

Contents lists available at ScienceDirect

Polymer



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Optimizing molecular alignment to reduce dark current via side-chain engineering for high-performance polymer photodetector



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ARTICLE INFO	A B S T R A C T				
Keywords: Photodetector Side-chain engineering Molecular alignment	Two low-bandgap polymers, PDTPN- α and PDTPN- β , containing diketopyrrolopyrrole (DPP) and dithienopyrrole (DTP) functionalized with two different side chains of α -naphthalene and β -naphthalene were synthesized. Experimental results show that subtle configuration changes at the side chains can effectively influence the molecular alignment, film morphology, and photodetector performance. As a result, the preferential edge-on orientation of PDTPN- β can effectively decrease the dark current density of the photodetector. This wealth of information on the strong correction between the variation in the molecular conformation and the device performance provides a novel avenue to prepare high-performance polymer photodetectors with superior specific detectivity.				

1. Introduction

Recently, solution-processed polymer photodetectors (PPDs) have drawn extensive attentions resulting from their intrinsic characteristics of low cost, light weight, flexibility and easy fabrication, which are recognized as promising candidates to the inorganic counterparts [1–6]. Owing to their easily optimized energy levels and band gaps, narrowband or broadband polymers for PPDs have been successfully designed and synthesized [7–11]. In general, the figure-of-the-merit of PPDs can be evaluated by the specific detectivity which is mainly dominated by the dark current and external quantum efficiency (EQE) [12–15]. However, the performance of PPDs is usually limited by the relatively high dark current density, which will dramatically depress the signal/noise ratio and the corresponding specific detectivity. Therefore, some efficient strategies are required to control the dark current density of PPDs.

Currently, some effective strategies, such as interface modification, thickening blend film and controlling charge transport channels, have been developed to reduce dark current density of PPDs [16–21]. However, the corresponding EQE values of the devices inevitably decrease with the reduction of dark current density, resulting in a severe damage to sensitive photoresponse of the PPDs [22]. Besides the methods of device engineering, the rational design of conjugated polymers has also been proven to effectively reduce current density [23–30]. For example,

Liang et al. adopted 3,4-ethylenedioxythiophene (EDOT) as side chains to enhance the interaction between the conjugated polymer and PEDOT layer, leading to the significantly lowered dark current due to polymer-rich layer accumulating at the surface of PEDOT [31]. Surprisingly, the dark current of the PPDs decreased about two orders of magnitude, while only little effect on EQE was observed. Furthermore, Wang et al. adjusted the solubility of polymer by introducing alkyl side chains, which can improve the film morphology to depress dark current [5,32]. On the basis of recently reported studies, side-chain engineering of the conjugated polymers opens a new avenue to construct high-performance PPDs [33–35]. However, the influence of side chains on the performance of PPDs is complicated when taking the diversity and multifunction of the side chain into consideration [24-26,36]. Therefore, revealing the relationships between side chain structures and device performance is beneficial to simultaneously realize low dark current and good EQE.

To achieve broad detection from ultraviolet (UV) to near infrared (NIR) region, the low-bandgap conjugated polymers were synthesized with strong acceptor and donor as monomers. Benefiting from the merits of strong electron deficiency and good planar backbone, diketopyrrolopyrrole (DPP) moiety has been usually used to build low-bandgap polymers. Meanwhile, dithienopyrrole (DTP) unit is chosen as donor due to its strong electron-donating property. The device performance has been found to be very sensitive to the size and the position of alkyl

https://doi.org/10.1016/j.polymer.2021.123728

Received 17 January 2021; Received in revised form 28 March 2021; Accepted 29 March 2021 Available online 1 April 2021 0032-3861/© 2021 Elsevier Ltd. All rights reserved.

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chains for polymer based on PDTPN [37–39]. To investigate how the molecular conformation variation due to the existence of steric torsions with the conjugated backbones on molecular stacking, film morphology and PPDs performance, two isomeric conjugated polymers, PDTPN- α and PDTPN- β , were designed and synthesized via changing the substitution position of naphthyl on the DTP unit. Taking advantage of the fine disparity of the steric effect at different substitution positions of naphthyl, we can create a steric distortion variation between conjugated backbone and side chains. The molecular conformation variation endows the two polymers with different aggregation behaviors and optoelectronic properties. Finally, the polymer of PDTPN- β with edge-on orientation exhibits the decreased dark current density and maintained EQE values.

2. Experimental section

2.1. Materials

2,5-bis(2-octyldodecyl)-3,6-bis(5-(trimethylstannyl)thiophen-2-yl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP-2tin) was purchased from Derthon and used without further purification. The solvents for chemical synthesis were purified by distillation. The reactions were performed under a nitrogen atmosphere. Unless otherwise stated, all of the chemicals were purchased from commercial sources and used as received.

3,3'-Dibromo-2,2'-bithiophene (Compound 1). 3-Bromothiophene (12.23 g, 75 mmol) was added in dry THF (80 mL) and cooled to 0 °C under nitrogen, lithium diisopropylamide (75 mmol) was added slowly via syringe. The reaction was continued at 0 °C for 2 h under stirring. The solution was then cooled to -78 °C before CuCl₂ (20.17 g, 150 mmol) was added. The reaction was stirred overnight at room temperature and then quenched with water, extracted with dichloromethane. The organic phase was washed with brine and dried over anhydrous Na₂SO₄. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica powder with petroleum ether and dichloromethane (10:1) as the eluent. The pure product as a pale-yellow solid around 4.80 g was finally obtained with a yield of 39.50%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.41 (d, 2H, J = 5.2 Hz), 7.09 (d, 2H, J = 5.6 Hz).

4-(*naphthalen*-1-yl)-4*H*-dithieno[3,2-b:2',3'-d]pyrrole (Compound 2a). To a anhydrous flask containing compound 1 (648.11 mg, 2 mmol), NaO^tBu (0.48 g, 5 mmol), Pd₂(dba)₃ (0.056 g, 0.06 mmol), 1,1'-Bis (diphenylphosphino)ferrocene (0.13 g, 0.25 mmol) and anhydrous toluene were added in 1-aminonaphthalene (0.34 g, 2.4 mmol) via syringe under N₂. The solution was reacted at 110 °C overnight in dark. After cooling the room temperature, the mixture was extracted with dichloromethane, and washed with brine. The organic extract was dried over anhydrous Na₂SO₄, concentrated at reduced pressure and purified with silica gel column chromatography using petroleum ether as the eluent to give 0.50 g pure product as a white solid. (yield, 81.60%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.76 (d, 2H, J = 5.2 Hz), 7.12 (d, 2H, J = 5.2 Hz), 7.45 (t, 1H, J = 7.6 Hz), 7.58 (m, 3H), 7.69 (d, 1H, J = 8.4 Hz), 7.97 (t, 2H, J = 9.6 Hz).

4-(*naphthalen*-2-yl)-4*H*-dithieno[3,2-b:2',3'-d]pyrrole (Compound 2b). Compound 2b was prepared according to the procedure for **2a** from 2amineonaphthalen (0.34 g, 2.4 mmol) with a yield of 80.26%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.20 (d, 2H, J = 5.6 Hz), 7.38 (d, 2H, J = 5.2 Hz), 7.54 (m, 2H), 7.76 (d, 1H, J = 2.4 Hz), 7.89 (q, 2H, J = 7.2Hz), 8.00 (d, 2H, J = 9.6 Hz).

2,6-dibromo-4-(naphthalen-1-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (Compound 3a). N-Bromosuccinimide (1.17g, 6.60 mmol) in 10 mL CHCl₃ was added dropwisely via syringe into a solution of Compound 2a (0.92 g, 3 mmol) in 10 mL chloroform in an ice bath under nitrogen. The reaction was stirred overnight at room temperature and then quenched with water, extracted with dichloromethane, and dried over anhydrous Na₂SO₄. The pure product (0.86 g, yield 61.61%) was obtained as a dark-red solid after being purified with silica gel column chromatography using petroleum ether as the eluent. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.77 (s, 2H), 7.56 (m, 5H), 7.98 (t, 2H, J = 6.8 Hz).

2,6-dibromo-4-(naphthalen-2-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (*Compound 3b*). Compound 3a (0.87 g, yield 62.57%) was obtained from compound 2b (0.92 g, 3 mmol) according to the procedure **3a**. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.22 (s, 2H), 7.57 (m, 2H), 7.63 (d, 1H, J =2,4 Hz), 7.90 (q, 3H, J = 6.2 Hz), 8.00 (d, 1H, J = 8.8 Hz).

Preparation of PDTPN-α. 25 mL of round-bottom flask was introduced compound 3a (138.96 mg, 0.3 mmol), DPP-2tin (356.11 mg, 0.3 mmol) before being transferred to a glovebox where Pd(PPh₃)₄ (6.93 mg 0.006 mmol) and anhydrous toluene (2 mL) were added in. The mixture was then stirred at reflux for 72 h under N₂. After cooling down to room temperature, the mixture was added into 200 mL of methanol dropwisely. The precipitated solid was collected by filtration and extracted in a Soxhlet with acetone, hexane, chloroform sequentially. The chloroform solution was then concentrated, reprecipitated into 150 mL of methanol, filtered and dried under vacuum to afford the final product as a dark-green solid (308.10 mg, yield 86.09%, $M_n = 74.70$ kDa, PDI = 3.61).

Preparation of PDTPN-β. The polymer PDTPN-β (300.40 mg) was prepared according to the procedure for **PDTPN-α** from compound 3b (138.96 mg, 0.3 mmol) and DPP-2tin (356.11 mg, 0.3 mmol) with a yield of 83.94% ($M_n = 102.40$ kDa, PDI = 2.61).

3. Results and discussion

3.1. Synthesis and characterizations

The target copolymers of PDTPN- α and PDTPN- β with α -naphthalene and β -naphthalene as aryl side chains, respectively, are presented in Scheme 1. The copolymers were synthesized via Stille cross-coupling reaction using toluene as the solvent and Pd(PPh₃)₄ as the catalyst. These two copolymers display good solubility in common organic solvents, such as chloroform, toluene, chlorobenzene, etc. The numberaverage molecular weights (M_n) of PDTPN- α and PDTPN- β are 74.70 kDa and 102.40 kDa, with the polydispersity index (PDI) of 3.61 and 2.61, respectively, as measured by gel permeation chromatography (GPC) in tetrahydrofuran against polystyrene standards (Table 1). The phase transition and thermal properties of the copolymers were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under nitrogen. Both of the copolymers exhibited sufficient thermal stability with loss of weight less than 5% on heating to about 400 °C, and no obvious thermal transitions in the second heating and cooling scans were observed. (Fig. S1 and Fig. S2).

3.2. Optical and electrochemical properties

The UV-vis absorption spectra of the two copolymers in dilute chloroform solution and in film at room temperature were presented in Fig. S3 and Fig. 1a, respectively. As can be seen from Fig. 1a, each copolymer shows two main absorption profiles in the region of 300-500 nm and 500–1000 nm. In the thin film, PDTPN- α and PDTPN- β give rise to maximum absorption wavelengths of 806 nm and 905 nm, respectively. Notably, obviously bathochromic shift is observed for PDTPN-β compared with that of PDTPN- α , and this result is demonstrated by absorption of the blending films as well (Fig. S4), indicative of the stronger intramolecular packing of PDTPN-β. In addition, the film absorption spectra of PDTPN- β exhibits obvious shoulder peak compared with its solution absorption spectra, suggesting that PDTPN- β film behaves more obvious molecular orientation. Moreover, the polymer of PDTPN- β (1.16 eV) displays smaller optical band gaps (E_g^{opt}) than that of PDTPN- α (1.24 eV), which is beneficial to achieve broad response photodetector.

The electrochemical properties of these two copolymers were further studied by cyclic voltammetry (CV) in Fig. S5. From onset potentials of



Scheme 1. Synthetic route of the polymers PDTPN- α and PDTPN- β . Reagents and conditions : (i) NaO^tBu, Pd₂(dba)₃, dppf, toluene, 110 °C. (ii) NBS, chloroform, 0 °C ~ room temperature. (iii) DPP-2tin, Pd(PPh₃)₄, toluene, 110 °C.

Table 1

Characterizations of PDTPN- $\!\alpha$ and PDTPN- $\!\beta$

Polymer	$M_{ m n}$ (kDa)	PDI	$T_{\rm d}$ (°C)	$\lambda_{\max}^{\text{film}}$ (nm)	$E_{\rm g}^{\rm opt}$ (eV) ^a	$E_{\rm HOMO}~({\rm eV})^{\rm b}$	$E_{\rm LUMO} (\rm eV)^{\rm b}$	E_{g}^{EC} (eV) ^c
PDTPN-α	74.7	3.61	389.9	806	1.24	-5.22	-3.48	1.74
PDTPN-β	102.4	2.61	400.9	905	1.16	-5.08	-3.53	1.55

^a Calculated from the onset of the electronic absorption of the polymer films ($E_g^{opt} = 1240/\lambda$ (nm)).

^b Estimated from the oxidation and reduction onset by the equation of $E_{\text{HOMO}} = -e(E_{\text{on}}^{\text{ox}} + 4.43)$ and $E_{\text{LUMO}} = -e(E_{\text{on}}^{\text{red}} + 4.43)$, respectively.

^c Estimated by the equation of $E_{g}^{EC} = E_{HOMO} - E_{LUMO}$.



Fig. 1. (a) Absorption spectra of PDTPN- α and PDTPN- β in neat thin films at room temperature; (b) Energy level diagram of polymers and PC₆₁BM.

the first oxidation and reduction peaks, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels can be calculated, respectively. As displayed in Table 1, the HOMO/LUMO energy levels are -5.22/-3.48 and -5.08/-3.53 eV for PDTPN- α and PDTPN- β , respectively. A smaller electrochemical bandgap is also obtained for PDTPN- β (1.55 eV) than that of PDTPN- α (1.74 eV), which is in accordance with the results of optical band gaps. However, driving force for exciton dissociation of PDTPN- β slightly reduced resulting from the smaller Δ LUMO between donor polymer and PC₆₁BM, further leading to the recession in EQE (Fig. 1b).

3.3. Theoretical calculations and molecular stacking

Considering significant variation in optoelectronic properties between PDTPN- α and PDTPN- β , we firstly tried density functional theory (DFT) to investigate coplanarity by calculating the energy levels and dihedral angles between the backbone and naphthyl using Gaussian 09 at the B3LYP/6-31G(d) level. As shown in Fig. 2, the alkyl chains are replaced by methyl groups, and three repeating units are used as alternatives for simplicity of calculation [40]. As displayed in Fig. S6, no obvious influence of the side chains on energy levels according to the DFT calculations. Moreover, the PDTPN- β exhibited more coplanarity compared with PDTPN- α , suggesting that PDTPN- β could be expected to obtain a much ordered molecular packing because higher planar structure can help enhance molecular interactions.

To further gain insight into the different molecular stacking for PDTPN- α and PDTPN- β , the X-ray diffraction (XRD) measurements were carried out. As displayed in Fig. 3, no apparent peaks are observed with the polymer of PDTPN- α , indicating the amorphous structure in PDTPN- α film. In contrast to PDTPN- α , PDTPN- β exhibited a strong peak at $2\theta = 3.91^{\circ}$, corresponding to the (100) diffraction with a *d* spacing of 21.2 Å. At the same time, weak but visible (200) diffraction peaks at 8.31° for PDTPN- β can also be observed, indicating the featured lamellar molecular packing. This is a somewhat superior result of the solid-state



Fig. 2. The optimized molecular geometries (3 repeat units) of PDTPN-α and PDTPN-β.



Fig. 3. XRD profiles of PDTPN- α and PDTPN- β films.

ordering features for PDTPN- β , which is one important characteristic for photodetectors. It can be reasonably explained that the alkyl side chains of the polymers are angled toward the electrode in the edge-on molecular orientation, which may spontaneously form an insulating alkyl layer between the active layer and the metal electrode [41]. Thus, the dark current of the device could be effectively reduced by block the hole

injection at negative bias. Briefly, the results indicate that it is an important means to regulate the molecular packing and orientation by optimizing naphthyl isomer, which can affect the device photodetector performance.

3.4. Photodetector performance

To evaluate the photodetector performance of two copolymers as the donor materials, we chose $PC_{61}BM$ as the acceptor, and fabricated the device structure of ITO/PEDOT:PSS/active layer/ C_{60} /Al (Fig. 4a) [38, 42,43]. The energy level diagrams of the electronic materials are depicted in Fig. 1b, which clearly indicates energetically favorable electron transfer and charge transport. The active layers were spin-coated from the polymer: $PC_{61}BM$ solutions in chlorobenzene with the concentration of 24 mg/mL. The optimal film thickness and weight ratio of polymer: $PC_{61}BM$ in the blends was found to be 100 nm and 1:1 for the two copolymers (Table. S1). To optimize the phase separation, 3% DIO was used as solvent additive [43–47].

It can be found that the optimized dark current density (J_d) was reached with 3% DIO (v/v) in chlorobenzene as the processing condition during the device fabrication. In addition, to further minimize the dark current, C₆₀ (10 nm) was applied as hole blocking layer. As displayed in



Fig. 4. (a) Schematic device structure; (b) Specific detectivity and dark current density under 500 and 900 nm; (c) External Quantum Efficiency under -0.1 V bias for PDTPN- α and PDTPN- β ; (d) Specific detectivity under -0.1 V bias for PDTPN- α and PDTPN- β .

Fig. 4b and Table 2, the best $J_{\rm d}$ of 2×10^{-7} A/cm² was obtained for the PDTPN-α. Encouragingly, the $J_{\rm d}$ was dramatically reduced to 6.1×10^{-8} A/cm² at -0.1 V bias using PDTPN-β, considerably lower than that achieved for PDTPN-α.

The external quantum efficiency (EQE) spectra of the devices for both polymers are depicted in Fig. 4c. The responsivity (*R*) spectra of the devices for both polymers are depicted in Fig. S8. Under -0.1 V bias, the devices of both polymers yield broad EQE spectra from 300 nm to 1000 nm. The EQE values of 14.05% and 17.07% at 500 nm and 20.98% and 24.76% at 900 nm are achieved based on PDTPN- α and PDTPN- β , respectively. The R values of 56.65 mA/W and 68.65 mA/W at 500 nm and 152.25 mA/W and 179.71 mA/W at 900 nm are achieved based on PDTPN- α and PDTPN- β , respectively. As a result, isomerization of naphthyl as side chains only exhibit slight effect on the EQE and R for two copolymers. Considering dark current as the major contributor to the noise, the specific detectivity (D^*) could be calculated by the equation of $D^* = R/(2qJ_d)^{1/2} = EQE \times (\lambda/1240)/(2qJ_d)^{1/2}$, where *q* is the absolute charge (1.6 \times 10⁻¹⁹ C), λ is the wavelength and J_d is the dark current density. As shown in Fig. 4b, the D^* of PDTPN- β is much higher than that of PDTPN- α . It should be noted that both copolymers exhibit similar EQE values, and the higher D^* based on PDTPN- β should be attributed to the decreased dark current density. Therefore, the subtle conformational transform on the naphthyl side chain of two copolymers can lead to a negligible impact on EQE but a distinct one on dark current density. In addition, the electron mobility of the two polymers was also evaluated with the device structure of ITO/ZnO/active layer/pdino/Al. The resulting fitting curves are shown in the Fig. S9, and the electron mobilities of 1.60 \times 10^{-5} cm 2 V $^{-1}$ s $^{-1}$ and 2.85 \times 10^{-7} cm 2 V $^{-1}$ s $^{-1}$ are obtained for PDTPN- α and PDTPN- β , respectively, which are consistent with their dark current density.

3.5. Film morphology

Besides the preferred edge-on orientation behavior of PDTPN- β , we recognized that its decreased dark current density may be influenced by the more optimized blend film morphology as well. Thence, the surface morphology of the polymer:PC₆₁BM blends was investigated by tapping-mode atomic force microscopy (AFM) [48–51]. As shown in Fig. 5, the optimized blend films give a root-mean-square (RMS) roughness of 4.7 nm for PDTPN- α :PC₆₁BM whereas of 3.6 nm for PDTPN- β :PC₆₁BM. In contrast, the blend film based PDTPN- β exhibits relatively smooth surface morphology, which could prevent metal electrode from penetrating into the blend film and depress the leakage current in PPDs.

4. Conclusion

In this work, two isomeric copolymers of PDTPN- α and PDTPN- β with the donor unit of dithienopyrrole (DTP) and the acceptor of diketopyrrolopyrrole (DPP) were synthesized. PDTPN- α with α -naphthyl as side chain exhibits twisted molecular structure, while PDTPN-β with β-naphthyl as side chain is observed with much planar molecular structure, leading to the strong intermolecular interactions and preferred edge-on orientation. This strong intermolecular interactions facilitates the transfer of charge between molecules, thus reducing the dark current density, from 2×10^{-7} A/cm² to 6.1×10^{-8} A/cm². Finally, the observed totally different molecular packing affects the performance in PPDs seriously, in which a much lower dark current density of 6.1 imes 10^{-8} A/cm² and a specific detectivity over 10^{12} between 700 nm and 1000 nm were achieved for PDTPN-β-based PPDs. This complementary insight on the impact of backbone steric distortions due to isomeric on the polymer properties, film morphology and device performance could provide meaningful guidance for optimizing the chemical structure toward highly efficient PPDs.

Table 2

Performance parameters of photodetectors with PDTPN- α :PC₆₁BM and PDTPN- β :PC₆₁BM blends.

Polymer	$J_{\rm d}$	EQE900nm	R _{900nm}	D*900nm
	(A/cm ²)	(%)	(mA/W)	(Jones)
PDTPN-α PDTPN-β	$\begin{array}{c} 2\times10^{-7}\\ 6.1\times10^{-8}\end{array}$	20.98 24.76	152.25 179.71	$\begin{array}{c} 5.99 \times 10^{11} \\ 1.29 \times 10^{12} \end{array}$



Fig. 5. Tapping-mode AFM images (2 μm \times 2 $\mu m)$ of optimized polymer: $PC_{61}BM$ blends.

Declaration of competing interest

We declare that we have on financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51973169).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2021.123728.

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