

1,2,5,6-Naphthalenediimide-based Conjugated Copolymers Linked by Ethynyl Units*

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Abstract Two copolymers of **P1** and **P2** comprising benzothiadiazole, 1,4-bis(dodecyloxy)-benzene units were synthesized by Sonogashira coupling polymerization based on ethynyl-linked 1,2,5,6-naphthalenediimide. Their thermal, optical, electrochemical as well as charge transport properties were studied. Bottom-gate top-contact organic field-effect transistors (OFETs) measurements of **P1** and **P2** thin films showed different charge transport behaviors. **P1** displayed pure electron transport behaviors in OFETs with electron mobility up to $10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, while **P2** exhibited hole transport features. The molecular structure analysis revealed that the structure of **P1** has the acceptor-linker-acceptor' (A-L-A') characteristic, and **P2** possesses the donor-linker-acceptor (D-L-A) structure feature. The results demonstrate that different molecular structures lead them to have distinct charge transport behaviors. In particular, the first pure electron transport copolymer in OFETs based on 1,2,5,6-naphthalenediimide is achieved.

Keywords Poly(phenylene ethynylene)s; Ethynyl; 1,2,5,6-Naphthalenediimide; Organic field-effect transistors

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INTRODUCTION

Electron acceptors have been a subject of great interest during the past decades^[1–4], of which imide-functionalized arylenes have attracted ever increasing attention due to their excellent optoelectronic properties^[5–9]. Among imide-functionalized arylenes, 1,4,5,8-naphthalenediimides (1,4,5,8-NDIs) are the most popular acceptor moieties owing to their electron-deficient NDI cores with the low-lying lowest unoccupied molecular orbital (LUMO) energies and excellent electron transport performance^[6, 10, 11]. With the advancement of synthetic methods, the substitutions on the imide and NDI core positions have been reported to manipulate solubility, molecular orbital energies, molecular self-assembly, thin film morphology and the optoelectronic properties^[12, 13]. It is a popular strategy to use electron accepting building blocks and electron donating ones for

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constructing donor-acceptor (D-A) conjugated polymers that usually have high device performance^[14–18]. A large amount of electron donor monomers have been copolymerized with 1,4,5,8-NDI units, and these copolymers show excellent device performance^[5, 6, 19]. The highest occupied molecular orbital (HOMO) energies can be fine-tuned by donor units for 1,4,5,8-NDI-based copolymers. But the tuning of E_{LUMO} is difficult because the LUMO electron density mainly locates on the NDI units^[19, 20]. The optimized E_{LUMO} values of polymeric electron acceptors should be about -3.6 eV for all polymer solar cells (all-PSCs) to obtain high open circuit voltage (V_{oc}) values and thus high power conversion efficiencies (PCEs)^[21–23]. However, the E_{LUMO} values of 1,4,5,8-NDI-based copolymers are usually low (about -3.85 eV), which leads to low V_{oc} values and thus limits the further improvement of PCEs of all-PSCs^[24–32].

Recently, novel angular-shaped 1,2,5,6-NDIs have been developed as new acceptors and applied in the field of organic field-effect transistors (OFETs)^[33–35] and polymer solar cells (PSCs)^[36–38], which show different physicochemical properties from those of 1,4,5,8-NDIs. For instance, the LUMO energy values of 1,2,5,6-NDIs are higher than those of 1,4,5,8-NDIs by about 0.3 eV^[34], and 1,2,5,6-NDI-based copolymers used in PSCs always show high V_{oc} values (about 0.90 V)^[36–38]. In addition, OFETs based on 1,2,5,6-NDI copolymers exhibited hole dominant transport characteristics^[34] or pure hole transport characteristics^[35], while 1,4,5,8-NDI-based copolymers displayed electron dominant transport characteristics^[19]. Up to now, there are still no 1,2,5,6-NDI-based copolymers with pure electron transport characteristics in OFETs.

Poly(phenylene ethynylene)s (PPEs, Fig. 1)^[39, 40] with the aromatic units linked by alkyne triple bonds are a kind of fantastic materials used in many areas, such as sensors^[41–44], molecular wires^[45–47], polymer light-emitting diodes (PLEDs)^[48, 49] and so on. In 2012, Malika and coworkers reported ethynyl-linked benzobisoxazoles (BBOs)-based copolymer PBOP-D (Fig. 1) and applied it as the active layers for PLEDs; the luminous efficiency was improved a lot than those of other reported BBO-based PLEDs^[50]. David *et al.* reported the synthesis and characterization of ethynyl-linked PQE(EH) (Fig. 1) that had a low band gap of 2.25 eV and red-shifted absorption in comparison with those of polymers without ethynylene linkages between monomers^[51]. Thayumanavan and coworkers reported ethynyl-linked P(BODIPY-*alt*-NDI) (Fig. 1). They used it as the active layers for OFETs. The polymer exhibited an electron mobility of about $3.9 \times 10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ with an on/off ratio of 10^3 ^[52]. In 2013, Howard *et al.* reported OFETs based on ethynyl-linked P(PyDI-E) (Fig. 1), which showed an electron mobility of $2.0 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and an on/off ratio of 10^3 ^[53]. Up to now, PPEs and their analogues have not been extensively studied in OFETs^[54, 55] and PSCs devices^[56–58] due to their large band gaps

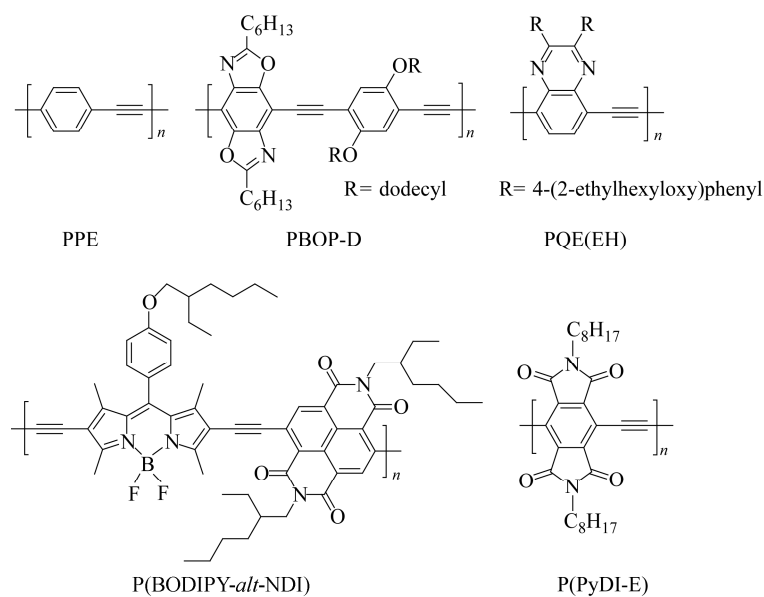
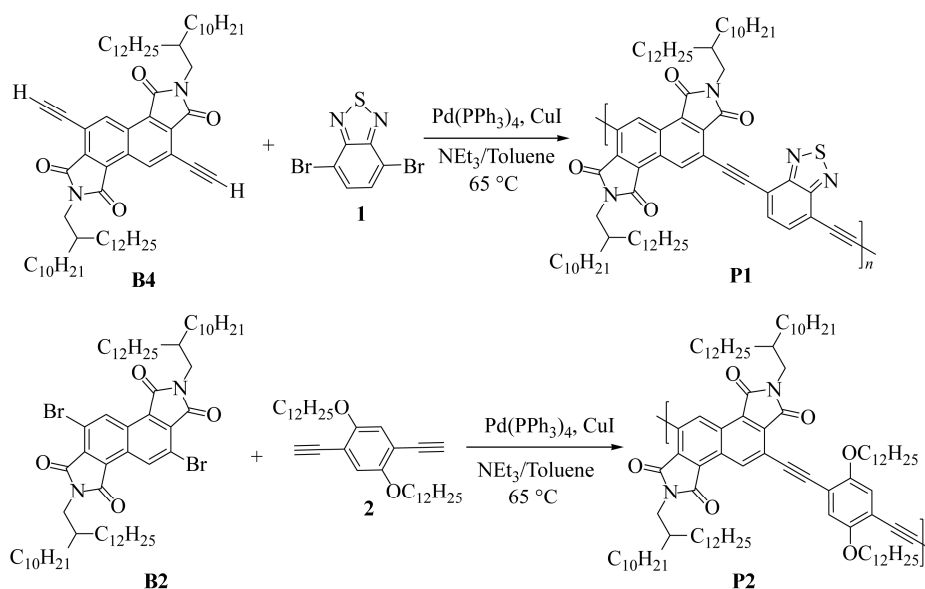


Fig. 1 Chemical structures of the representative copolymers

(~2.5 eV) and unsatisfied frontier molecular orbital energy (such as the deep HOMO energy levels: -5.9 ~ -6.3 eV)^[59], which limits the further enhancement of device performance.

Herein, we report the molecular design, synthesis and characterizations of two ethynyl-linked 1,2,5,6-NDI-based copolymers **P1** and **P2** (Scheme 1) comprising of benzothiadiazole, 1,4-bis(dodecyloxy)-benzene units, respectively. Optical and electrochemical properties of **P1** and **P2** were investigated. It was found that **P1** and **P2** in solution and in solid state both exhibited fluorescence, and their band gaps (< 2.2 eV) were lower than those of common PPEs (about 2.5 eV)^[59]. OFETs based on **P1** showed pure electron transport behaviors, which made **P1** as the first example of pure electron transport copolymers in OFETs based on 1,2,5,6-NDI. The electron mobility of **P1** was up to $10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which is comparable or even higher than those of recent reported electron-deficient PPEs-like copolymers^[52, 53, 60]. From the structure analysis, it can be seen that **P1** has the acceptor-linker-acceptor' (A-L-A') structure feature, where A = 1,2,5,6-NDI, L = triple bond and A' = benzothiadiazole, while **P2** possesses the donor-linker-acceptor (D-L-A) structure characteristic, where D = 1,4-bis(dodecyloxy)-benzene, L = triple bond and A = 1,2,5,6-NDI. The different molecular structures greatly impacted the charge transport behaviors of **P1** and **P2**, *i.e.* **P1** showed pure electron transport behaviors, while **P2** exhibited hole transport features.



Scheme 1 Synthetic routes to **P1** and **P2**

EXPERIMENTAL

Chemicals

Iso-NDI2DT-2Br (**B2**)^[35] and 1,4-bis(dodecyloxy)-2,5-di(ethynyl)benzene (**2**)^[61] were synthesized according to the methods reported in the literature (Scheme S1, in supporting information, SI). 4,7-Dibromo-2,1,3-benzothiadiazole (**1**) and other compounds were purchased from commercial suppliers and used without further purification. Tetrahydrofuran and toluene were distilled from sodium/benzophenone under nitrogen atmosphere.

Synthesis of Polymers

Synthesis of **P1**

B4 (100 mg, 0.1 mmol) and **1** were added to a 25 mL Schlenk flask. Pd(PPh₃)₄ (5.8 mg, 0.005 mmol) and CuI (0.9 mg, 0.005 mmol) were added to the flask under nitrogen atmosphere. The dry toluene (6 mL) and triethylamine (3 mL) were added by syringe into the Schlenk flask under nitrogen, and the mixture was stirred at 65 °C for 9 h. Then, methanol (100 mL) was added into the reaction mixture. The crude polymer was collected

via gravity filtration and purified by Soxhlet extraction with methanol, acetone, petroleum ether and chloroform, respectively. Finally the product was dissolved in chloroform and precipitated in methanol. The product was dried in vacuum, giving **P1** as a red solid (87 mg, 80%). GPC (CHCl₃): M_n = 23.6 kDa, M_w = 41.9 kDa, PDI = 1.8. IR (KBr, cm⁻¹): 2922 and 2852 (vs, —CH₂— and —CH₃), 2212 (w, C≡C), 1707 (vs, C=O); Anal. Calcd. for C₇₂H₁₀₂N₄O₄S₁: C, 77.23, H, 9.18, N, 5.0. Found: C, 76.40, H, 8.89, N, 4.48.

Synthesis of **P2**

Preparation of **P2** was carried out according to the above procedure for the synthesis of **P1**. Dark-red solid of **P2** (103 mg, 75%) was obtained. GPC (CHCl₃): M_n = 14.9 kDa, M_w = 33.3 kDa, PDI = 2.2. IR (KBr, cm⁻¹): 2922 and 2852 (vs, —CH₂— and —CH₃), 2208 (s, C≡C), 1706 (s, C=O), 1221 (s, Ph—OR), Anal. Calcd. for C₉₆H₁₅₂N₂O₆: C, 80.62, H, 10.71, N, 1.96. Found: C, 79.68, H, 10.44, N, 1.92.

Characterization

¹H-NMR spectra and ¹³C-NMR spectra were measured on Varian Mercury (300 or 400 MHz) in CDCl₃ with tetramethylsilane as the internal reference. Elemental analyses were performed on an Elemental Vario EL III elemental analyzer. Infrared (IR) spectroscopy was measured on a Thermo Nicolet Iz-10 spectrometer. The gel permeation chromatography (GPC) measurements were conducted on alliance Waters e2695. Electronic absorption spectra were determined by a U-3900 UV-Vis spectrophotometer. Fluorescence spectra were measured on a HITACHI F-2700 spectrophotometer. Thermogravimetric analysis (TGA) measurements were carried out on a TA Q500 instrument under a dry nitrogen flow at a heating rate of 10 K·min⁻¹, heating from room temperature to 500 °C. Differential scanning calorimetry (DSC) analyses were performed on a Perkin Elmer Pyris I instrument under nitrogen atmosphere at a heating (cooling) scan rate of 10 K·min⁻¹, heating from room temperature to 400 °C. Cyclic voltammetry (CV) measurements were carried out in a conventional three-electrode cell using a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/Ag⁺ (0.1 mol/L AgNO₃ in acetonitrile) as the reference electrode on a computer-controlled CHI610D electrochemical workstation. X-ray diffraction (XRD) measurements were carried out in the reflection mode using a 2-kW Rigaku X-ray diffraction system. AFM was recorded on a JPK NanoWizard atomic force microscope (AFM) in tapping mode. Corresponding NMR (Figs. S1–S7, in SI), IR (Figs. S8 and S9, in SI), TGA (Fig. S10, in SI), DSC (Fig. S11, in SI) and emission spectra of polymers (in films, Fig. S12, in SI) can be found in supporting information.

RESULTS AND DISCUSSION

Synthesis

The synthetic routes for the monomers and polymers are depicted in Scheme S1 (in SI) and Scheme 1, respectively. 1,4-Bis(dodecyloxy)-2,5-di(ethynyl)benzene (**2**)^[61] and **B2**^[35] were synthesized according to the methods reported in the literature. The synthetic procedures of monomers are described in SI. **P1** and **P2** were prepared by Sonogashira cross-coupling reaction of **B4** with **1**, **B2** with **2**, respectively. The crude polymers were collected via gravity filtration and purified by Soxhlet extraction with methanol, acetone, petroleum ether and chloroform, respectively. After purification, **P1** (red) and **P2** (dark-red) were obtained in 80% and 75% yields. The molecular weights (M_n , M_w) and polydispersity indexes (PDI) of polymers were measured by gel permeation chromatography (GPC) with chloroform as an eluent and calibrated with polystyrene standards. As depicted in Table 1, the number-average molecular weights (M_n) of **P1** and **P2** are 23.6 and 14.9 kDa, and the PDI are 1.8 and 2.2, respectively. The IR spectra (Figs. S8 and S9, in SI) showed ν (C≡C) peak at about 2200 cm⁻¹, ν (—CH₂—, —CH₃) peaks at about 2900 and 2850 cm⁻¹, ν (C=O) peak at about 1700 cm⁻¹ and ν (Ph—OR) peak at about 1221 cm⁻¹.

Table 1 Molecular weights of **P1** and **P2**

Polymer	Yield (%)	M_n^a (kDa)	M_w^a (kDa)	PDI
P1	80	23.6	41.9	1.8
P2	75	14.9	33.3	2.2

^a GPC versus polystyrene standards, chloroform as the eluent.

Thermal Properties

Thermal stability of **P1** and **P2** was evaluated by using thermogravimetric analysis (TGA) with a heating ramp rate of 10 K·min⁻¹ under nitrogen (Fig. S10, in SI). The 5% decomposition temperatures of **P1** and **P2** are 420 and 387 °C, respectively, demonstrating their good thermal stability. The relatively lower decomposition temperature of **P2** may be due to the decomposition of dodecyloxy side chains^[62]. Differential scanning calorimetry (DSC) was carried out at a scan rate of 10 K·min⁻¹ to evaluate the phase transition of **P1** and **P2**; however, no phase transition was observed from the entire scanning ranges of DSC (Fig. S11, in SI).

Optical Properties

The UV-Vis absorption spectra and fluorescence spectra of **P1** and **P2** (in solution) are shown in Figs. 2 and 3, and the related data are summarized in Table 2. As depicted in Fig. 2, the absorption spectrum of **P1** in solution consists of two bands: a higher energy band at 470 nm and a lower energy band at 506 nm. The absorption spectra of **P2** is quite different from that of **P1**, with only one band at 465 nm. The absorption of **P1** and **P2** in thin films is red-shifted 9 and 10 nm, relative to those measured in solution. Optical energy gaps (E_g^{opt}) of **P1** and **P2** (measured from the onset absorptions of the thin films) are 2.18 and 2.02 eV. **P1** and **P2** have different fluorescence in solution with emission at 544 and 620 nm, respectively. As shown in Fig. 3, the Stokes shift of **P2** (155 nm) is larger than that of **P1** (38 nm), which may be due to the intramolecular charge transfer (ICT)^[63, 64] or the excited-state proton transfer^[65]. To examine the fluorescence spectra, the thin films of **P1** and **P2** were prepared by static-casting their solutions onto quartz substrates. As shown in Fig. S12 (in SI), the photoluminescence of **P2** (at 627 nm) is decreased relative to that of **P1** (at 560 nm) due to the intra-chain charge transfer (CT) between the donor and acceptor units of **P2**^[66].

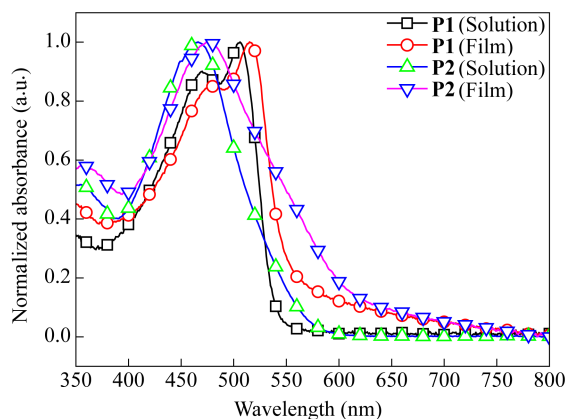


Fig. 2 UV-Vis absorption spectra of **P1** and **P2** in dichloromethane solution and in thin films

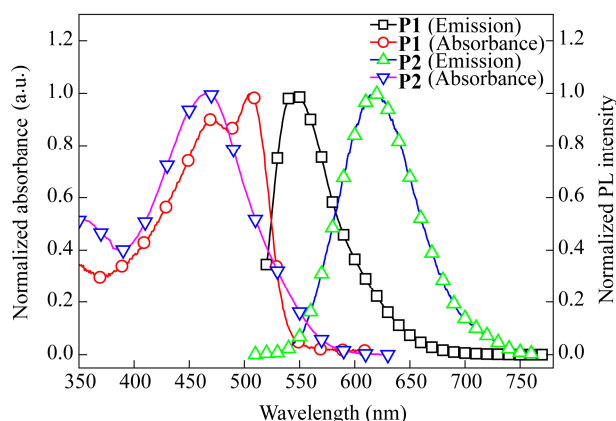


Fig. 3 Absorption and emission spectra of **P1** and **P2** in dichloromethane

Table 2 Optical and electrochemical properties of **P1** and **P2**

Polymer	Solution		Thin film					
	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\lambda_{\text{max}}^{\text{PL}}$ (nm)	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\lambda_{\text{max}}^{\text{PL}}$ (nm)	$E_g^{\text{opt a}}$ (eV)	$E_{\text{LUMO}}^{\text{b}}$ (eV)	$E_{\text{HOMO}}^{\text{c}}$ (eV)	$E_{\text{red}}^{1/2}$ (eV)
P1	506	544	515	560	2.18	-3.49	-5.67	-1.19
P2	465	620	475	627	2.02	-3.54	-5.56	-1.14

^a Calculated from the onset of thin-film absorption spectra; ^b $E_{\text{LUMO}} = -(E_{\text{red}}^{1/2} - E^{1/2}(\text{Fc}/\text{Fc}^+) + 4.8)$ eV; ^c $E_{\text{HOMO}} = -(E_g^{\text{opt}} - E_{\text{LUMO}})$ eV

Electrochemical Properties

The electrochemical properties of **P1** and **P2** were measured by cyclic voltammetry (CV). As shown in Fig. 4, **P1** and **P2** show only reduction waves with the onset reduction ($E_{\text{red}}^{1/2}$) values of -1.19 and -1.14 eV, respectively. The HOMO and LUMO energy levels of **P1** and **P2** were estimated according to the Eqs. (1)

and (2).

$$E_{\text{LUMO}} = -(E_{\text{red}}^{1/2} - E^{1/2}(\text{Fc}/\text{Fc}^+) + 4.8) \text{ eV} \quad (1)$$

$$E_{\text{HOMO}} = -(E_{\text{g}}^{\text{opt}} - E_{\text{LUMO}}) \text{ eV} \quad (2)$$

The electrochemical parameters and HOMO/LUMO energy levels are summarized in Table 2. In comparison with **P2** (E_{LUMO} : -3.54 eV), the LUMO energy level of **P1** (-3.49 eV) showed a slight increase, although an electron-withdrawing benzothiadiazole unit was introduced into the polymeric backbone; the similar phenomenon was also reported in the literature^[35]. But the HOMO energy level of **P2** (-5.56 eV) was increased by 0.11 eV relative to that of **P1** (-5.67 eV) due to the introduction of electron donors to the main chain of **P2**.

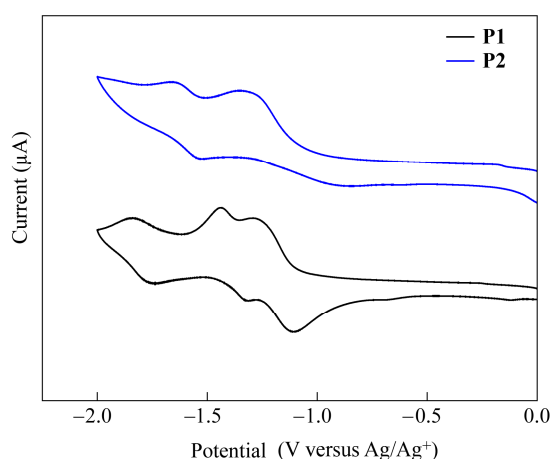


Fig. 4 Cyclic voltammograms of thin films of **P1** and **P2** in 0.1 mol/L $\text{Bu}_4\text{N}^+\text{PF}_6^-$ solution in acetonitrile at a scan rate of 100 mV/s

Field-effect Transistors

To investigate the charge transport properties of **P1** and **P2**, their bottom-gate top-contact OFETs were fabricated (see SI for details). The devices were measured under nitrogen conditions. Figure 5 shows the typical transfer curves of OFETs based on **P1** and **P2**, and the device performance data are summarized in Table S1 (in SI). **P1** showed pure electron transport characteristics with the electron mobility of up to $10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and an on/off ratio of 10^3 , while **P2** exhibited hole transport behaviors ($\mu_{\text{h}} = 10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$). **P1** is the first example of pure electron transport copolymers in OFETs based on 1,2,5,6-naphthalenediimide, with the electron mobility comparable to or even higher than those of recent reported electron-deficient PPEs-

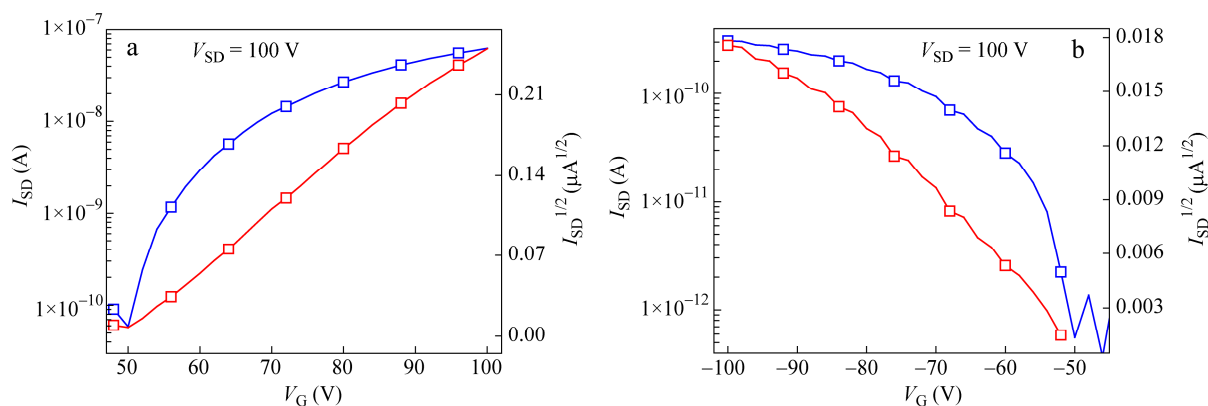


Fig. 5 Transfer characteristics of OFET based on **P1** (a) and **P2** (b)

like copolymers^[52, 53, 60]. From the molecular structure analysis, **P1** has the acceptor-linker-acceptor' (A-L-A') structure feature and **P2** possesses the donor-linker-acceptor (D-L-A) structure characteristic. The different molecular structures greatly impact on the charge transport behaviors of **P1** (n-type) and **P2** (p-type). The first pure electron transport copolymer in OFETs is achieved by the construction of A-L-A' structure based on 1,2,5,6-naphthalenediimide.

Film Morphology

Morphology and microstructure of the spin-coated thin films of **P1** and **P2** were studied by X-ray diffraction (XRD) and atom force microscopy (AFM). As shown in Fig. 6, no obvious diffraction peaks in XRD plots are observed even at high annealing temperature of 160 °C, indicating non-crystallizable nature of these polymers. As depicted in Fig. 7, the AFM images of thin films of **P1** and **P2** show featureless morphology without obvious crystalline domains. The morphology of films is slightly varied even at high thermal annealing temperatures. The above results together with the comparable maximum mobility ($\mu_{\max}$) and average mobility (μ_{avg}) values indicate the amorphous-like features of thin films of **P1** and **P2**, which is important for preparing large-area electronic devices.

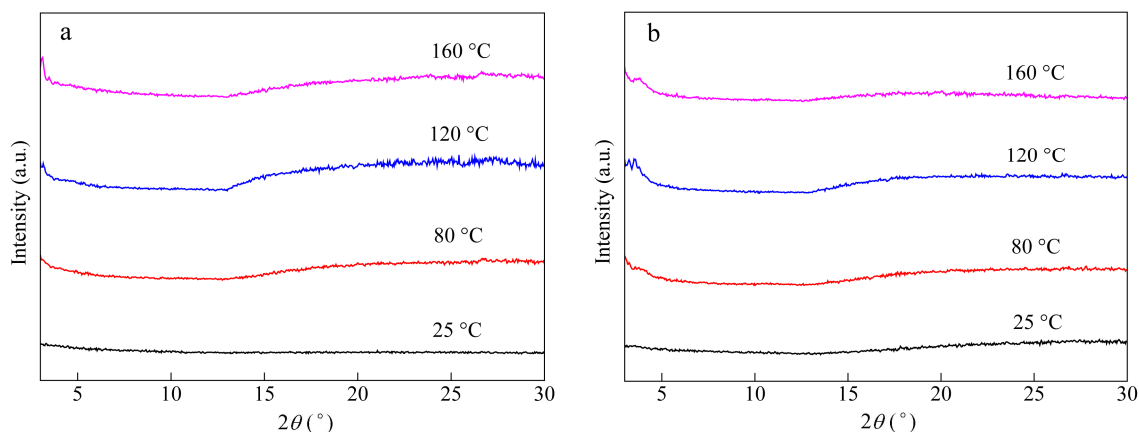


Fig. 6 X-ray diffraction patterns of thin films of **P1** (a) and **P2** (b) with as-spun and thermal annealed films

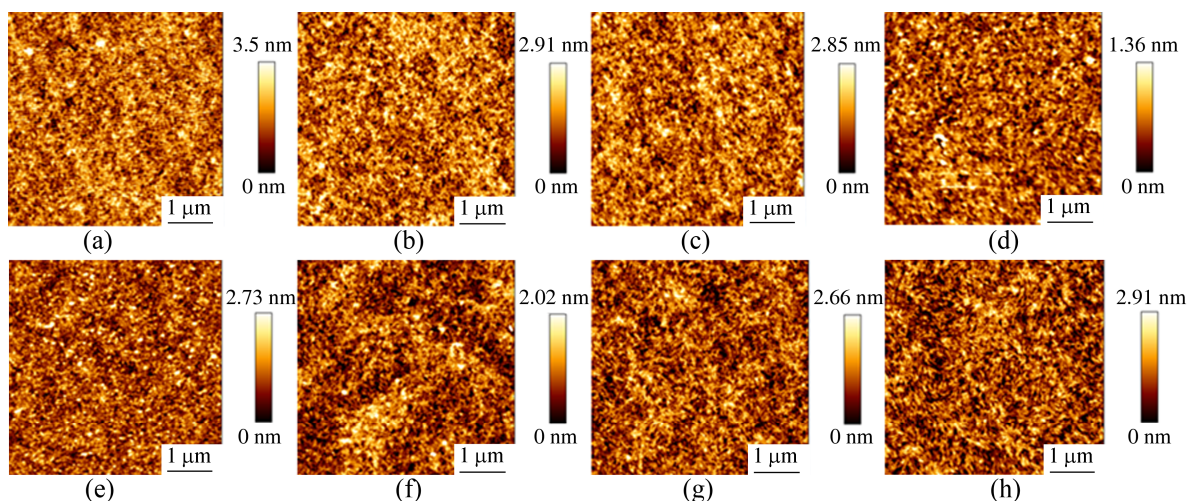


Fig. 7 AFM images of thin films of **P1** (a–d) and **P2** (e–h) with as-spun (a, e) and thermal annealed films at temperatures (b, f for 80 °C; c, g for 120 °C; d, h for 160 °C)

CONCLUSIONS

Two ethynyl-linked 1,2,5,6-naphthalenediimide-based conjugated copolymers (**P1** and **P2**), comprising of benzothiadiazole, 1,4-bis(dodecyloxy)-benzene units, were synthesized by Sonogashira coupling polymerization. The thermal, optical, electrochemical as well as charge transport properties of the polymers were investigated. **P1** and **P2** were luminescent both in solution and in solid state, and displayed lower band gaps (< 2.2 eV) than those of common PPEs (about 2.5 eV). The two copolymers showed comparable LUMO energy levels of about -3.5 eV, but the HOMO energy level of **P2** (-5.56 eV) was increased by 0.11 eV relative to that of **P1** (-5.67 eV) due to the introduction of electron donors to the main chain of **P2**. Bottom-gate top-contact OFETs based on **P1** and **P2** were fabricated in order to investigate their charge transport behaviors. From the molecular structure analysis, it can be found that the different structure features of **P1** and **P2** (A-L-A' and D-L-A, respectively) greatly impact on their charge transport behaviors, *i.e.* **P1** showed only n-type charge transport behaviors, while **P2** exhibited p-type charge transport features. It should be noted that **P1** is the first example of pure electron transport copolymers in OFETs based on 1,2,5,6-NDI, with the electron mobility comparable to or even higher than those of recent reported electron-deficient PPEs-like copolymers. The results demonstrate that the construction of A-L-A' structure is an effective strategy to achieve pure electron transport 1,2,5,6-NDI-based copolymers.

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