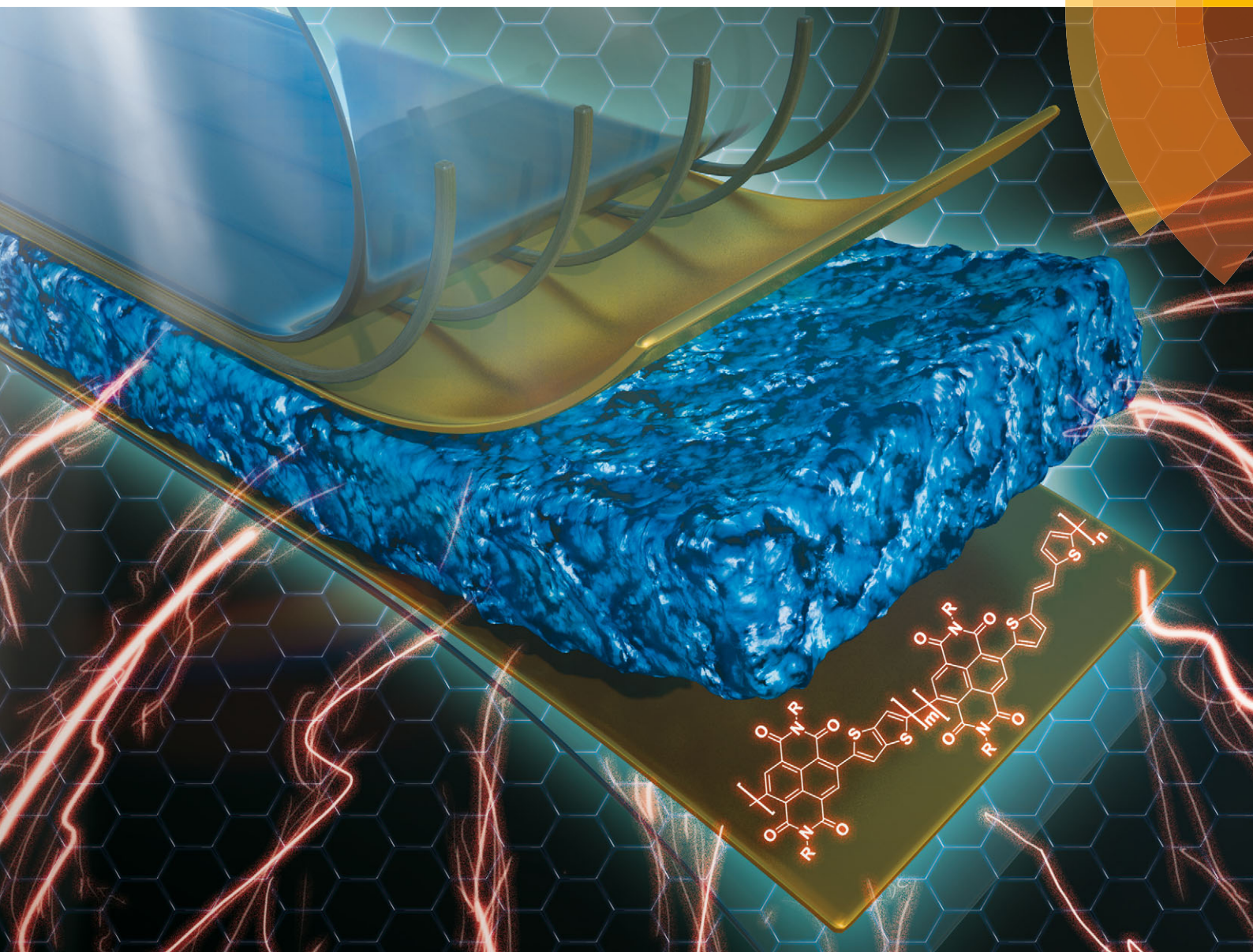


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A random copolymer approach to develop nonfullerene acceptors for all-polymer solar cells†

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We report a donor–acceptor type of random copolymer PNDI-TT-TVT as a replacement for fullerene-based acceptors in organic solar cells (OSCs). PNDI-TT-TVT is composed of naphthalene tetracarboxylic diimide (NDI) acceptor units, randomly distributed thieno[3,2-*b*]-thiophene (TT) and thienylene-vinylene-thienylene (TVT) donor units. OSCs fabricated from a blend of PTB7-Th and PNDI-TT-TVT exhibit a power conversion efficiency of 4.86%, which is significantly higher than the PCEs of the devices based on alternating copolymers of PNDI-TT and PNDI-TVT. The results indicate that random copolymerization is a promising approach to develop novel polymer acceptors for organic photovoltaics.

All-polymer solar cells (all-PSCs) that utilize a mixture of electron-donating and electron-accepting polymers as the photo-active layers have attracted significant research interest. The all-PSCs are superior to conventional polymer/fullerene based solar cells due to (i) the potential to tune the molecular energy levels and bandgaps of the acceptors, (ii) light harvesting and exciton generation by both donors and acceptors and (iii) an improvement of device stability by replacing optically instable fullerenes.^{1–3} Although significant progress has been made for all-PSCs, the power conversion efficiencies (PCEs) of these devices are still limited to 7%,^{4,5} while those using polymer/fullerene blends can reach above 10%.^{6–8} To date, the most intriguing n-type conjugated polymers in all-PSCs are those with strong electron-withdrawing naphthalene tetracarboxylic diimides (NDIs) on the backbones for their high electron affinities (EAs) and high electron mobilities.^{9,10} Nevertheless, the performance of all-PSCs using NDI-based n-type polymers is still far below that of typical fullerene-based solar cells.⁵ The low PCEs for all-PSCs are attributed to many undesirable features of the bulk heterojunction (BHJ) films, *e.g.* mismatch

energy levels between the donors and acceptors, a large phase-separated domain size, inhomogeneous compositions in each phase, a low degree of ordering of polymer chains, *etc.*, which hamper the generation and transportation of free charge carriers in the films and thus the device performance.^{11–13} Hence, developing new materials that may address the above-listed issues is a current research focus.^{14,15} Synthesizing n-type polymers with new building blocks is an attractive approach.¹⁶ The other instant strategy is to construct random conjugated copolymers based on multiple existing building blocks, with which a wide range of new materials of controlled physical/chemical properties could be achieved. High performance random copolymer donors based on this approach have been developed for solar cells previously.^{17–21} However, very few acceptors with such a structure have been reported.^{22,23} It is expected that the bandgaps, the highest occupied molecular orbital (HOMO) and the low-lying lowest unoccupied molecular orbital (LUMO) energy levels, charge transport properties, and photovoltaic behaviors of random copolymer acceptors could be fine-tuned through adjusting the component ratio of the building blocks by simply varying the monomer feed ratio during synthesis.

In this communication, we present the synthesis of a novel random copolymer acceptor PNDI-TT-TVT from three well-known building blocks and its application in all-PSCs. NDI was employed as the electron deficient unit, and randomly distributed thieno[3,2-*b*]thiophene (TT) and thienylene-vinylene-thienylene (TVT) were used as the electron rich moieties in the donor–acceptor (D–A) type of polymer acceptors (Fig. 1). Alternating copolymers PNDI-TT and PNDI-TVT were prepared for comparison. Both of the donor units TT and TVT are universally used in alternating D–A polymers. Such a structure allows better coplanarity of the polymer backbone, which reduces the packing distance between the polymer chains, promotes long-range ordering of the molecules and increases the charge carrier mobility in the films.^{24,25} For example, the alternating copolymers PNDI-TT and PNDI-TVT (Fig. 1) have exhibited high electron motilities in transistors and served as acceptors in all-PSCs.²⁶ Recently, Kim *et al.* reported that all-PSCs using PNDI-TVT as the acceptor presented

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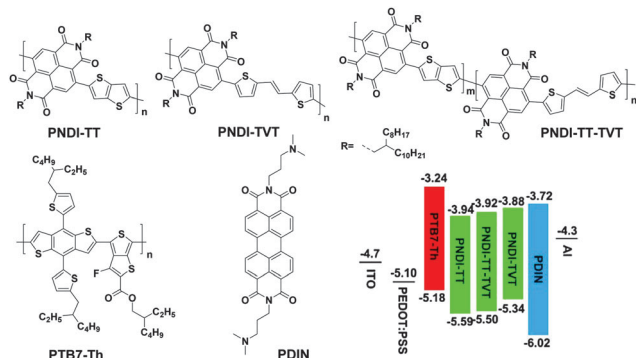


Fig. 1 Chemical structures of the materials used in the solar cell stacks and the energy diagram showing their respective energy levels.

decent performance.²⁷ Here, we report a significant PCE increment in all-PSCs by introducing a new random copolymer acceptor (PNDI-TT-TVT) instead of alternating copolymers PNDI-TT or PNDI-TVT. The findings in this work suggest that the random copolymer approach is a simple and effective approach to develop novel high performance n-type polymers for organic photovoltaics.

PNDI-TT-TVT was synthesized *via* the Stille coupling reaction between 4,9-dibromo-2,7-bis(2-octyldodecyl)-benzo[*lmn*][3,8]-phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone, 2,5-bis(trimethylstannyl)-thieno[3,2-*b*]-thiophene, and (*E*)-1,2-bis(5-(trimethylstannyl) thiophen-2-yl)-ethene in a molar ratio of 2 : 1 : 1 with a yield of 79%. Following the same method, PNDI-TT and PNDI-TVT were synthesized from the respective monomers in similar yields. The successful synthesis of the polymers was evidenced by ¹H NMR and gel permeation chromatography (GPC) (ESI[†]). The m/n ratio of PNDI-TT-TVT was 1 : 1, which was obtained from the ¹H NMR spectrum of PNDI-TT-TVT. The weight average molecular weight (*M_w*), number average molecular weight (*M_n*) and polydispersity index (pdi, *M_w*/*M_n*) of the polymers were measured using GPC against polystyrene standards in *o*-dichlorobenzene (DCB) at 120 °C. PNDI-TT, PNDI-TT-TVT, and PNDI-TVT had *M_n* values of 26.7, 36.5 and 31.4 kDa with pdi of 1.5, 1.6 and 1.6, respectively. The three copolymers exhibit excellent thermal stability with a 5% weight loss between 438 and 441 °C measured by thermogravimetric analysis (TGA) (Fig. S2, ESI[†]). The DSC trace for PNDI-TVT exhibits a very sharp endothermic peak on heating at 267 °C and an exothermic peak upon cooling at 256 °C (Fig. S2b, ESI[†]), which are attributed to the melting and crystallization transitions of the polymer.²⁸ The sharp endothermic and exothermic peaks of DSC trace for PNDI-TVT indicate that PNDI-TVT had better crystallinity. No obvious endothermic peak and exothermic peak are found for PNDI-TT. It is interesting to note that PNDI-TT-TVT, which contains both TT and TVT building blocks in the polymer, demonstrates a very broad endothermic band on heating and an exothermic band on cooling and peaked at 289 °C and 284 °C respectively in the DSC trace. The significant differences of the DSC traces for the three polymers suggest TT and TVT units were randomly distributed within the PNDI-TT-TVT backbone without long PNDI-TVT polymeric blocks.

The UV-vis absorption spectra of the three polymers in dilute chloroform and as thin films (95–110 nm on glass) are shown in Fig. 2. In solution, each polymer exhibited typical NDI-based

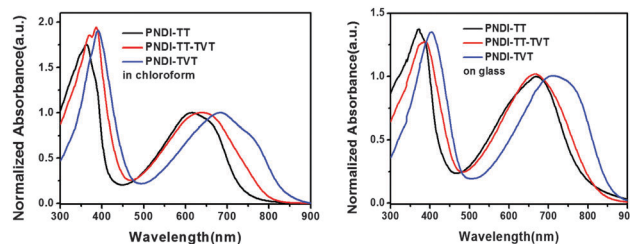


Fig. 2 UV-vis absorption spectra of the polymers in chloroform solution (left) and as thin films on glass (right).

D-A polymer absorptions with two distinct bands between 300–450 nm and 500–800 nm, which are assigned to be the π - π^* transitions and an intramolecular charge transfer (ICT) band, respectively.²⁹ The ICT absorption band in the solution of the random copolymer PNDI-TT-TVT showed a red-shift of 26 nm and a blue-shift of 43 nm compared with that of PNDI-TT and PNDI-TVT, respectively. The absorption spectra of the polymers in thin films were red-shifted compared with those in solutions, which indicates the aggregation of the polymer chains in the solid state. The optical bandgaps were estimated using the absorption edges of the thin films and found to be 1.65, 1.58, and 1.46 eV for PNDI-TT, PNDI-TT-TVT, and PNDI-TVT, respectively (Table S1, ESI[†]). The optical bandgap of PNDI-TT-TVT lies between those of PNDI-TT and PNDI-TVT polymers, suggesting that fine-tuning of the bandgap of the random copolymer is feasible by adjusting the ratio of TT to TVT.

The redox properties of the polymers were investigated using cyclic voltammetry (CV) on the polymer films. The LUMOs were estimated from the onset of the reduction waves, referred to the Ag/AgCl redox couple, and were found to be -3.94, -3.92 and -3.88 eV for PNDI-TT, PNDI-TT-TVT, and PNDI-TVT, respectively (Table S1, ESI[†]). The low lying LUMO levels suggest that all the three polymers are suitable for serving as electron acceptors. The similarity among their LUMO energy levels suggested that the LUMO distributions of the polymers were dominated by the NDI units and can be slightly modulated by the donor units incorporated. The HOMO levels of the three polymers were calculated using the polymer optical bandgaps and their LUMOs. They are -5.59, -5.50, and -5.34 eV for PNDI-TT, PNDI-TT-TVT, and PNDI-TVT, respectively. An energy level diagram for the polymer acceptors is shown in Fig. 1. Similar as the bandgap of PNDI-TT-TVT, the HOMO and LUMO levels of this random copolymer also lie between the two alternating copolymers of PNDI-TT and PNDI-TVT. The HOMO and LUMO levels of the polymer acceptors match well with the donor polymer PTB7-Th and the interfacial material PDIN.

The photovoltaic behaviors of the three polymer acceptors were characterized in all-PSC devices using PTB7-Th as the donor material. Such devices were fabricated in a conventional configuration of ITO/PEDOT:PSS/PTB7-Th:acceptor/PDIN/Al and tested under an AM 1.5G simulated solar light at 100 mW cm⁻². PEDOT:PSS was used as a hole injection layer and 2,9-bis(3-(dimethylamino)propyl)anthra[2,1,9-*def*:6,5,10-*d'**e'**f'*']diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (PDIN) as a cathode interlayer.³⁰ *o*-Dichlorobenzene was used as the solvent due to the good solubility to the polymers.

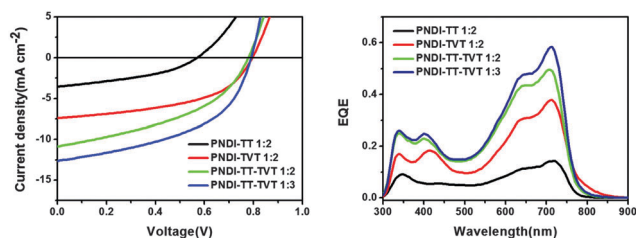


Fig. 3 J - V curves (left) and EQE spectra (right) of PTB7-Th:polymer acceptor solar cells with a device structure ITO/PEDOT:PSS/PTB7-Th:polymer acceptor/PDIN/Al.

The J - V curves of the devices are shown in Fig. 3. V_{OC} , J_{SC} , FF, and PCEs are summarized in Table 1. The devices using alternating copolymers (PNDI-TT and PNDI-TVT) exhibited inferior performance. The optimized device using a blend of PTB7-Th:PNDI-TT (2:1 wt%) demonstrated a PCE of 0.79% with a V_{OC} of 0.570 V, J_{SC} of 3.56 mA cm⁻², and FF of 0.391. Under the same conditions, the optimized device using PNDI-TVT as the acceptor exhibited an improved PCE of 2.94% with a J_{SC} of 7.41 mA cm⁻², V_{OC} of 0.795 V and FF of 0.499. The all-PSC using a blend of PTB7-Th:PNDI-TT-TVT (2:1 wt%) showed a significant improvement in PCE when compared with those using PNDI-TT or PNDI-TVT. The device exhibited a PCE of 3.65% at a J_{SC} of 10.86 mA cm⁻², V_{OC} of 0.779 V and FF of 0.431, which was 265% and 24% higher than those devices based on the two alternating copolymers. The all-PSCs containing PNDI-TT-TVT were further optimized by adjusting the PTB7-Th:PNDI-TT-TVT weight ratio to 3:1. This led to device PCE of up to 4.86% (J_{SC} = 12.66 mA cm⁻², V_{OC} = 0.790 V and FF = 0.486). The significant improvement was attributed to the increased J_{SC} . The devices fabricated from the random copolymer PNDI-TT-TVT exhibited higher EQEs over the wavelength range from 300 nm to 800 nm than those using PNDI-TT and PNDI-TVT, which is consistent with the higher J_{SC} values observed for the PNDI-TT-TVT based devices. The EQE spectra in the high energy region (300–500 nm) indicate clearly that photo excitation also occurred within the acceptor and contributed to the power conversion. Notably, these devices were only fabricated using a simple spin-coating process and optimized by tuning the donor-to-acceptor ratio. Further improvement in the device performance is expected through formulation (*i.e.* solvents and additives optimization) and process optimization (*i.e.* thermal annealing and/or solvent annealing). The results obtained indicate the development of random conjugated copolymers is a promising method to synthesize active materials for high performance organic solar cells.

Space-charge-limited current (SCLC) measurement was carried out to investigate the bulk charge transport in the blend films

toward a better understanding of the photovoltaic properties of the materials. Hole-only devices with a structure of ITO/PEDOT:PSS/blend/MoOx/Al and electron-only devices with a structure of ITO/ZnO/blend/Ca/Al were fabricated and characterized. Charge carrier mobilities obtained from the SCLC fittings to the current-voltage characteristics of the hole-only devices (Fig. S4a, ESI†) and electron-only devices (Fig. S4b, ESI†) are summarized in Table S2 (ESI†). The blend of PTB7-Th:PNDI-TT (2:1 wt%) exhibited hole and electron mobilities of 1.56×10^{-5} cm² V⁻¹ s⁻¹ and 2.89×10^{-5} cm² V⁻¹ s⁻¹, respectively (μ_h/μ_e = 0.54). The hole mobility and electron mobility of PTB7-Th:PNDI-TVT (2:1 wt%) blend films were found to be 3.23×10^{-5} cm² V⁻¹ s⁻¹ and 4.23×10^{-5} cm² V⁻¹ s⁻¹ (μ_h/μ_e = 0.76), respectively. The all-PSC using a blend of PTB7-Th:PNDI-TT-TVT (2:1 wt%) exhibited a better balanced charge transport (μ_h = 2.78×10^{-5} cm² V⁻¹ s⁻¹, μ_e = 3.45×10^{-5} cm² V⁻¹ s⁻¹, μ_h/μ_e = 0.81) when compared with PNDI-TT and PNDI-TVT based devices. The blend of PTB7-Th:PNDI-TT-TVT (3:1 wt%) demonstrated the highest charge mobilities and the most balanced charge transport properties (μ_h = 4.34×10^{-5} cm² V⁻¹ s⁻¹, μ_e = 4.26×10^{-5} cm² V⁻¹ s⁻¹, μ_h/μ_e = 1.02). The improvement in charge transport in the PNDI-TT-TVT based devices may be the key factor that accounts for the higher J_{SC} values.

Atomic force microscopy (AFM) was used to investigate the surface morphology of the active layers of the devices. AFM topographical images (2 μ m \times 2 μ m) are shown in Fig. 4. There was no significant difference among the films containing different polymeric acceptors. However, the surface roughness for these films was found to be 2.01, 1.92, and 1.77 nm for films with PNDI-TT, PNDI-TVT, and PNDI-TT-TVT, respectively (2:1 D/A by weight). The roughness of the active layer may form some shunt paths in the devices and cause charge accumulation/charge recombination at the interface between the active layer and the cathode. This should partially account for the low V_{OC} for the device of PTB7-Th:PNDI-TT and low J_{SC} for both of the devices of PTB7-Th:PNDI-TT and PTB7-Th:PNDI-TVT.^{31,32} Apparently, the lower surface roughness is correlated with the higher J_{SC} of the devices, thus the superior PCEs and more balanced hole and electron motilities in the films. As the ratio

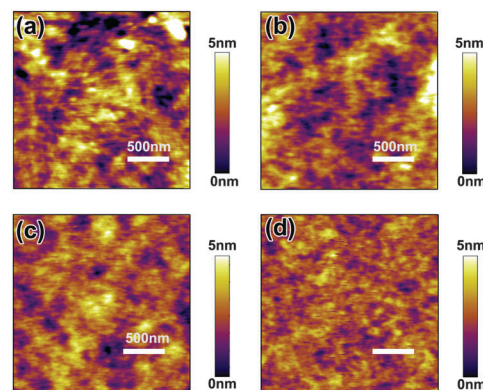


Fig. 4 AFM topographical images (2 μ m \times 2 μ m) of the surfaces of the all-PSCs: (a) PTB7-Th:PNDI-TT (2:1), (b) PTB7-Th:PNDI-TVT (2:1), (c) PTB7-Th:PNDI-TT-TVT (2:1), and (d) PTB7-Th:PNDI-TT-TVT (3:1).

Table 1 Photovoltaic properties of the devices

Donor:acceptor (w/w)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE ^a (%)
PTB7-Th:PNDI-TT (2:1)	0.570	3.56	39.1	0.79 (0.65 \pm 0.14)
PTB7-Th:PNDI-TVT (2:1)	0.795	7.41	49.9	2.94 (2.75 \pm 0.19)
PTB7-Th:PNDI-TT-TVT (2:1)	0.779	10.86	43.1	3.65 (3.56 \pm 0.09)
PTB7-Th:PNDI-TT-TVT (3:1)	0.790	12.66	48.6	4.86 (4.80 \pm 0.06)

^a The PCEs were averaged over 8 devices.

of PTB7-Th:PNDI-TT-TVT was increased to 3:1, the surface roughness further decreased to 1.62 nm. The lower surface roughness suggested enhanced the mixing between the donor (PTB7-Th) and the acceptor polymer (PNDI-TT, PNDI-TVT, or PNDI-TT-TVT), which is beneficial to the devices by creating more favorable phase-separated domains with more efficient exciton dissociation and charge migration. This helps explaining the significantly higher J_{SC} and PCE values observed for PNDI-TT-TVT based devices.³³ However, it should be noted that the blend surface morphology does not represent the bulk morphology due to the possible blends vertical phase segregation of the donor and acceptor polymers.³⁴ Therefore, further investigation of the correlation between the blend surface and bulk morphologies is necessary in the future.

Conclusions

In summary, we have developed a random donor-acceptor (D-A) type of semiconducting copolymer PNDI-TT-TVT, which contains NDI as the acceptor unit and randomly distributed TT and TVT as the donor units. The BHJ solar cells using the blends of PTB7-Th:PNDI-TT-TVT showed a high PCE of 4.86%. The PNDI-TT-TVT based devices exhibited higher and more balanced charge mobility, subsequently, a significant increase in device performance, compared to devices using the corresponding alternating copolymers. The random copolymerization method reported here is a simple and immediate approach to develop novel n-type materials using state-of-the-art building blocks with desired chemical/physical properties for OPV applications. Systematic work on tuning the composition and properties of the copolymers and their photovoltaic behaviors is under way, and will be reported shortly.

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