



## Effects of flanked units on optoelectronic properties of diketopyrrolopyrrole based $\pi$ -conjugated polymers



Jing Yue, Junfei Liang, Sheng Sun, Wenkai Zhong, Linfeng Lan, Lei Ying\*, Wei Yang\*, Yong Cao

State Key Laboratory of Luminescent Materials and Devices, and Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou 510640, China

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### ABSTRACT

Two novel donor–acceptor  $\pi$ -conjugated copolymers comprising (*E*)-1,2-di(thiophen-2-yl)ethylene as the electron-donating unit, and diketopyrrolopyrrole flanked with phenyl or 2-pyridyl moiety as the electron-accepting unit were synthesized through a palladium-catalyzed Stille polymerization. With respect to the copolymer based on diketopyrrolopyrrole flanked with phenyl unit (PTDPP-Ph), the copolymer counterpart containing the 2-pyridyl moiety (PTDPP-Py) as the flanked unit exhibited increased coplanarity, bathochromic shift in absorption, decreased lowest unoccupied molecular orbital energy levels, as well as the about one order of magnitude increase in hole mobility. Of particular interests is that the bulk heterojunction solar cell based on PTDPP-Py exhibited an improved power conversion efficiency of 3.26% relative to the power conversion efficiency of 2.51% as attained by PTDPP-Ph. These results indicated that the replacement of flanked phenyl with 2-pyridyl moiety of the diketopyrrolopyrrole core unit can be an effective strategy for the construction of conjugated polymers with improved optoelectronic properties.

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### 1. Introduction

Organic photovoltaics (OPVs) have attracted much attention over the past decade owing to their specific advantages of fabricating light-weight and large-area devices through cost-effective solution processing techniques [1,2]. Recent advantages of organic semiconducting polymers allowed for the systematically tunable optoelectronic properties through the delicate molecular design, which can provide optimum frontier molecular orbital levels, appropriate absorbance, favorable film morphology as well as high charge carrier mobility. One of the most extensively used strategies to construct conjugated polymers was the integration of the electron-rich donor (D) and the electron-deficient acceptor (A) units along the polymer backbone in an alternating fashion, which can result in excellent optoelectronic performances of conjugated polymers [2–5].

Diketopyrrolopyrrole (DPP) unit has been extensively utilized as the electron-deficient building block for the construction of organic semiconductors due to its planar architecture and high charge carrier mobility [6–9]. A range of DPP-based organic semiconducting polymers have been developed for high performance organic OPVs [10–13] and organic field effect transistors (OFETs) [14–18]. The most successful DPP based conjugated polymers consisted two thiophene units flanked on both sides of the DPP core unit, while the optoelectronic properties in terms of charge carrier mobility and frontier molecular orbitals of these copolymers can be affected by replacing the sulfur atom in thiophene moiety with oxygen or selenium atom. In contrast, copolymers comprising the DPP unit flanked with two phenyl rings (DPP-Ph) exhibited less pronounced optoelectronic performances, which can be attributed to the poor coplanarity as a result of a large dihedral angle of  $\sim 20$ – $40^\circ$  between the phenyl ring and the DPP core unit that can impede charge carrier transportations and lead to reduced conjugation of the polymer backbone. Recently, conjugated polymers comprising 2-pyridinyl unit flanked DPP unit (DPP-Py) has emerged as promising electron-donating materials for OPV [19] and as the semiconducting layer for OFETs [20,21]. Considering that the nitrogen atom in the proximal position of DPP unit

\* Corresponding authors. Tel.: +86 20 87114346 17; fax: +86 20 87110606.

E-mail addresses: [msleijing@scut.edu.cn](mailto:msleijing@scut.edu.cn) (L. Ying), [pswyang@scut.edu.cn](mailto:pswyang@scut.edu.cn) (W. Yang).

exhibited reduced steric hindrance with respect to the C–H species in phenyl ring that adjacent to the central DPP core unit, nearly coplanar geometry can be accessed for DPP-Py, and high electron mobility over  $6.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  has been recognized on the basis of DPP-Py based copolymer [21].

Here we introduced two donor–acceptor type of conjugated polymers based on phenyl or 2-pyridyl unit flanked DPP unit as the electron-accepting unit. These copolymers were constructed by copolymerizing two electron-deficient DPP based dibromo-derivatives with an electron-rich (*E*)-1,2-di(thiophen-2-yl)ethylene based bis-stannyl monomer. We chose (*E*)-1,2-di(thiophen-2-yl)ethylene (TVT) moiety as the electron-donating units because it can effectively extend the co-planarity and promote intermolecular  $\pi$ – $\pi$  stacking, and the intermolecular distances can also be reduced which is beneficial for charge transportation. It was recognized that the flanked phenyl or 2-pyridyl unit of can significantly affect the molecular geometry, absorbance, frontier molecular orbital energy levels, and in turn the charge carrier mobility and photovoltaic performances of the resultant copolymers.

## 2. Experimental section

### 2.1. General measurement and characterization

$^1\text{H}$  NMR spectra were collected on a Bruker AV-500 (500 MHz) in deuterated chloroform with tetramethylsilane as a reference. The molecular weights of the polymers were determined by waters GPC 2410 using THF as eluant. Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 at a heating rate of  $20 \text{ }^\circ\text{C min}^{-1}$  under a nitrogen atmosphere. The differential scanning calorimetry (DSC) characteristics were measured on a Netzsch DSC 204 under  $\text{N}_2$  flow at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  and cooling rate of  $40 \text{ }^\circ\text{C min}^{-1}$ . UV–vis absorption spectra were obtained with a Shimadzu UV-3600 UV–vis–NIR spectrometer. Cyclic voltammetry (CV) data were measured on a CHI630E electrochemical workstation equipped with a glassy carbon working electrode, a saturated calomel electrode as the reference electrode, and a platinum wire counter electrode. The measurements were carried out with anhydrous acetonitrile tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of  $100 \text{ mV s}^{-1}$ . The polymers were deposited on the electrode. Potentials were referenced to the ferrocene/ferrocenium couple by using ferrocene as the standard. The oxidation potential of ferrocene was set at  $-4.80 \text{ eV}$  with respect to zero vacuum level. The HOMO energy levels were calculated according to the equation of  $E_{\text{HOMO}} = -[4.8 + e(E_{\text{OX}} - E_{\text{Fc/Fc}^+})]$  (eV). Atomic force microscopy (AFM) measurements were carried out by using a Digital Instrumental DI Multimode Nanoscope IIIa in tapping mode.

### 2.2. Fabrication and characterization of organic field effect transistors (OFETs)

OFETs were fabricated in a bottom-gate and top-contact geometry. First the Al:Nd film was deposited under vacuum on the glass, and the polymethyl methacrylate (PMMA) was spin-coated. Then the copolymers films ( $\sim 30 \text{ nm}$ ) were spin-coated on the substrates, and the films were annealed at  $100 \text{ }^\circ\text{C}$  for 10 min. Finally, the gold film ( $45 \text{ nm}$ ) was deposited under vacuum as the source and drain electrodes, defining a channel width/length ( $W/L$ ) of  $500/70 \text{ }\mu\text{m}$ . The OFETs characterizations were performed in air by using a probe station and a semiconductor parameter analyzer (Agilent 4155C).

### 2.3. Fabrication and characterization of solar cells

All devices were fabricated using a conventional structure: ITO/PEDOT:PSS/polymer:PC<sub>61</sub>BM/PFN/Al through solution process. A  $40 \text{ nm}$ -thick PEDOT:PSS was spin-coated on ITO-coated glass substrates treated by 4 min oxygen plasma, then annealed at  $120 \text{ }^\circ\text{C}$  on a hotplate for 20 min. The polymer:PC<sub>61</sub>BM active blend layer with a thickness of around  $100 \text{ nm}$  was prepared by spin-coating the  $\text{CHCl}_3$  (CF) solution on the top of the PEDOT:PSS layer. Then the poly[(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) interlayer material was dissolved in methanol in the presence of a small amount of acetic acid ( $1.5 \text{ }\mu\text{L mL}^{-1}$ ), and the solution (concentration,  $0.02 \text{ mg mL}^{-1}$ ) was spin-coated on the top of the active layer. Aluminum cathode ( $100 \text{ nm}$ ) (thickness monitored with an STM-100/MF Sycon quartz crystal) was thermally evaporated under vacuum (about  $1.0 \times 10^{-6} \text{ mbar}$ ) through a shadow mask defining an active device area of  $0.16 \text{ cm}^2$ . We used Keithley 2400 sourcemeter to measure current density–voltage ( $J$ – $V$ ) curves under 1 sun (AM 1.5 G spectrum), which generated from a class solar simulator (Japan, SAN-EI, XES-40S1). The thicknesses of PEDOT:PSS and active layer were measured by a Tencor Alpha-step 500 Surface Profilometer.

### 2.4. Synthesis of PTDPP-Ph

To a microwave vial was added 3,6-bis(4-bromophenyl)-2,5-bis(2-octyldodecyl)-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**Br<sub>2</sub>-DPP-Ph**) (151 mg, 0.15 mmol), (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethylene (77.65 mg, 0.15 mmol). Xylenes (5 mL) were added and the solution degassed before addition of  $\text{Pd}(\text{PPh}_3)_4$  (9 mg, 0.05 mmol). The reaction mixture was further degassed and subsequently sealed. The vial was heated in a microwave reactor at  $80 \text{ }^\circ\text{C}$  for 2 min,  $120 \text{ }^\circ\text{C}$  for 2 min,  $160 \text{ }^\circ\text{C}$  for 2 min, and finally  $180 \text{ }^\circ\text{C}$  for 30 min. After cooling to room temperature, the reaction mixture was poured into methanol. The crude product was filtered off and purified by subsequent Soxhlet extraction with methanol, acetone and hexane. After cooling to room temperature, the organic fraction was extracted with water, and concentrated in vacuo. The resulting residue was dissolved in a minimum amount of chloroform and added dropwise to a vigorously stirred methanol (250 mL). The resulting precipitate was isolated by filtration and dried in vacuo to afford the desired polymer (115 mg, 72%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.58 (br, ArH), 7.33 (br, ArH), 7.07–7.04 (br, ArH), 6.90 (br, ArH), 6.77 (br, ArH), 3.86 (br, N–CH<sub>2</sub>), 3.54 (br, N–CH<sub>2</sub>), 1.55 (br, CH), 1.23–1.09 (m, CH<sub>2</sub>), 0.89–0.82 (m, CH<sub>3</sub>). GPC:  $M_n = 20.9 \text{ kDa}$ ,  $M_w = 40.3 \text{ kDa}$ , PDI = 1.93.

### 2.5. Synthesis of PTDPP-Py

The copolymer PTDPP-Py was prepared by the same procedure as that for PTDPP-Ph, where the 3,6-bis(5-bromopyridin-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo-[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**Br<sub>2</sub>-DPP-Py**) (152 mg, 0.15 mmol), (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethylene (77.65 mg, 0.15 mmol) were used as the monomers. After dried in vacuo the target polymer was afforded as the dark-red solids (140 mg, 87%). GPC:  $M_n = 63.5 \text{ kDa}$ ,  $M_w = 181.8 \text{ kDa}$ , PDI = 2.87.

## 3. Results and discussion

### 3.1. Synthesis and thermal properties

Scheme 1 shows the synthetic routes of the polymers. The monomers 3,6-bis(4-bromophenyl)-2,5-bis(2-octyldodecyl)

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