Macromolecules

Two-Dimensional Conjugated Polymer Based on sp²-Carbon Bridged Indacenodithiophene for Efficient Polymer Solar Cells

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S Supporting Information

ABSTRACT: Molecular electronic structure plays a vital role in the photovoltaic performances in polymer solar cells (PSCs) due to their influences on light-harvesting, charge carrier transfer, $\pi - \pi$ stacking, etc. Indacenodithiophene as a star unit has been well studied in PSCs; various structural derivation methods have been tried, but they are still not efficient in improvement of power conversion efficiencies (PCE) due to the narrow optical absorptions. In this contribution, a novel planar DMIDT with extended lateral π -electron delocalization is efficiently synthesized via introduction of sp² hybrid carbons as the bridge atoms. Based on this novel building block, a twodimensional conjugated polymer PDMIDT-TPD is prepared, and the unique structure improves the conjugation at the lateral direction, enlarges the electron delocalization area, and greatly broadens the absorption spectrum with a full coverage from 350 to 700 nm. Finally, a PCE of 8.26% is achieved when blended with PC71BM, which is the highest result among the IDT-based



polymer donors. Meanwhile, PDMIDT-TPD also presents good compatibility with the non-fullerene acceptor, and a preliminary PCE of 6.88% is obtained. In all, this work not only provides an excellent donor material but also offers a general and simple derivation strategy for fused aromatic building blocks.

1. INTRODUCTION

Polymer solar cells (PSCs) have attracted more and more attention due to the relatively high efficiency, easy fabrication, low cost roll-to-roll process, and light weight. The impressive power conversion efficiencies (PCEs) have been achieved over 12% for single junction PSCs by several groups.¹⁻³ Up to now, great efforts have been devoted to modulating the conjugated structures of polymer donors in the active layers, which have strongly advanced the development of this field in the past decade. Generally, the open-circuit voltage (V_{oc}) , short-circuit current density (J_{sc}) , and fill factor (FF) are crucial parameters to impact the final PCEs, which are closely related to the chemical and electronic structures of the polymer donors. The exploration of effective polymer donors with appropriate bandgaps and frontier molecular orbital energy levels remains a major challenge for PSCs.

Currently, construction of donor-acceptor (D-A) alternating copolymers is the most effective way for polymer donor designing in PSCs due to its tunability at the bandgaps, energy levels, absorption spectra, etc. In order to achieve better PCEs and higher mobility in solid films, planar polymer chains are required for close packing, so the rigid and coplanar ladder-type aromatic molecules have been utilized as D or A sections in the backbones to enhance the coplanarity of the final polymer main chains. Indacenodithiophene (IDT), a popular electrondonating building block, has been widely used in p-type

conjugated polymers for organic field effect transistors⁴ and PSCs applications.^{5–10} Various chemical modification methods have been applied on IDT skeleton by altering the bridging atoms,^{11,12} replacing the central benzene ring or end-capped thiophene with larger fused aromatic rings, and/or changing the substituted side chains to generate a variety of π -conjugation extended ladder-type aromatic building blocks for more planar conjugated polymers. The motivation is to prevent rotational disorder to reduce reorganization energy, facilitate π -electron delocalization along the polymer backbones, enhance the charge carrier mobility, and reduce their bandgaps by means of extending the conjugation length of the ladder-type donor unit. Unfortunately, these derivation strategies can only enhance the carrier mobility¹³ but cannot broaden the absorption spectrum. The narrower absorption for IDT-based polymers will restrict the enhancement of J_{sc} and thus photovoltaic performances, resulting in PCEs around 6% for most IDT-derivative-based PSCs.^{12,14,15}

In the meanwhile, two-dimensional (2D) conjugated polymers possess extended conjugation at two directions and may provide broadened absorption spectra, better interchain $\pi - \pi$ overlapping, and higher charge mobility compared with

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Scheme 1. Synthesis of DMIDT Monomer (Compound 7) and Polymers (PDMIDT-TPD and PIDT-TPD)



their one-dimensional conjugated counterparts. Benzodithiophene (BDT)-based conjugated polymer donors as one typical representative of the 2D-conjugated polymers have been well studied and made great progress in PSCs by Li^{16-19} and Hou^{20,21} et al. Via replacing the conjugated side chains, a variety of BDT-based 2D-conjugated polymers have been prepared;^{18,22} very recently, a trialkylsilyl-substituted 2D polymer J71 has been reported, and a PCE of 11.41% with a J_{sc} of 17.32 mA cm⁻² is achieved,¹⁶ demonstrating that 2D strategy is effective at broadening the absorption spectra. In addition, we have previously reported that planar conjugated polymers could be obtained via the replacement of sp³hybridized carbon at 9-position of fluorene by sp²-hybridized carbon, which also favors the improvement of the $J_{\text{sc}}^{-23,24}$

Considering the fascinating properties of 2D conjugated polymers and the weak light-harvesting abilities for IDT-based polymers, in this article, we designed and developed a novel methylene-modified IDT building block (DMIDT) as shown in Scheme 1, in which two ethylene bridges were grafted onto the conjugated IDT main core and the sp²-hybridized bridged carbon atoms were successfully introduced to the novel building block. Very recently, a similar idea was reported by Li, and a PCE of 7.3% was obtained.²⁵ In addition, four flanking phenyl rings at lateral direction are effectively conjugated with the IDT segment in our DMIDT unit, which may enlarge the π -electron delocalization region and broaden the absorption spectrum. Such structural modification could greatly reduce the steric hindrance of the phenyl rings and generate more planar structures, resulting in improved charge transport mobility. Finally, this novel building block was first applied for the D-A polymer; since supramolecular interactions have been widely utilized in conjugated backbones as soft conformational "locks"

(e.g., S…O, F…H, F…S, etc.)^{26,27} to generate planar π conjugated structures for higher performance PSCs, thieno-[3,4-*c*]pyrrole-4,6-dione (TPD) was selected as the electronaccepting comonomer in this work in virtue of the S…O supramolecular locks in between the ending thiophenes of DMIDT and carbonyl groups from the TPD unit. Meanwhile, a polymer based on IDT and TPD was prepared as the control.

Benefiting from the two perpendicular ethylene side bridge, which are in the same plane with the conjugated backbone, could greatly reduce the steric hindrance for $\pi - \pi$ stacking (as shown in Figure 1) and provide better lateral conjugation, polymer PDMIDT-TPD presents a broader and red-shifted absorption spectrum compared with the control polymer (PIDT-TPD). The syntheses, thermal stability, photophysical properties, electrochemical properties, and DFT calculations along with the photovoltaic device performances of the two polymers are described. Finally, a PCE of 8.26% is achieved by PDMIDT-TPD when blended with PC71BM, which is the champion PCE result among the IDT-based polymer donors to the best of our knowledge. In the meantime, this polymer also presents good compatibility with non-fullerene acceptor, and a preliminary PCE of 6.88% is obtained when blended with ITIC, indicating a universal utilization of this polymer.

2. RESULTS AND DISCUSSION

Synthesis. The synthetic routes of all the monomers are shown in Scheme 1. Starting from the commercially available compound 1, two flanking thiophene rings could be attached via Suzuki cross-coupling in a yield of 52%. After the hydrolysis and Friedel–Crafts reactions, the diketone precursors (5) could be obtained as a dark-blue solid in a yield of 83%. Then, the crucial tetrabromide intermediate (6) carrying two perpendic-



Figure 1. Molecular structures (a) IDT and (b) DMIDT; front and side view of crystal structures for IDT (c, e) and DMIDT (d, f); carbon and sulfur atoms are depicted with thermal ellipsoids set at 50%; crystal packing structures of IDT (g) and DMIDT (h).

ular ethylene bridges could be generated as red solids in a yield of 80% via the Corey–Fuchs reaction in the presence of CBr_4 and triethoxyphosphine. Subsequently, Suzuki cross-coupling of **6** and 4-hexylphenylboronic ester afforded the key intermediate DMIDT in a yield of 55%. Finally, via the deprotonation and quenching with trimethylstannanylium chloride, the monomer (7) could be prepared as red solids in a yield of 60%. Compound **8** is prepared according to the literature,¹⁵ and the final polymers are prepared via the microwave-assisted Stille polymerization in *o*-xylene/DMF (5:1), aiming at higher molecular weights.

Molecular Weights and Thermal Properties. With enough alkyl chains attached on the conjugated backbones, both of the two polymers displayed good solubility in chloroform (CF), chlorobenzene (CB), and 1,2-dichlorobenzene (DCB) at room temperature. The GPC results are summarized in Table S5, and the number-averaged molecular weights for PIDT-TPD and PDMIDT-TPD are 67.2 and 13.9 kg/mol, respectively. Both of the two polymers are thermally stable below 400 °C as shown in Figure S12, and the 5% weight loss temperatures for PIDT-TPD and PDMIDT-TPD are 404 and 437 °C, respectively.

X-ray Crystal Structures. Fortunately, the molecular structures of IDT and DMIDT were obtained and confirmed by single-crystal X-ray analysis as shown in Figure 1, and both of the two molecules belong to space group triclinic P-1(2). In

Figure 1c, the two flanking hexylphenyl side groups are perpendicular to the IDT core along the z-direction (as shown in Figure 1c) due to the sp³-hybridized character of the bridged carbons, which will hinder the molecular packing of the IDT core. However, when the sp³-hybridized carbons are replaced by sp²-hybridized carbons in Figure 1d and the ethylene bridges are successfully grafted onto the IDT core along the *y*-direction, the steric hindrance of the two phenyl groups is greatly reduced. From the side view as shown in Figure 1f, DMIDT with a more planar structure is achieved, which may facilitate the molecular packing in solid state and enhance the charge carrier mobility. Meanwhile, their crystal packing structures are shown in Figure 1. Interestingly, the crystal for IDT grows along two directions, but there is only one packing style for DMIDT, which may lead to varied charge transport properties.

Table 1. Optical and Electrochemical Properties of thePolymers

| | solution | | film | | | | |
|----------------|------------------|---------------------------|-----------------------|---------------------------|-------------------------------|--------------|--------------|
| polymer | λ_{\max} | $\lambda_{ m onset}$ (nm) | λ_{\max} (nm) | $\lambda_{ m onset}$ (nm) | $E_{\rm g}^{\rm opt}$ (eV) | HOMO (eV) | LUMO (eV) |
| PIDT-TPD | 584 | 620 | 584 | 620 | 2.00 | -5.59 | -3.59 |
| PMDIDT- TPD | 597 | 688 | 640 | 700 | 1.77 | -5.46 | -3.69 |



Figure 2. Normalized optical absorption spectra of (a) PIDT-TPD and (b) PDMIDT-TPD: measured spectra in dilute CB solutions (red solid lines), spectra on quartz substrates (black solid lines), and spectra computed within the TD-DFT/PCM approaches based on CAM-B3LYP (dash dot lines). (c) Energy level diagrams of polymer donor, $PC_{71}BM$ and ITIC. (d) Cyclic voltammograms of polymer films in 0.1 M Bu_4NPF_6 -CH₃CN solutions at a scanning rate of 100 mV/s.

Photophysical and Electrochemical Properties. The UV-vis absorption spectra of PIDT-TPD and PDMIDT-TPD in chlorobenzene solution and/or on quartz substrates were measured, and very different absorption behaviors were observed as shown in Figure 2. The solution of polymer PIDT-TPD presented one narrow absorption band bearing two clear peaks at 538 and 586 nm, which is ascribed as the intramolecular charge transfer (ICT) peak, and no bathochromic shift was observed even in its thin film spectrum. Surprisingly, PDMIDT-TPD in both solution and as film exhibited a much broad absorption ranging from 350 to 700 nm with two bands, which is expected to enhance the I_{sc} of devices. A shorter wavelength band located around 350-490 nm (band II) may be attributed to $\pi \to \pi^*$ transitions in the polymer chains, and the longer wavelength band located around 490-700 nm (band I) can be ascribed to the strong intramolecular charge transfer (ICT) interactions. In thin film, a slightly redshifted ICT band and a sharp shoulder peak at 638 nm are observed; the bathochromic absorption might be attributed to the strong intermolecular interactions (interchain packing or aggregation) induced by the extended π -conjugated structure of DMIDT segments in the polymer backbones. In the meanwhile, the temperature-dependent absorption spectra (TD- $(Abs)^{28}$ in dilute solutions were carried for both polymers, and the results are shown in Figure S13. It is worth noting that these two polymers have similar main chains, but different optical bandgaps are obtained. PIDT-TPD belongs to the category of wide bandgap conjugated polymer with an E_g of 2.0 eV (estimated from the absorption edge in the thin films), whereas PMDIDT-TPD is classified as medium bandgap polymer with an E_{g} of 1.77 eV; such broad and red-shifted absorption character is expected for efficient PSCs with elevated J_{sc} .

Meanwhile, quantum chemistry calculations were performed with Gaussian 09 suite by the TD-DFT/PCM approach at the 6-31G(d,p) level to provide further insight into the transition

contributions to the UV-vis spectra. The predicted spectra are consistent with the experimental curves as shown in Figure 2 and the selected transition contributions are listed in Table S1. From the calculated results, it is clear that the main absorption band of PIDT-TPD is produced by excitations of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_3$, which are mainly associated with the HOMO \rightarrow LUMO and H-1 \rightarrow L+1 transitions, whereas the energy excitations and electron distributions for PDMIDT-TPD became slightly complicated. The band I at the long wavelength resulted from the low-lying energy excitation of $S_0 \rightarrow S_1$ associated mainly with the HOMO \rightarrow LUMO transition. As for the band II at the short wavelength, it is contributed by the combined higher energy excitations of $S_0 \rightarrow S_6$, $S_0 \rightarrow S_7$, and S_0 \rightarrow S₉ related to mixed transitions as shown in Table S1. Meanwhile, the frontier orbitals for PDMIDT-TPD depicted in Figure S10 demonstrated that the electron migration between the side chains and backbones is responsible for the varied absorption activity.

With the structural differences, these two polymers displayed varied electrochemical properties, which were investigated by cyclic voltammetry with a standard three-electrode electrochemical cell in acetonitrile solution containing 0.1 M Bu₄NPF₆ at room temperature under a nitrogen atmosphere with a scanning rate of 100 mV/s. Ag/AgNO3 was used as the reference electrode and a standard ferrocene/ferrocenium redox system was used as the internal standard. The CV curves of PIDT-TPD and PDMIDT-TPD are shown in Figure 2d, and their HOMO energy levels, which were calculated from the onset oxidation potential (E_{ox}) of these polymers according to the equations $E_{\text{HOMO}} = -e[(E_{\text{ox}} - E(F_c/F_c^+) + 4.8] \text{ (eV)})$, are -5.59 and -5.46 eV, respectively, indicating that both polymers should be good candidates as donor materials for high V_{oc} . The LUMO energy levels of PIDT-TPD and PMDIDT-TPD were calculated to be -3.59 and -3.69 eV, which are higher than that of PC71BM, guaranteeing the photoinduced electron efficiently transfers from the donor to



Figure 3. Top (a, b), front (c, d), and side (e, f) views for the trimers for PIDT-TPD and PDMIDT-TPD; (g) XRD patterns of PIDT-TPD and PDMIDT-TPD films.



Figure 4. (a) J-V curves and (b) EQE curves of PSCs fabricated from blend of polymer and PC₇₁BM based on the device structure of ITO/ PEDOT:PSS/poly mer:PC₇₁BM/LiF/Al. (c) J-V curves and (d) EQE curves for PSCs fabricated from polymers and ITIC blend based on the inverted device structure of ITO/ZnO/polymer:ITIC/MoO₃/Ag.

acceptor. In addition, from the energy level diagram, polymer PMDIDT-TPD should be also compatible with ITIC as shown in Figure 2c.

X-ray Diffraction Analysis and Quantum Calculations for Chemical Structures. To evaluate the packing properties for the polymers, an X-ray diffraction (XRD) experiment was performed, and the results are shown in Figure 3. According to the single crystal structures for the two IDT building blocks, PDMIDT-TPD was supposed to present more planar polymer mainchains and closer packing than that of PIDT-TPD. Surprisingly, the XRD results for the polymer thin films did not follow the tendency of crystal orders, and contrary results are observed. As shown in Figure 3g, both of the PDMIDT-TPD and PIDT-TPD polymers exhibit two diffraction peaks in the XRD curves. The first peaks in a small-angle region, which reflex the distance of polymer backbones separated by the flexible side chains, are located at 2θ of 4.44° and 5.93° for PDMIDT-TPD and PIDT-TPD, corresponding to distances of 19.91 and 14.90 Å, respectively. The second peaks in the wideangle region are related to the π – π stacking distances between polymer backbones, which are located at 2θ of 19.07° for PDMIDT-TPD and 21.22° for PIDT-TPD, corresponding to

| Table 2. PSC Devices Based on ITO/PEDOT:PSS/Polymer:PC ₇₁ BM/LiF/A | /iF/Al |
|---|--------|
|---|--------|

| active layer | additive | $V_{\rm oc}$ (V) | $J_{\rm sc}~({\rm mA/cm^2})$ | FF (%) | PCE (av) (%) |
|--|---------------------------------|--------------------|--------------------------------------|-------------------|--------------------|
| PIDT-TPD:PC ₇₁ BM = $1:3^{a}$ | no | 1.03 | 10.30 | 49.82 | 5.27 (5.05) |
| PIDT-TPD:PC ₇₁ BM = $1:3^{a}$ | 3% DPE | 1.03 | 10.90 | 50.76 | 5.70 (5.52) |
| PDMIDT-TPD:PC ₇₁ BM = $1:1.5^{a}$ | no | 0.89 | 10.50 | 67.41 | 6.27 (6.16) |
| PDMIDT-TPD:PC ₇₁ BM = $1:1.5^{a}$ | 5% 1-CN | 0.89 | 13.40 | 69.83 | 8.26 (8.01) |
| PIDT-TPD:ITIC = $1:1^{b}$ | no | 1.08 | 4.26 | 35.73 | 1.65 (1.56) |
| PIDT-TPD: ITIC = $1:1^{b}$ | 3% DPE | 1.09 | 5.15 | 40.06 | 2.25 (2.03) |
| PDMIDT-TPD: ITIC = $1:1.5^{b}$ | no | 0.91 | 13.91 | 57.45 | 6.88 (6.70) |
| PDMIDT-TPD: ITIC = $1:1.5^{b}$ | 5% 1-CN | 0.89 | 4.41 | 36.94 | 1.46 (1.37) |
| ^a PSC cells based on ITO/PEDOT:PSS/ | polymer:PC ₇₁ BM/LiF | /Al device configu | aration. ^b PSC cells base | d on inverted ITC | D/ZnO/polymer:ITIC |

MoO₃/Ag device configuration.

distances of 4.65 and 4.19 Å, respectively. In summary, PIDT-TPD presented closer packing distances in both *d*-spacing and π - π stacking than that of the PDMIDT-TPD. To figure out the reason for this exceptional phenomenon, the geometry optimization via quantum chemistry calculation was applied to the trimers with density functional theory (DFT) at B3LYP/ 6-31G(d,p) employed as the basis set. Because of the strong S... O interactions produced by TPD in the final polymers,^{29,30} the conjugated backbones of the D-A polymer displayed planar or nearly flat configurations as shown in Figure 3. Similar to the Xray crystal results, the flanking side hexylphenyl groups are perpendicular to the IDT cores due to the sp³-hybridized character of the bridged carbons (Figure 3a), and it guarantees the side chains freely rotating and stretching in space without disturbing the conjugated main chains, leading to planar conjugated backbones as shown in Figure 3c. However, due to the steric hindrance of the neighboring 4-hexylphenyl side groups as shown in Figure 3b, the conjugated polymer backbones of PDMIDT-TPD are not produced as superplanar as anticipated, and a slightly twisted structure is obtained even when alkyl chains are replaced by methyl groups to simplify the calculations (Figure 3d). So in the real solid thin films, this repulsion effects may be amplified due to the longer hexyl chains and the polymer aggregation, resulting in larger dspacing and $\pi - \pi$ stacking distances for PDMIDT-TPD.

Photovoltaic Properties. Photovoltaic properties of these two polymers were first investigated in a typical device architecture of ITO/PEDOT:PSS/polymer:PC71BM/FLi/Al in this work. The performance of devices was optimized by varying of the weight ratio of polymer to PC₇₁BM, concentrations of blend solution, and additive effects. For polymer PIDT-TPD, the optimum ratio of polymer to PC₇₁BM was 1:3 (w/w), and its PCE reached 5.70% (V_{oc} = 1.03 V, J_{sc} = 10.90 mA/cm², and FF = 50.76%) with 3.0 vol % diphenyl ether (DPE) as the additive, which is higher than that of the similar conjugated structures reported in the literature.³¹ This photovoltaic performance improvement might be attributed to the elevated molecular weight by microwave assisted polymerization. As for PDMIDT-TPD, an enhanced Jsc of 13.40 mA/ cm² achieved a PCE of 8.26% with 1-chloronaphthalene (1-CN) as the effective additive. Obviously, neither the moderate molecular weight nor the crystallinity is the key factor for enhancing the performance of PDMIDT-TPD-based devices, but the extended lateral conjugation in each repeating unit, which can expanded π -delocalization area and enhance the hole mobility of blend films (vide infra), could be the main reason. The J-V curves and external quantum efficiencies (EQE) curves are shown in Figures 4a and 4b, where it can be seen that PDMIDT-TPD displayed a wide light harvesting region

and the maximum intensity has reached 70%. The detailed device optimization results are provided in Table S2 of the Supporting Information.

PSCs based on fused non-fullerene acceptors have aroused intensive interest in the past two years, and ITIC series molecules became the star acceptors with which the PCEs reached 12%.² However, donor materials that match well with both fullerene and non-fullerene acceptors are limited. So, the compatibility with ITIC for the two polymers was also investigated in this contribution, and the devices were fabricated in an inverted configuration of ITO/ZnO/polymer:-ITIC/MoO₃/Ag. Finally, the optimized ratio for control blend (PIDT-TPD:ITIC) changed to 1:1 (w/w); the V_{oc} was increased to 1.08 V, but the $J_{\rm sc}$ was restricted to 4.26 mA/ cm², leading to a lower PCE of 1.65% even after optimization as shown in Figure 4c and Table 2. However, PDMIDT-TPD presents better compatibility with ITIC and a PCE of 6.88% $(V_{oc} = 0.91 \text{ V}, J_{sc} = 13.91 \text{ mA/cm}^2$, and FF = 57.45%) without additive, which is higher than its corresponding PC71BM-based cells. Obviously, ITIC cells based on both polymers provided higher Voc should be attributed to the enlarged energy gap between polymer donor's HOMO and acceptor's LUMO. In addition, ITIC-based cells gave broader EQE spectra (300-800 nm) than the $PC_{71}BM$ ones (300–740 nm), which can be ascribed to the absorption compensation at long wavelength contributed by ITIC. However, when additives are applied to the fabrication of these devices, disparate results are observed. Via addition of the 3% DPE, the PCEs for cells made from the control blend (PIDT-TPD:ITIC) are elevated to about 2.25%; but on the contrary, the addition of additives remarkably decline of the PCEs to 1.46% when 5% 1-CN is applied to the blend of PDMIDT-TPD:ITIC.

Charge Carrier Mobilities. Charge transport property plays an important role in the photovoltaic performances in PSCs, and balanced hole/electron mobilities, which are in favor of reducing charge recombination and increasing the J_{sc} and FF, are desired for high performance devices. Therefore, the charge transport properties of the polymers were investigated in a typical device structures of ITO/PEDOT:PSS/active layer/Au and ITO/ZnO/active layer/Al via the space-charge-limited current (SCLC) mode for hole and electron mobilities, respectively. The $J^{1/2}-V$ curves and detailed results are shown in Figure S11 and Table S4, which indicated that in PDMITD-TPD/PC71BM cells possessed the most balanced hole and electron mobilities. The ratio of $\mu_{\rm h}/\mu_{\rm e}$ for the blend of PDMITD-TPD/PC71BM is equal to 1.16 at the optimized processing condition, and it is quite consistent with the photovoltaic performances for this systems. The imbalanced



Figure 5. AFM height images: (a) PIDT-TPD/PC₇₁BM, (b) PIDT-TPD/PC₇₁BM with 3% DPE, (c) PIDT-TPD/ITIC with 3% DPE, (d) PMDIDT-TPD/PC₇₁BM, (e) PDMIDT-TPD/PC₇₁BM with 5% 1-CN, and (f) PDMIDT-TPD/ITIC and TEM images (g–l) for the for the corresponding blend films, respectively.

ratios for the other PSC cells might be one of the reasons for their relative lower PCEs.

Morphological Properties. Morphology of blend films can largely affect the charge separation and transport. In order to get further insight into the relationships between polymer structures and the device performances, morphologies of blend films were investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM) measurements for more details at surface or in-depth levels as shown in Figure 5. Generally, the films based on PIDT-TPD or PDMIDT-TPD displayed different morphology when blended with either PC71BM or ITIC. In polymer/PC71BM blend systems, PIDT-TPD blend film presented a really smooth surface with a rootmean-square (RMS) roughness of 0.36 nm in Figure 5a, but that of PDMIDT-TPD was 8.13 nm in Figure 5d. When the polymer/PC₇₁BM blend films were processed at the optimum conditions with additives, the PIDT-TPD blend film did not decreased so much with a RMS of 0.29 nm with 3% DPE in Figure 5b, whereas the RMS for PDMIDT-TPD/PC71BM blend film was reduced significantly to 2.65 nm by adding 5% 1-CN (Figure 5e,k), and obvious morphology change is observed. However, polymer/ITIC blend films prepared at the optimum conditions bear higher RMS values of 1.15 nm (Figure 5c) and 3.92 nm (Figure 5f) for PIDT-TPD and PDMIDT-TPD, respectively. TEM offered in-depth morphology for the compositions in active layers; it is clear that all blend films presented bicontinuous polymer/acceptor interpenetrating networks and the variations are at the domain sizes. Thinner domain sizes below 10 nm are observed for PIDT-TPD blend films regardless of the acceptor types and/or addition of additive (Figure 5g-i), whereas the original domain size for the PDMIDT-TPD/PC71BM blend film is about 10 nm (Figure 5j), and it is increased to the preferred domain size of 14-18 nm by adding 1-CN as the additive (Figure 5k). But, the domain size becomes more thinner (2-4 nm) when the

polymer blended with ITIC as shown in Figure 5l, which may explain the variation in photovoltaic performances from the microscopic level.

3. CONCLUSION

In conclusion, a simple and universal method has been developed for the ethylene-modified building block with fused aromatic rings (DMIDT) and a novel 2D conjugated polymer PDMIDT-TPD was designed and prepared based on it. By introducing lateral ethylene bridge, the π -electrons expanded and delocalized along two directions, which could facilitate the charge transport mobility. Interestingly, with such structural design strategy, PDMIDT-TPD is able to broaden and red-shift the UV-vis absorption spectrum to 700 nm in relative to the control polymer PIDT-TPD (~620 nm), resulting in an elevated J_{sc} . Most importantly, the PDMIDT-TPD:PC₇₁BM blend could achieve a PCE of 8.26% ($V_{oc} = 0.89$ V, $J_{sc} = 13.40 \text{ mA/cm}^2$, and FF = 69.83%), which is the champion result among the IDT-based polymer donors to the best of our knowledge; even its molecular weight is moderate, and the crystallinity is not as good as that of the control PIDT-TPD. It is clear that molecular electronic structures play a vital role in the photovoltaic performances in this case and the enhanced photovoltaic performance might be also related to the balanced charge carrier mobility and suitable domain sizes for the D/A components of about 14-18 nm. Finally, PDMIDT-TPD is applied for non-fullerene PSCs fabrication and a PCE of 6.88% is achieved without additive, demonstrating a good compatibility and universal utilization of this polymer.

4. EXPERIMENTAL SECTION

Synthesis of 4,9-Bis(dibromomethylene)-4,9-dihydro-sindaceno[1,2-b:5,6-b']dithiophene (6). A mixture of 5 (640 mg, 2.1743 mmol, 1.0 equiv) and carbon tetrabromide (2.16 g, 6.52 mmol, 3.0 equiv) was dissolved in anhydrous dichloromethane (30 mL). To the solution was added a solution of $P(OEt)_3$ (2.25 mL, 13.05 mmol, 6.0 equiv) in dichloromethane (10 mL) dropwise at 0 °C, and then the reaction mixture was warmed up slowly to room temperature and stirred overnight. Then, the reaction mixture was poured into ice diluted hydrochloric acid, then filtered, and washed by water and dichloromethane for several times to yield a red solid (1.08 g, 81.8%), which could was used for the next step without any further purification. HRMS (MALDI-FT/DHB) m/z [M + H]⁺ Calcd for [C₆₆H₇₄S₂] 602.6644. Found 602.6717.

Synthesis of 4,9-Bis(bis(4-hexylphenyl)methylene)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (DMIDT). A mixture of 6 (209 mg, 0.34 mmol, 1.0 equiv), A (497 mg, 1.72 mmol, 5.0 equiv), potassium carbonate (238 mg, 1.72 mmol, 5.0 equiv), and Pd(PPh₃)₄ (12.0 mg, 0.003 mmol) was dissolved in anhydrous THF (30 mL) and water (10 mL), which was refluxing for 24 h under argon. Then, the mixture was cooled down to room temperature and extracted with dichloromethane (50 mL \times 3). The combined organic layers were dried over MgSO4, the solvent removed under vacuum, and the residue was purified by column chromatography with hexane to afford 6 as a red solid (188.6 mg, 58.7%); mp 148-149 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.15 (m, 16H), 6.81 (d, J = 6.0 Hz, 2H), 6.50 (s, 2H), 6.08 (d, J = 6.0 Hz, 2H), 2.74–2.61 (m, 8H), 1.79–1.59 (m, 8H), 1.50–1.26 (m, 24 H), 0.96–0.86 (m, 12H). ¹³C NMR (75 MHz, CDCl₂) δ 144.7, 144.6, 144.3, 143.8, 143.4, 140.1, 139.9, 139.3, 134.2, 131.4, 130.5, 128.7, 128.4, 124.4, 123.2, 115.6, 36.1, 36.0, 32.0, 32.0, 31.9, 31.5, 29.3, 29.2, 22.8, 22.8, 14.4, 14.2. HRMS (DART) m/z [M + H]⁺ Calcd for $[C_{66}H_{74}S_2]$ 931.5232. Found 931.5304.

Synthesis of (4,9-Bis(bis(4-hexylphenyl)methylene)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis-(trimethylstannane) (7). To a solution of DMIDT (948.8 mg, 1.0186 mmol, 1.0 equiv) in anhydrous THF (70 mL) was added freshly made LDA (2.3429 mmol, 2.3 equiv) dropwise at -78 °C. After being stirred for 30 min, the reaction mixture was warmed slowly up to 0 °C. For another 3 h, Sn(CH₃)₃Cl (2.45 mL, 2.45 mmol) was added dropwise at -78 °C, and the reaction was warmed up to the room temperature and stirred overnight. Finally, the reaction mixture was quenched with water, extracted with diethyl ether (50 mL \times 3), and washed with water (20 mL \times 3). The organic phase was dried over MgSO₄; the solvent was removed under vacuum and to get the aimed compound 7 as a red solid (800 mg, 62.5%). ¹H NMR (300 MHz, $CDCl_3$) δ 7.34–7.15 (m, 16H), 6.55 (s, 2H), 6.05 (s, 2H), 2.76–2.60 (m, 8H), 1.82-1.59 (m, 8H), 1.53-1.27 (m, 24H), 0.99-0.84 (m, 9H), 0.21 (s, 18 H). ¹³C NMR (75 MHz, CDCl₃) δ 150.7, 146.4, 144.1, 143.7, 143.4, 140.5, 140.2, 139.3, 137.6, 134.2, 131.2, 130.8, 130.5, 130.5, 128.7, 128.3, 115.9, 36.1, 36.1, 32.0, 31.9, 29.3, 22.8, 22.8, 14.3, 14.3, -8.28. HRMS (MALDI-EF/DHB) m/z [M + H]⁺ Calcd for [C₇₂H₉₀S₂Sn₂] 1256.4522. Found 1256.4516.

Synthesis of PDMIDT-TPD. A mixture of compound 7 (127.8 mg, 0.1017 mmol), compound 9 (43.0 mg, 0.1017 mmol), and Pd(PPh₃)₄ (4 mg) was placed in a 10 mL microwave tube. After purging with argon for 1 h, anhydrous o-xylenes (2.0 mL) and anhydrous DMF (0.4 mL) were added under the protection of argon. Then, the reaction mixture was heated to 160 °C for 2 h in a microwave reactor. After cooling down to room temperature, bromobenzene (0.1 mL) was added to the reaction solution for 20 min at 160 °C. Then, the reaction mixture was poured into methanol, and the precipitate was collected. Finally, the precipitate was subjected to Soxhlet extraction with methanol, acetone, dichloromethane, and chloroform 12 h each. The chloroform fraction was concentrated and poured into acetone to get the targeted polymer PDMIDT-TPD as a deep red solid (119.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.27 (mbr, 16H), 6.95 (br, 2H), 6.62 (br, 2H), 2.88-2.63 (mbr, 10H), 1.88-1.65 (mbr, 10H), 1.44-1.15 (mbr, 34H), 0.95-0.86 (mbr, 3H), 0.85-0.75 (mbr, 12H).

Synthesis of PIDT-TPD. The control polymer PIDT-TPD was prepared according to the similar method of PDMIDT-TPD; compound 8 (130.0 mg, 0.1054 mmol), compound 9 (44.6 mg, 0.1054 mmol), and Pd(PPh₃)₄ (4 mg) were used. The chloroform fraction was collected and the final PIDT-TPD polymer was obtained as a deep red solid (90 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (br,

2H), 7.47 (br, 2H), 7.24–7.13 (mbr, 8H), 7.13–7.01 (mbr, 8H), 2.73–2.40 (mbr, 10H), 1.77–1.58 (mbr, 10H), 1.47–1.09 (mbr, 34H), 0.99–0.72 (mbr, 15H).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.7b01738.

NMR, HRMS data, and detailed device optimization (PDF)

X-ray crystallographic data for CCDC 1559268 (DMIDT) (CIF)

X-ray crystallographic data for CCDC 1559269 (IDT) (CIF)

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Notes

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