

# Solar Cell and Transistor Applications of Naphthodithiophene-Based Polymers

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## Abstract

We report the synthesis and characterization of two novel semiconducting polymers based on naphthodithiophene and their applications to bulk heterojunction solar cells and transistors. The naphthodithiophene based copolymers exhibit a low optical bandgap of  $\sim 1.35$  eV with the high field-effect hole motility of  $2.77 \times 10^{-2}$  cm<sup>2</sup>/(Vs). The solar cells made from the polymers yielded power conversion efficiencies of 3.09% and 3.29% under AM 1.5 G irradiation (100mW/cm<sup>2</sup>) for PNDDTD12 and PzNDDTD12 respectively.

## 1. Introduction

Polymer solar cells (PSCs) based on blends of conjugated polymers and fullerene derivatives are now recognized as a promising approach for future renewable energy production because of their low production cost, mechanical flexibility, and solution processability.<sup>1</sup> Development of a new low-band gap polymer and control over nanoscale morphologies of interpenetrating donor/acceptor networks play important roles to enhance the performances of PSCs.<sup>2</sup> To obtain the low-bandgap polymers and modulate their electronic properties, the use of donor-acceptor system (D-A) in the semiconducting materials has become an efficient strategy.<sup>3,4</sup> Recently, the naphthodithiophenes (NDT) based polymers with the D-A structure have been reported with high mobility and high power conversion efficiencies (PCE).<sup>5,6</sup> Here, we report the synthesis and characterization of two novel semiconducting copolymers based on naphthodithiophene and dithiophene diketopyrrolopyrrole (PNDDTD12 and PzNDDTD12) and their applications to bulk heterojunction solar cells (BHJ) and organic field-effect transistors (OFETs).

## 2. Experiment

2,7-Bis(trimethyltin)-4,9-bis(2-ethylhexyloxy)naphtho[2,3-b:6,7-b']dithiophene (NDT),<sup>7</sup> 2,7-Bis(trimethyltin)-4,9-bis(2-ethylhexyloxy)naphtho[1,2-b:5,6-b']dithiophene (zNDT),<sup>8</sup> 3,6-Di(2-bromothiophene-5-yl)-2,5-di(2-butylactyl)pyrrolo[3,4-c]pyrrole-1,4-dione (DTDPP)<sup>9</sup> were synthesized according to the reported procedures. The PNDDTD12 and PzNDDTD12 (Fig. 1) were synthesized through the Stille coupling reaction of NDT or zNDT with DTDPP using

Pd<sub>2</sub>(dba)<sub>3</sub>/P(o-tolyl)<sub>3</sub> as the catalyst.

BHJ solar cells were fabricated with the structure of ITO/PEDOT:PSS(40nm)/Polymer:PC<sub>61</sub>BM/LiF(1nm)/Al (100nm). The photoactive layer was deposited by spin-coating a solution containing 10 mg/mL of polymer with a respective amount of PC<sub>61</sub>BM (polymer/PC<sub>61</sub>BM ratio of 1:2.5). The solvent was a mix solvent of 88.5% v/v chloroform, 10% v/v chlorobenzene and 1.5% v/v 1,8-diiodooctane (DIO). The thicknesses of the active layers were 130 nm and 140 nm for PNDDTD12 and PzNDDTD12, respectively. The active area of the cells was 0.02 cm<sup>2</sup>.

OFETs were fabricated on heavily doped n<sup>+</sup>-Si gate electrode covered with a 400 nm SiO<sub>2</sub> dielectric layer. After hexamethyl-disilazane treatment, a 75-nm PNDDTD12 or 55-nm PzNDDTD12 was deposited on the SiO<sub>2</sub> dielectric by spin-coating. Finally, gold source-drain electrodes (50 nm) were finally vacuum-deposited on top of the polymer layer ( $L=50$  μm;  $W=5000$  μm).

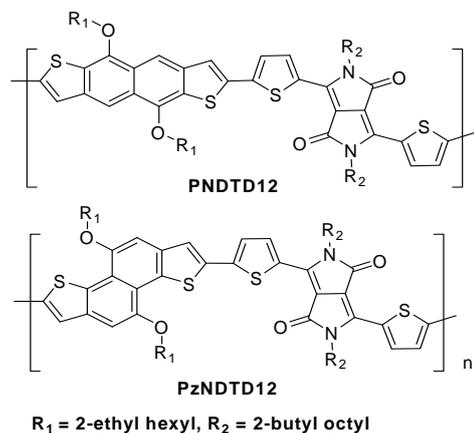


Fig. 1 Chemical structure of PNDDTD12 (top) and PzNDDTD12 (bottom).

## 3. Results and discussion

The UV-vis absorption spectra, cyclic voltammograms and photoelectron spectra of the synthesized polymers are shown in Fig. 2. The optical and the electrochemical properties are summarized in Table I. Due to the extended  $\pi$ -conjugation length of naphthodithiophene structure, both polymers show broad absorption spectra up to 900 nm which allows better sunlight harvesting.<sup>6</sup>

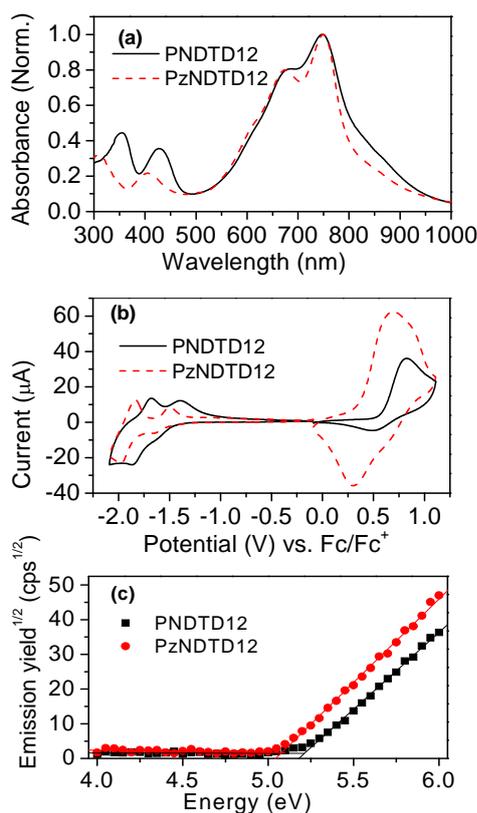


Fig. 2 UV-vis absorption spectra (a), cyclic voltammograms (b) and photoelectron spectra (c) of the polymers.

The current density-voltage ( $J$ - $V$ ) curves of BHJ solar cells are shown in Fig. 3. The PNDTD12-device showed the highest PCE of 3.09% with  $J_{SC} = 9.13 \text{ mA/cm}^2$ ,  $V_{OC} = 0.70 \text{ V}$  and  $FF = 0.48$  and the PzNDDTD12-device showed the highest PCE of 3.29% with  $J_{SC} = 9.67 \text{ mA/cm}^2$ ,  $V_{OC} = 0.61 \text{ V}$  and  $FF = 0.55$  under AM 1.5 G irradiation. The  $V_{OC}$  of PNDTD12-device was higher than that of PzNDDTD12-device because theoretical achievable  $V_{OC}$  depends on the difference of energy between the highest occupied molecular orbital (HOMO) of the electron donor material and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor material.<sup>10</sup>

Characteristics of OFETs using the naphthodithiophene based polymers are depicted in Fig. 4. The field-effect hole mobility ( $\mu$ ) of OFETs with PNDTD12 and PzNDDTD12 were calculated using a saturation-regime equation to be  $1.43 \times 10^{-2}$  and  $2.77 \times 10^{-2} \text{ cm}^2/(\text{Vs})$ , respecti-

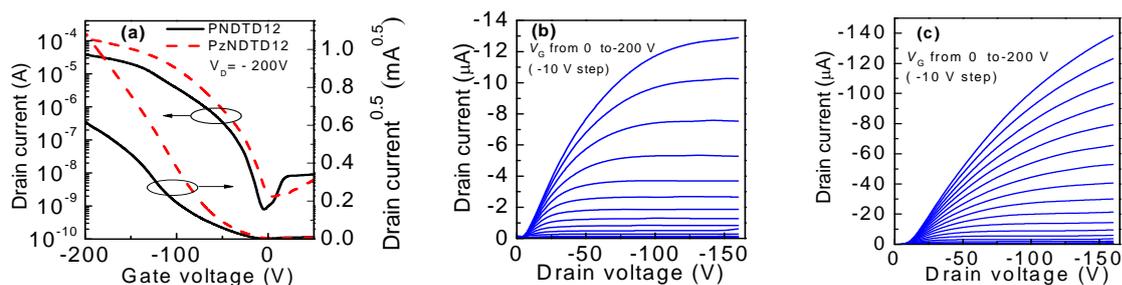


Fig. 4 (a) Typical transfer curves of OFETs, (b) output curves of PNDTD12 – based and (c) PzNDDTD12 – based devices.

vely. The obtained higher  $J_{SC}$  and  $\mu$  in the devices with PzNDDTD12 is most likely as a result of, in part, the more compact  $\pi$ -system of nonlinear structure zNDT.<sup>8</sup>

Table I Optical and electrochemical properties of the polymers

Polymer	$\lambda_{\text{max}}^{\text{film}}$ (nm)	IPs (eV) <sup>a</sup>	HOMO (eV) <sup>b</sup>	LUMO (eV)	$E_g$ (eV)	$E_g^{\text{opt}}$ (eV) <sup>c</sup>
PNDTD12	748	5.21	-5.28	-3.58	1.70	1.34
PzNDDTD12	746	5.08	-5.07	-3.55	1.52	1.38

a. Photoelectron spectroscopy in air.

b. Cyclic voltammetry (CV). c. From absorption onset in film.

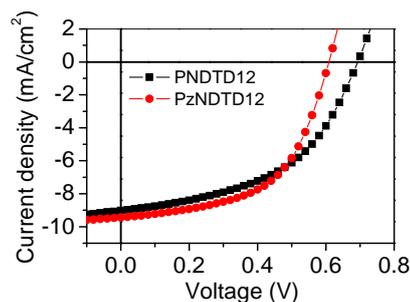


Fig. 3  $J$ - $V$  curves of BHJ solar cells fabricated from the polymers

#### 4. Conclusions

In summary, we have synthesized and characterized two new semiconducting polymers with low optical bandgap and high hole mobility. The BHJ solar cells based on the polymers exhibited an efficiency over 3% which overcomes the performances of the commonly used P3HT:PCBM blend in our laboratory. Considering the photovoltaic and OFETs properties, naphthodithiophene based polymers are promising candidates for high performance materials in the field of organic electronics.

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