Fig. 2 UV-Vis absorption spectra of the polymers in a chloroform solution (a) and as a thin film (b)

Table 2 Absorption and energy levels of the polymers

Copolymer	$\lambda_{s, \max}^a$ (nm)	$\lambda_{f, \max}^b$ (nm)	E_{HOMO}^c (eV)	E_{LUMO}^d (eV)	$E_{\text{gap}}^{\text{cv} e}$ (eV)	$E_{\text{gap}}^{\text{opt} f}$ (eV)
PDI-CNTVT	426, 582	430, 594	−5.83	−3.93	1.90	1.68
NDI-CNTVT	392, 604	408, 652	−5.97	−3.94	2.03	1.63

^a Absorption maximum of a CHCl_3 solution; ^b Absorption maximum of a thin film; ^c Estimated from the onset oxidation potentials; ^d Estimated from the onset reduction potentials; ^e HOMO-LUMO gap estimated from cyclic voltammetry data; ^f Optical bandgap estimated from the absorption edge of a solid film

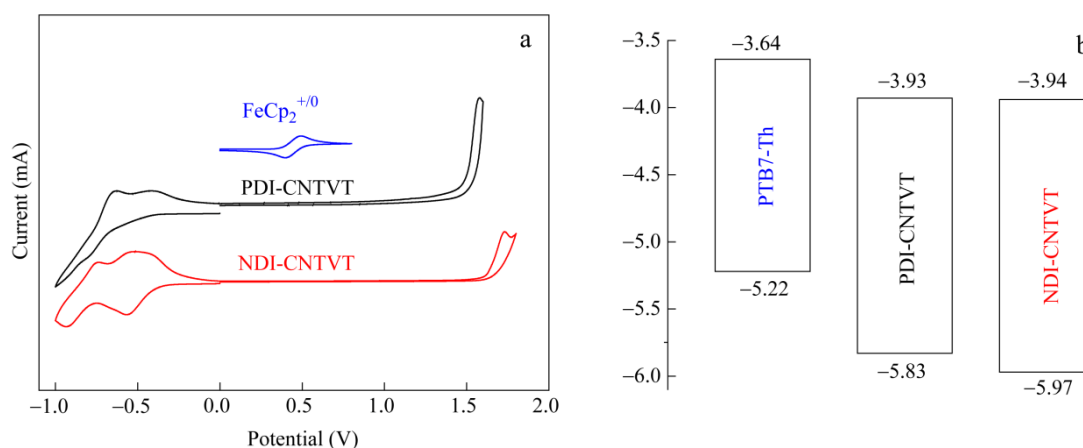


Fig. 3 Cyclic voltammograms (a) and energy alignment for the polymers (b)

Photovoltaic Properties

We fabricated BHJ OSCs with a structure of ITO/PEDOT:PSS/donor:acceptor/Ca/Al by using PTB7-Th as a donor to blend with the polymer acceptors. The V_{oc} , J_{sc} , fill factor (FF) and PCE data of OSCs with different PTB7-Th:polymer acceptor weight ratios are summarized in Table 3. The J - V curves of the best OSCs are shown in Fig. 4(a). For the PTB7-Th:PDI-CNTVT blend, when the D/A ratio is 1:1, the device shows the best performance with V_{oc} of 0.66 V, J_{sc} of $7.32 \text{ mA}\cdot\text{cm}^{-2}$, FF of 35.8% and PCE of 1.74%. When 1% 1,8-diiodooctane (DIO) is added into the blend, the PCE decreases. For the PTB7-Th:NDI-CNTVT blend, when the D/A ratio is 2:1, the device shows the best performance with V_{oc} of 0.69 V, J_{sc} of $8.39 \text{ mA}\cdot\text{cm}^{-2}$, FF of 47.7%

and PCE of 2.76%. When 1% DIO is added into the blend, the J_{sc} , FF and PCE is improved to 10.6 mA·cm⁻², 52.6% and 3.80%, respectively. The devices exhibit low V_{oc} of 0.66–0.69 V, probably due to the low LUMO levels (−3.94 and −3.93 eV) of the two new polymer electron acceptors.

Table 3 Performance of the OSCs based on PTB7-Th (D) and polymer acceptor (A) blends

Acceptor	PTB7-Th:acceptor (<i>W:W</i>)	DIO (%)	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	FF (%)	PCE (%)	
						Best	Average
PDI-CNTVT	2:1	0	0.66	5.68	35.0	1.33	1.28
PDI-CNTVT	1:1	0	0.66	7.32	35.8	1.74	1.68
PDI-CNTVT	1:2	0	0.69	6.28	33.7	1.46	1.39
PDI-CNTVT	1:1	1	0.65	4.76	35.1	1.09	1.05
NDI-CNTVT	3:1	0	0.69	7.69	40.6	2.14	2.01
NDI-CNTVT	2:1	0	0.69	8.39	47.7	2.76	2.62
NDI-CNTVT	1:1	0	0.68	8.77	41.5	2.47	2.30
NDI-CNTVT	2:1	1	0.68	10.6	52.6	3.80	3.67

The IPCE spectra of the blended films are shown in Fig. 4(b). The OSCs based on two blended films exhibit a broad photoresponse extending from 300 nm to 800 nm. Compared with the PTB7-Th:PDI-CNTVT blend, the PTB7-Th:NDI-CNTVT blend shows larger IPCE value, which is consistent with the higher J_{sc} .

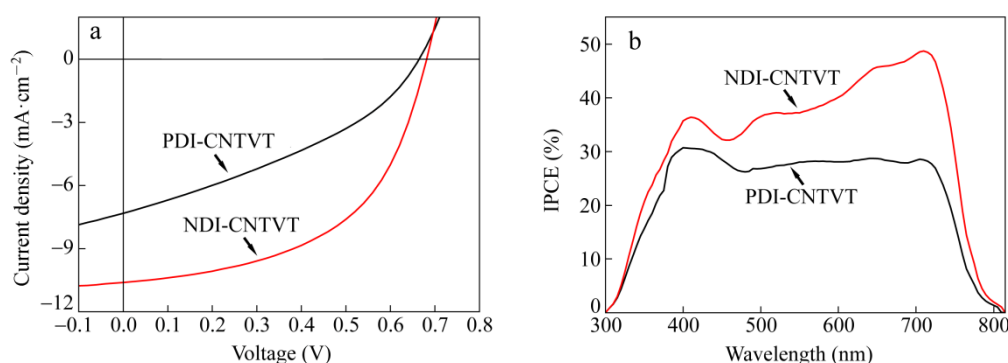


Fig. 4 J - V characteristics (a) and IPCE spectra of the best OSCs (b)

Hole and Electron Mobility

The hole and electron mobility of the blended films was measured *via* the SCLC^[46] method to understand the influence of the charge transport properties on the photovoltaic performance (Fig. 5). The PTB7-Th:PDI-CNTVT and PTB7-Th:NDI-CNTVT blends exhibit hole mobility of 4.7×10^{-5} and 1.4×10^{-4} cm²·V⁻¹·s⁻¹, electron mobility of 4.7×10^{-6} and 2.0×10^{-5} cm²·V⁻¹·s⁻¹, respectively (Table 4). The higher hole and electron mobility of PTB7-Th:NDI-CNTVT blend is beneficial to the higher J_{sc} and FF. The XRD patterns of NDI-CNTVT shows stronger π - π stacking peak at $2\theta = 23^\circ$ (Fig. 6) than PDI-CNTVT owing to the more planar backbone, which facilitates charge transport.

Table 4 SCLC data of hole-only and electron-only devices based on the blends

Blend	μ_h (cm ² ·V ⁻¹ ·s ⁻¹)	μ_e (cm ² ·V ⁻¹ ·s ⁻¹)
PTB7-Th:PDI-CNTVT (1:1, <i>W:W</i>)	4.7×10^{-5}	4.7×10^{-6}
PTB7-Th:NDI-CNTVT (2:1, <i>W:W</i> ; 1% DIO)	1.4×10^{-4}	2.0×10^{-5}

Film Morphology

The morphology of the BHJ active layer was examined using atomic force microscope (AFM) in the tapping mode. Figure 7 shows the AFM height images and the phase images of PTB7-Th:PDI-CNTVT (1:1, *W:W*) and PTB7-Th:NDI-CNTVT (2:1, *W:W*; 1% DIO) blended films. The PTB7-Th:PDI-CNTVT blended film exhibits

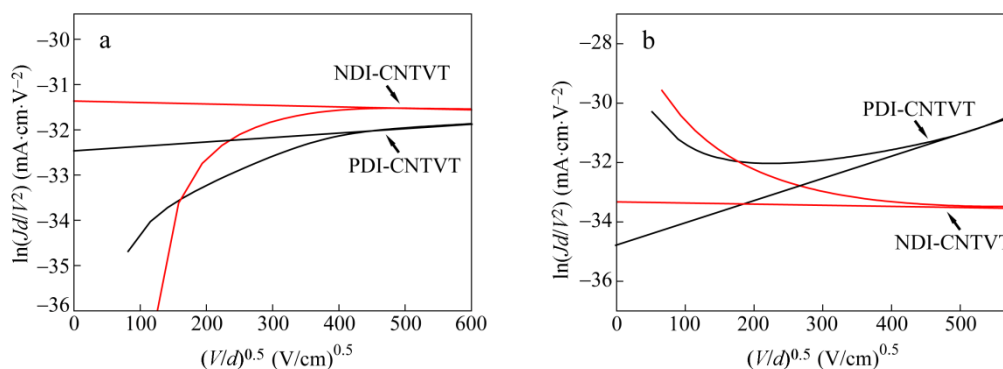


Fig. 5 J - V characteristics measured under dark for (a) hole-only and (b) electron-only devices based on PTB7-Th:polymer acceptor blended films

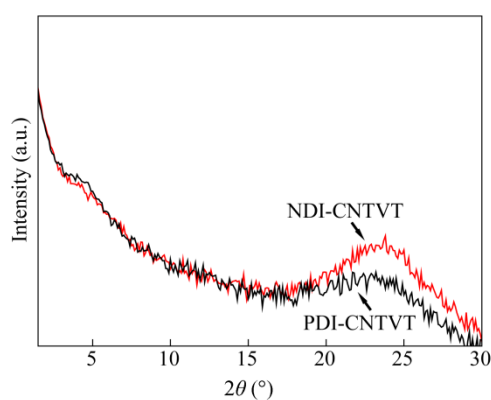


Fig. 6 XRD patterns of the polymers

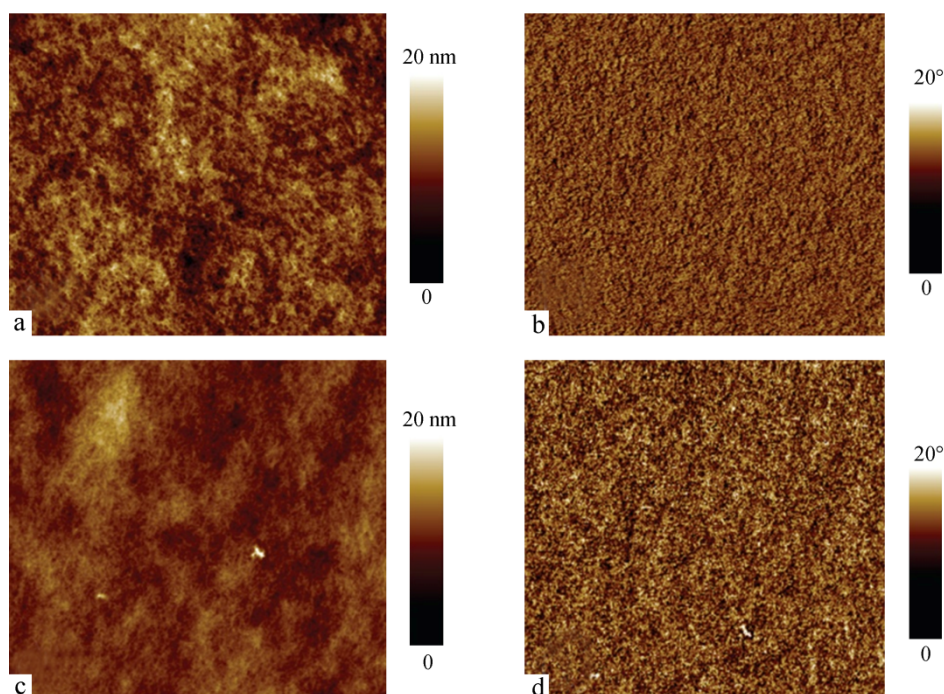


Fig. 7 AFM height (a, c) and phase images (b, d) of PTB7-Th:PDI-CNTVT (1:1, $W:W$) (a, b) and the PTB7-Th:NDI-CNTVT (2:1, $W:W$; 1% DIO) (c, d) blended films spin-coated on ITO/PEDOT:PSS substrates (The scan size for all images is $1\ \mu\text{m} \times 1\ \mu\text{m}$.)

smooth and uniform surface with root-mean-square (RMS) roughness value of 0.67 nm, while PTB7-Th:NDI-CNTVT shows rougher surface with larger RMS roughness of 1.14 nm. The PTB7-Th:PDI-CNTVT blend exhibits smaller phase separation than the PTB7-Th:NDI-CNTVT blend, thus leading to worse charge transport, more serious bimolecular recombination, and lower FF.

CONCLUSIONS

Two polymer acceptor materials based on CNTVT as a donor unit and PDI or NDI as an acceptor unit have been developed for the application in the solution-processed OSCs. Both polymers exhibit good solubility, broad absorption, similar LUMO energy level and similar V_{oc} in the OSCs. The NDI polymer has more planar backbone and stronger π - π stacking than the PDI polymer, which facilitates charge transport. Relative to the PTB7-Th:PDI-CNTVT blend, the PTB7-Th:NDI-CNTVT blend shows higher mobility and better balanced charge transport, leading to the higher J_{sc} and higher FF. The OSCs based on the PTB7-Th:NDI-CNTVT blend display the best PCE of up to 3.80%, much higher than that of the PTB7-Th:PDI-CNTVT blend (1.74%).

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