

Unsymmetric Side Chains of Indacenodithiophene Copolymers Lead to Improved Packing and Device Performance

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Electronic Supplementary Information

Abstract Two conjugated polymers (PuIDTBD and PuIDTQ) with unsymmetric side chains have been prepared for polymer solar cells using two other polymers (PIDTBD and PIDTQ) with symmetric side chains as control compounds. The combination of methyl and 4-hexylphenyl side chains on the same bridged carbon can ensure good solubility, decrease π - π stacking distances, and bring proper miscibility with PC₇₁BM simultaneously. Therefore, the corresponding polymer solar cells (PSCs) based on donor polymers with unsymmetric side chains exhibited enhanced short-circuit current density (J_{sc}) and power conversion efficiency (PCE) compared with those of control polymers. The PIDTBD and PIDTQ based devices possessed low PCE of 2.13% and 1.48%, while PCEs of devices based on PuIDTBD and PuIDTQ were improved to 3.93% and 4.12%, respectively. The results demonstrate that unsymmetric side chain engineering of conjugated polymers is an effective approach to achieve high performance PSCs.

Keywords Polymer solar cell; Indacenodithiophene; Side-chain engineering; Unsymmetric

Citation: Yang, Y.; Shan, T.; Cao, J.; Wang, H. C.; Wang, J. K.; Zhong, H. L.; Xu, Y. X. Unsymmetric side chains of indacenodithiophene copolymers lead to improved packing and device performance. *Chinese J. Polym. Sci.* 2020, 38, 342–348.

INTRODUCTION

PSCs have attracted great interests in recent years due to several advantages such as low cost, semitransparency, flexibility, and light weight.^[1–6] Conjugated polymers as an important component of PSCs are usually designed with an alternating array of donor and acceptor moieties, which helps to well tune the light absorption and energy level.^[7–10]

Indacenodithiophene (IDT) as a common building block incorporates good solubility and highly planar structure into polymer backbone, which can enhance the degree of π -conjugation and lead to low reorganization energy.^[11] Since it has a larger rigid conjugated skeleton, its application in D/A copolymers is conducive to charge transfer.^[12] However, its side chains are not coplanar with the IDT skeleton, which weakens its stacking capacity and makes the IDT-based polymers mostly amorphous polymers.^[13] In order to enhance the stacking effect, the π -conjugated core structure can be further extended to larger numbered fused-ring such as pyran-bridged indacenodithiophene (IDTP) and indacenodithieno-

[3,2-*b*]thiophene (IDTT). However, the synthetic work will be more tedious and the phase size could be too large to ensure high efficiency.^[13–18] Alternatively, side chain engineering is an effective strategy to tune the packing behavior of IDT polymers and optimize phase morphology.^[13,14,19]

For conjugated polymers, side chains engineering not only provides the solubility required for the processing of photovoltaic devices, but also affects the intermolecular stacking strength and direction of polymers in the active layer. As for IDT polymers, the IDT side chains typically have alkyl side chains or alkyl aryl side chains. Compared to those containing alkyl aryl side chains, the polymers with alkyl side chains have smaller π - π stacking distance and higher charge mobility, but the phase size of the blended film is relatively large.^[20–22] To solve this problem, the short-branched alkyl side chains can be used to obtain better phase separation morphology, but it results in loose packing again.^[13,23] On the other hand, alkyl aryl side chains can inhibit extensive aggregation of the main chains, but bring larger π - π stacking distances and lower charge mobility. In view of this, it is envisioned that unsymmetric side chain engineering combining alkyl and aryl side chains on the same bridged carbon could be a desirable design, for it integrates the advantages of both kinds of side chains. There have been only a few reports on unsymmetric side chains so far, most of which focused on

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Received July 23, 2019; Accepted August 21, 2019; Published online October 24, 2019

electron acceptor materials.^[24–27]

In this work, we report a kind of IDT unit with unsymmetric side chains (uIDT) and two polymers (PuIDTBD and PuIDTQ) based on it. Besides, two other polymers (PIDTBD and PIDTQ) based on the IDT unit with symmetric side chains were synthesized as control compounds. By introducing a methyl group and a hexylphenyl group as side chains, the uIDT based polymers could achieve smaller π - π stacking distances through reducing steric hindrance compared to the traditional IDT compounds. Meanwhile, the unsymmetric structure can ensure good solubility in the processing solvent.^[20,27] PC₇₁BM was chosen as the acceptor to blend with these four polymers to fabricate PSCs. The photovoltaic devices based on PuIDTQ showed the maximum PCEs of 4.12%, and the devices based on PuIDTBD showed PCEs of 3.93%. In contrast, the symmetrical IDT based polymers PIDTQ and PIDTBD only showed low PCEs of 1.48% and 2.13%.

EXPERIMENTAL

Materials and General Characterization Methods

uIDT,^[28] PIDTBD, and PIDTQ^[16] were synthesized and characterized according to the methods described in our previous work. Compounds **M2**, **M3**, **M4**, and other reagents were purchased from commercial sources without further purification. UV-Vis spectra were obtained using a Shimadzu UV 3600 spectrophotometer. The ¹H- and ¹³C-NMR spectra were collected on a Bruker ASCEND 400 spectrometer operating at 400 MHz in deuterated chloroform solution with TMS as the reference. Cyclic voltammeteries of polymer films were conducted in acetonitrile with 0.1 mol·L⁻¹ tetrabutylammonium hexafluorophosphate. ITO, Ag/AgCl, and Pt mesh were used as working electrode, reference electrode, and counter electrode, respectively. More information on characterization measurements can be found in the electronic supplementary information (ESI).

Device Fabrication and Characterization

ITO glass substrates (15 Ω ·sq⁻¹) were cleaned in detergent, deion water, acetone, chloroform, acetone, and isopropanol sequentially by ultra-sonic bath for 15 min each, and further cleaned by UV-ozone machine for 5 min before use. The ZnO precursor solution was prepared by dissolving zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, Sigma-Aldrich, 99.0%, 1 g) and ethanolamine (NH₂CH₂CH₂OH, Acros, 99%, 0.28 g) in 2-methoxyethanol (CH₃OCH₂CH₂OH, Aladdin, 99.8%, 10 mL) under vigorous stirring for 15 h for the hydrolysis reaction and aging in air. The ZnO precursor solution was spin-cast on top of the ITO-glass substrate. The films were annealed at 200 °C for 20 min in air to have thickness of approximately 35 nm as determined by atomic force microscopy (AFM). Then, the ZnO-coated substrates were transferred into a nitrogen-filled glove box. The polymer:PC₇₁BM blends with different ratios (1:1, 1:1.5, or 1:2) were dissolved in dichlorobenzene (DCB) with 3 vol% 1,8-diiodooctane (DIO) at 80 °C and stirred overnight in a nitrogen-filled glove box. The active layers with optimized thicknesses were obtained by spin-coating the blend solution at 50 °C with the polymer concentrations of 10 mg·mL⁻¹ that was filtered by a PTFE (polytetrafluoroethylene) filter (pore size of 0.45 μ m) atop the ZnO layer. Next, approximately 9 nm of MoO₃ was evaporated on top of the active layer at a speed of 0.03 nm·s⁻¹. Finally, the anode, 120 nm Al was deposited at a speed of 0.3 nm·s⁻¹ through a shadow

mask by thermal evaporation in a vacuum chamber of under 4×10^{-4} Pa to complete the device fabrication. The active area of each device was 3.68 mm². The device *J*-*V* characteristics were recorded by a Keithley 2420 SourceMeter unit in forward direction under AM 1.5 G 1 sun irradiance (100 mW·cm⁻²) as generated by a 300 W Xe lamp solar simulator (Enlitech SS-F5-3A) at room temperature. The light intensity was calibrated using a standard Si diode with KG-5 filter. The EQE spectra were recorded using an Enlitech EQE system (Enlitech QE-M110) with a Si diode as the reference cell. Monochromatic light was generated from an Enlitech lamp source with a monochromator.

Synthesis

Synthesis of (4,9-bis(4-hexylphenyl)-4,9-dimethyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(trimethylstannane) (**M1**)

uIDT (210 mg, 0.34 mmol) was dissolved in dry THF (10 mL). The solution was cooled to -78 °C, and butyllithium (2.5 mol·L⁻¹, 0.4 mL, 1.00 mmol) was added dropwise over 10 min. The reaction was stirred at this temperature for 1 h and then at room temperature for another 0.5 h. The solution was cooled to -78 °C again, and trimethyltin chloride (1 mol·L⁻¹ in hexanes, 1.1 mL, 1.10 mmol) was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. Water was added, and the product was extracted with hexanes. The organic layer was washed with water and dried over magnesium sulfate. Evaporation of the solvent afforded the bis(trimethyltin) monomer (IDT-di-Tin, compound **M1**) as pale yellow solid (203 mg, 63%). ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 7.25 (d, *J* = 3.3 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 4H), 7.06 (d, *J* = 8.2 Hz, 4H), 6.97–6.89 (m, 2H), 2.61–2.48 (m, 4H), 1.86 (s, 6H), 1.66–1.51 (m, 8H), 1.31 (dd, *J* = 17.6, 6.0 Hz, 15H), 0.87 (dd, *J* = 9.4, 4.2 Hz, 6H), 0.46–0.23 (m, 18H). ¹³C-NMR (101 MHz, CDCl₃, δ , ppm): 159.81, 159.78, 156.29, 146.99, 141.45, 141.38, 141.07, 140.89, 134.40, 129.31, 129.31, 128.38, 126.26, 126.20, 115.21, 51.94, 35.58, 31.77, 31.41, 31.40, 29.21, 24.90, 24.76, 22.64, 14.15, -8.04.

Synthesis of PuIDTBD

M1 (82.6 mg, 0.088 mmol) and **M3** (64.1 mg, 0.084 mmol) were charged in a 25 mL three-neck flask under argon. After adding toluene (3 mL), the mixture was degassed by three freeze/pump/thaw cycles to remove O₂. Then, Pd₂(dba)₃ (3.9 mg) and P(o-tol)₃ (10.4 mg) were added. The mixture was degassed once more. Next, the mixture was heated at 120 °C for 2 days and poured into methanol after cooling to RT. The precipitate was collected and washed by Soxhlet extraction sequentially with acetone, hexane, and chloroform. The chloroform extraction was concentrated and precipitated in methanol. The solid was collected by filtration and dried to afford a brown solid (74 mg, 71%). *M_n*: 5.07×10^4 , *M_w*: 1.11×10^5 , PDI: 2.2.

Synthesis of PIDTBD

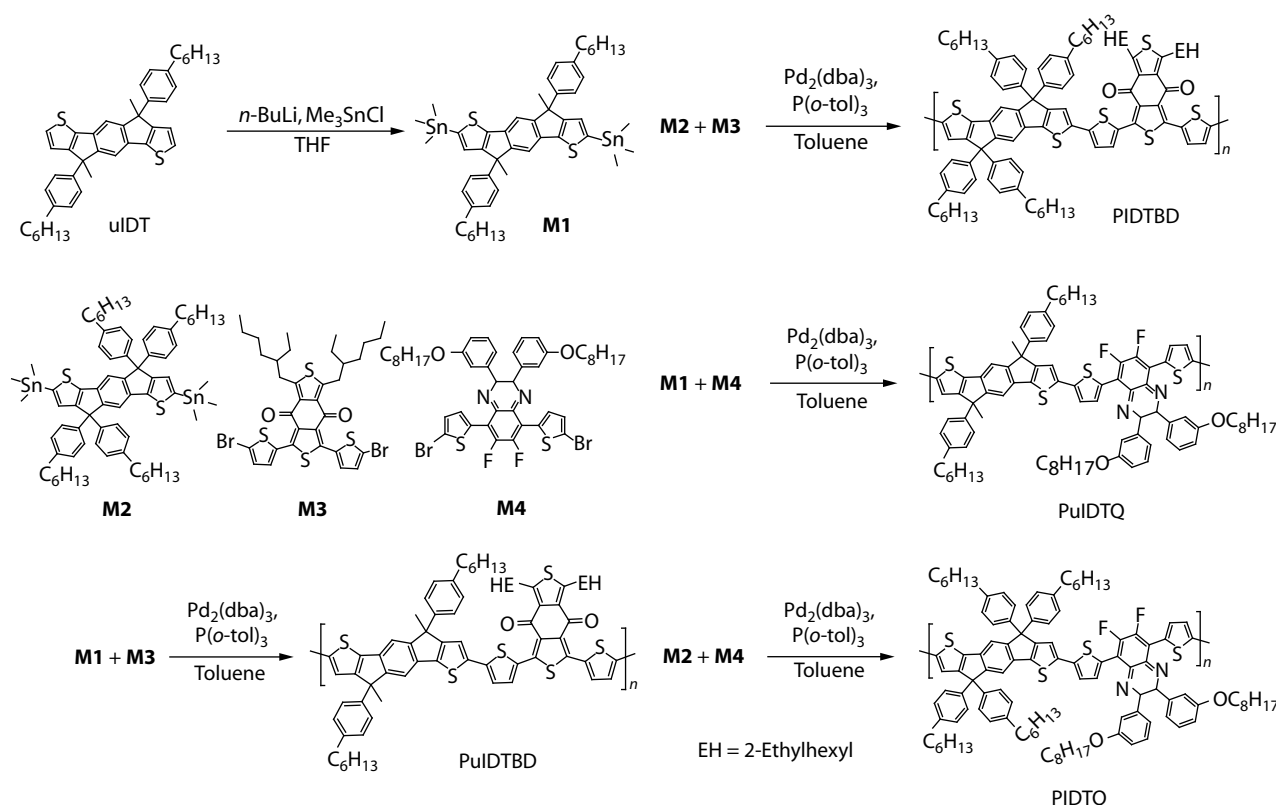
PIDTBD was synthesized with **M2** (102 mg, 0.082 mmol) and **M3** (60.1 mg, 0.078 mmol) following a similar procedure to that of PuIDBD (65 mg, 54%). *M_n*: 5.27×10^4 , *M_w*: 1.27×10^5 , PDI: 2.4.

Synthesis of PuIDTQ

PuIDTQ was synthesized with **M1** (90.1 mg, 0.096 mmol) and **M4** (81.8 mg, 0.091 mmol) following a similar procedure to that of PuIDTBD (84 mg, 67%). *M_n*: 5.22×10^4 , *M_w*: 1.12×10^5 , PDI: 2.1.

Synthesis of PIDTQ

PIDTQ was synthesized with **M2** (151 mg, 0.122 mmol) and **M4**



Scheme 1 Synthetic routes to polymers.

(104.6 mg, 0.117 mmol) following a similar procedure to that of PuIDBD (150 mg, 77%). M_n : 4.09×10^4 , M_w : 9.04×10^4 , PDI: 2.2.

RESULTS AND DISCUSSION

Synthesis

The synthetic routes to polymers PuIDTBD, PuIDTQ, PIDTBD, and PIDTQ are shown in Scheme 1. uIDT was lithiated by *n*-butyllithium followed by quenching with trimethyltin chloride to afford the distannyl compound **M1** with 63% yield (Figs. S1 and S2, in ESI). The target polymers were synthesized via Stille polycondensation using toluene as the solvent and tris(dibenzylideneacetone)dipalladium ($\text{Pd}_2(\text{dba})_3$) and tri(*o*-tolyl)phosphine ($\text{P}(\text{o-tol})_3$) as the catalysts (Figs. S3 and S4, in ESI). The polymers were purified by Soxhlet extraction with acetone and hexane to remove small molecules and residual catalysts, and collected in chloroform extract. The Tosoh Corporation HLC-8320 gel permeation chromatography (GPC) instrument was used to measure the molecular weights (M_n) of four polymers with chloroform as the mobile phase.

Thermal Properties

The thermal properties of the synthesized polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. The four polymers were found to be quite thermally stable. PIDTQ and PuIDTQ displayed onset decomposition temperatures above 270 °C for 5% weight loss (T_d). Furthermore, PIDTBD and PuIDTBD exhibited T_d above 440 °C. Obviously, the thermal stabilities of four polymers are more than adequate for use in OPVs and other optoelectronic devices.^[29] On the other hand, these four poly-

mers did not exhibit distinct endothermic peak or exothermic peak when heated from 40 °C to 250 °C in the DSC analysis, indicating that they would not crystallize during devices fabrication.

Optical Properties

The UV-Vis absorption spectra of four polymers in *o*-dichlorobenzene solution and in films are shown in Fig. 1. All four polymers displayed two distinct absorption bands in *o*-DCB solution. The higher energy bands were assigned to π - π^* transitions of the polymer backbone, while the lower-energy peaks were attributed to the intramolecular charge transfer between electron-rich units and electron-deficient units.^[30] All the four polymers showed similar absorption profiles.

Notably, PuIDTBD and PuIDTQ showed slightly lower molar extinction coefficients in solution ($\epsilon = 3.69 \times 10^4$ and $3.55 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) than those of PIDTBD and PIDTQ ($\epsilon = 4.78 \times 10^4$ and $4.34 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), which is common for aryl to alkyl side chain substitution.^[31] From the solution state to film state, the maximum absorption of PIDTBD was red-shifted slightly from 570 nm to 578 nm due to weak interaction in film, while the maximum absorption of PIDTQ was blue-shifted from 590 nm to 581 nm, most likely indicating some extent of H-type stacking.^[16] In contrast, PuIDTBD and PuIDTQ exhibited obvious red shifts of the maximum peaks from 573 nm to 608 nm and from 589 nm to 604 nm, respectively, indicating that uIDT based polymers can form close contact by stronger aggregation.

Electrochemical Properties

The electrochemical properties of polymers in the film state

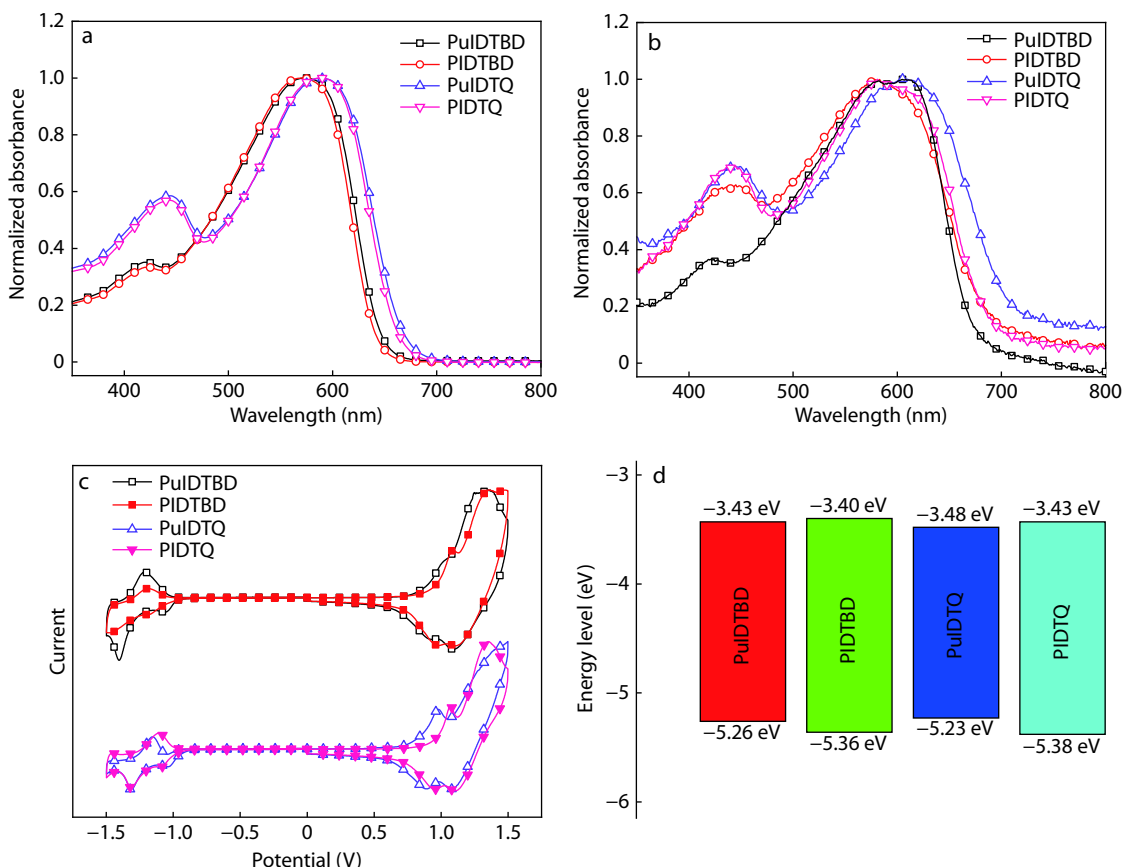


Fig. 1 UV-Vis spectra of polymers (a) in *o*-DCB solution and (b) as thin films; (c) Cyclic voltammograms of the polymers; (d) Energy levels of the polymers.

were investigated by cyclic voltammetry, as shown in Fig. 1(c). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were determined from the onset potentials of the first oxidation and reduction peaks, respectively. The LUMO/HOMO energy levels of four polymers are summarized in Table 1. The LUMO energy levels of PIDTBD and PIDTQ were -3.40 and -3.43 eV, respectively, and those of PuIDTBD and PuIDTQ were close to IDT based polymers, equalling -3.43 and -3.48 eV respectively. It seems that side chains only played a weak role in tuning the LUMO energy levels. On the other hand, the changes of HOMO energy levels were relatively obvious. The HOMO energy level of PuIDTBD (-5.26 eV) was 0.1 eV higher than that of PIDTBD (-5.36 eV). And the value offset was 0.15 eV for PuIDTQ (-5.23 eV) and PIDTQ (-5.38 eV). The higher HOMO energy levels of uIDT based polymers might lead to slightly lower open circuit voltage in the photovoltaic device.

Table 1 Optical properties and frontier molecular orbital energy levels of polymers.

Polymer	$\lambda_{\max}(\text{sol})$ (nm)	$\lambda_{\max}(\text{film})$ (nm)	$\epsilon(\text{sol}) \times 10^{-4}$ ($\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	HOMO (eV)	LUMO (eV)
PuIDTBD	573	608	3.69	-5.26	-3.43
PIDTBD	570	578	4.78	-5.36	-3.40
PuIDTQ	589	610	3.55	-5.23	-3.48
PIDTQ	590	581	4.34	-5.38	-3.43

Photovoltaic Properties

The photovoltaic properties of the polymers were investigated by using PC₇₁BM as the acceptor with a device configuration of ITO/ZnO/donor:PC₇₁BM/MoO_x/Al. The weight ratio of donor to acceptor was optimized to be 1:1.5 for PuIDTBD based device and 1:1 for other polymers based devices. The active layers were deposited by using *o*-DCB as the solvent and 1,8-diiodooctane (DIO) as the additive. The current density-voltage (*J*-*V*) curves of the devices are shown in Fig. 2(a), and the corresponding parameters are summarized in Table 2. The best PCE of 4.12% was obtained from PuIDTQ based device, with a J_{SC} of $8.99 \text{ mA} \cdot \text{cm}^{-2}$, an open-circuit voltage (V_{OC}) of 0.84 V , and a fill factor (FF) of 54.6%. The PuIDTBD based device showed a modest PCE of 3.93% with a J_{SC} of $8.45 \text{ mA} \cdot \text{cm}^{-2}$, a V_{OC} of 0.86 V , and an FF of 53.7%. The other two polymers based on IDT as the donor parts showed performance inferior to uIDT based polymers. The PIDTBD based device gave a PCE of 2.13% with a J_{SC} of $5.52 \text{ mA} \cdot \text{cm}^{-2}$, a V_{OC} of 0.92 V , and an FF of 42.0%, and the PIDTQ based device gave a PCE of 1.48% with a J_{SC} of $4.46 \text{ mA} \cdot \text{cm}^{-2}$, a V_{OC} of 0.88 V , and an FF of 37.6%. The uIDT based polymers generally showed shallower V_{OC} due to their higher HOMO levels. The slight reductions in V_{OC} values were overcompensated by the increase of J_{SC} and FF values for uIDT polymers-based devices. As shown in Fig. 2(b), both PIDTBD/PC₇₁BM and PIDTQ/PC₇₁BM devices displayed very low photo response from 350 nm to 700 nm. The EQE values were 30% in most wavelength

ranges for PIDTBD based devices and even lower than 25% for PIDTQ based devices from 400 nm to 600 nm. This result is consistent with the measured low J_{SC} in PIDTBD/PC₇₁BM and PIDTQ/PC₇₁BM devices. The EQE values of PuIDTBD and PuIDTQ based devices were much higher than those of PIDTBD and PIDTQ based devices in the range of 350 nm to 700 nm,

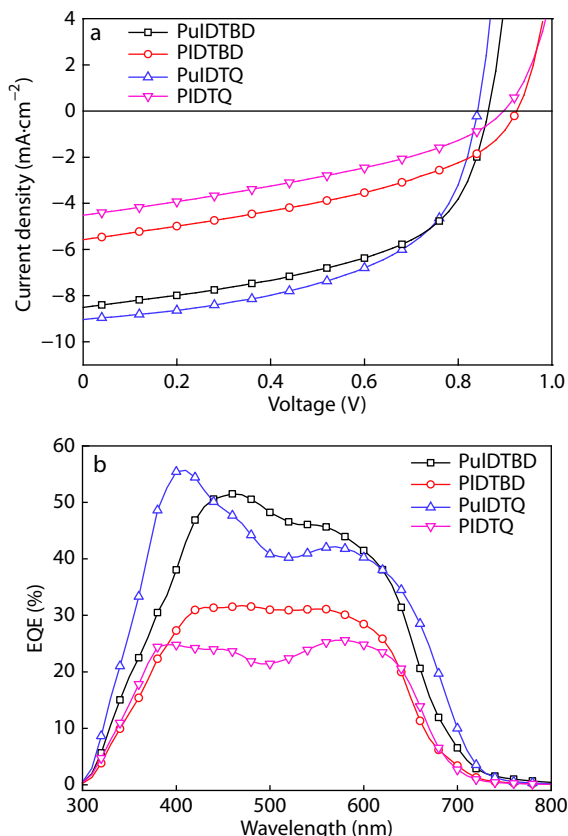


Fig. 2 (a) J - V curves of the devices based on polymer:PC₇₁BM and (b) EQE spectra of the corresponding devices.

remaining above 40% in most wavelength range. The EQE results indicate that the photoelectric conversion process was more efficient in PuIDTBD and PuIDTQ based devices, which explains their higher J_{SC} compared with PIDTBD and PIDTQ based devices.

As methyl side chains are expected to enhance interchain packing by decreasing steric hindrance, the thin-film morphology could possibly be influenced in the film casting process. X-ray diffraction (XRD) analysis was applied to study the packing behavior of polymers in films. As shown in Fig. 3, four polymers mainly exhibited broad peaks in the wide-angle region attributed to the π - π stacking of polymer backbones.

Table 2 Photovoltaic properties of solar cells based on devices using PC₇₁BM as the acceptor and PuIDTBD, PIDTBD, PuIDTQ, or PIDTQ as the donor.

Donor	D:A	V_{OC} (V)	J_{SC} ($\text{mA}\cdot\text{cm}^{-2}$)	FF (%)	PCE (%)
PuIDTBD	1:1.5	0.86	8.45	53.7	3.93
PIDTBD	1:1	0.92	5.52	42.0	2.13
PuIDTQ	1:1	0.84	8.99	54.6	4.12
PIDTQ	1:1	0.88	4.46	37.6	1.48

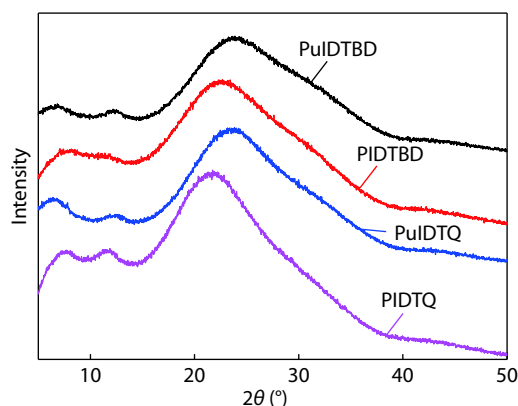


Fig. 3 XRD patterns of polymers.

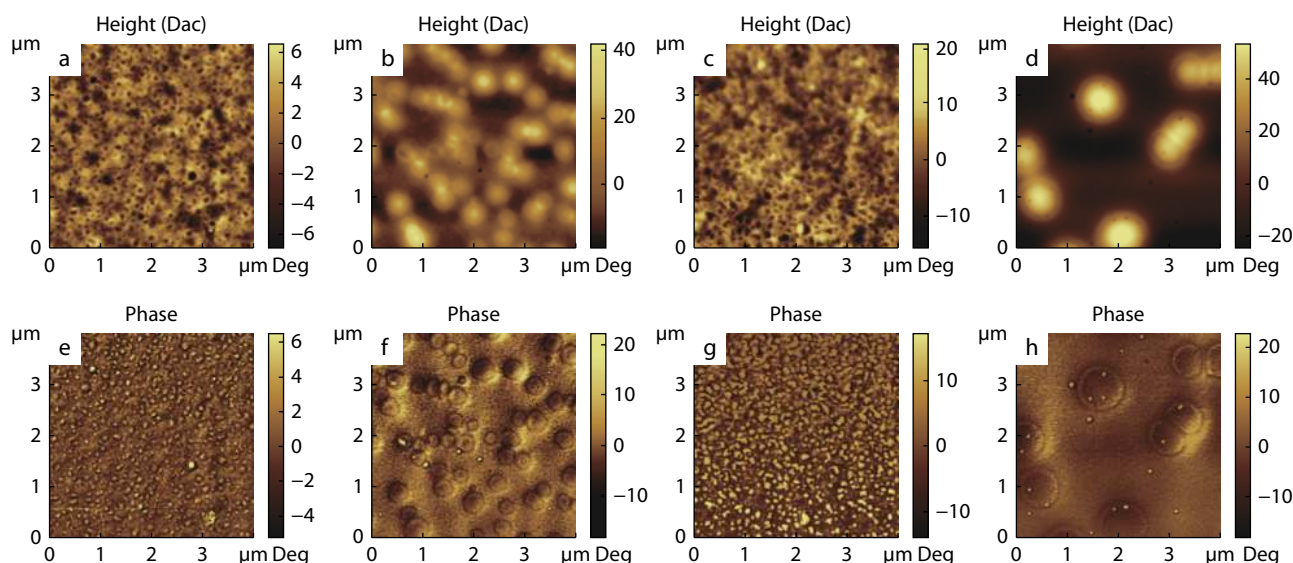


Fig. 4 AFM (a–d) height images and (e–h) phase images of photoactive layers of polymer solar cells based on (a, e) PuIDTBD:PC₇₁BM, (b, f) PIDTBD:PC₇₁BM, (c, g) PuIDTQ:PC₇₁BM, and (d, h) PIDTQ:PC₇₁BM (Tapping-mode, $4 \times 4 \mu\text{m}$).

The π - π stacking distances were 0.373 nm ($2\theta = 23.82^\circ$) and 0.376 nm ($2\theta = 23.62^\circ$) for PuIDTQ and PuIDTBD, respectively. However, the distances were 0.417 nm ($2\theta = 21.30^\circ$) for PIDTQ and 0.398 nm ($2\theta = 22.30^\circ$) for PIDTBD. By replacing 4-hexylphenyl group with methyl group on side chains, the π - π stacking distances of PuIDTQ and PuIDTBD became closer in comparison with those of PIDTQ and PIDTBD. The smaller π - π stacking distances may let PC₇₁BM disperse more uniformly.^[32]

To further understand the influence of unsymmetric side chains on the photovoltaic performance, morphologies of the polymers/PC₇₁BM blend films spin-coated under the optimized conditions were investigated by atomic force microscopy (AFM). As shown in Fig. 4, large aggregates were observed in the PIDTBD/PC₇₁BM and PIDTQ/PC₇₁BM blend films with a root-mean-square roughness (Rms) of 19.9 and 20.1 nm, respectively, which could be ascribed to different aggregation kinetics of polymers and PC₇₁BM. The domain size of PIDTBD/PC₇₁BM blend film was about 300 nm, and that of the PIDTQ/PC₇₁BM even reached ~700 nm. As for uIDT polymers, morphologies of the polymer/PC₇₁BM blend films have been improved greatly with domain size around ~70 nm for PuIDTBD and ~100 nm for PuIDTQ. Restricted by exciton diffusion length, extensive phase separation could result in severe exciton recombination.^[33] According to the result of AFM analysis, more suitable phase separation and less exciton recombination could cause the higher J_{SC} and FF values of PuIDTQ and PuIDTBD based devices.

CONCLUSIONS

In conclusion, we have reported two polymers based on the uIDT unit with unsymmetric side chains and compared them with IDT based polymers. By replacing 4-hexylphenyl side chain with methyl group, the π - π stacking distances of uIDT based polymers became closer. The blend films of PuIDTBD:PC₇₁BM and PuIDTQ:PC₇₁BM showed more proper phase separation compared to those of PIDTBD:PC₇₁BM and PIDTQ:PC₇₁BM. As a result, J_{SC} and FF values of PuIDTBD and PuIDTQ based devices improved remarkably and their PCEs reached 3.93% and 4.12%, respectively. The results indicate that unsymmetric side chains present an effective approach of side chain engineering to boost the efficiency of PSCs.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2342-9>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51403135) and Sichuan Science and Technology Program (No. 2019YJ0123).

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