**Synthesis, characterization, and field-effect properties of
(*E*)-2-(2-(thiophen-2-yl)vinyl)thiophen-based donor–acceptor copolymers**

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ABSTRACT

Two donor–acceptor copolymers, PTVTBT and PTVTBO, using the highly π -extended (*E*)-2-(2-(thiophen-2-yl)vinyl)thiophen as an electron-rich unit and benzodiathiazole or benzoxadiazole as an electron-deficient one, were designed and synthesized via a Pd-catalyzed Stille-coupling method. The copolymers possess high thermal stability, broad absorption, low band gap, and good film-forming ability. Meanwhile the two polymers exhibit excellent hole transport properties when used as the active layer in polymer field-effect transistor devices. The highest hole mobility can reach to 0.25 and 0.50 cm² V⁻¹ s⁻¹ for the PTVTBT and PTVTBO thin films, respectively. This work demonstrates that PTVTBT and PTVTBO would be promising semiconductors for developing cost-effective and large-scale production of flexible organic electronics.

Keywords: Conjugated copolymers; Field-effect transistor; Mobility

1. Introduction

Polymer field-effect transistors (PFETs) have been attracting considerable attention over the past decades due to their potential applications to large area flexible displays or ubiquitous cheap electronics through solution processed techniques [1–5]. In comparison to small molecules and organic crystallines, polymer semiconductors show a relatively low transporting capacity resulting from the film defects and weak crystalline. However, significant progress has been made in the performance of the field-effect transistors based on polymer semiconductors during the past few years, and it has been successfully proven that the utilization of electron donating and accepting building blocks in the main backbone of the π -conjugated copolymers is one of the most promising strategies to achieve high mobilities. The donor–acceptor (D–A) structures would be an effective way to achieve closed intermolecular π – π stacking, and in turn enhance crystalline and charge-transporting ability [6–8]. Also, a lower energy level of the highest occupied molecular orbital (HOMO) can be produced by selecting the D–A type of polymer, which can lead to higher air stability. At present, conjugated polymers with (*E*)-2-(2-(thiophen-2-yl)vinyl)thiophen (TVT) [9,10], thienothiophene (TT) [11] or naphthalene [12,13] as donor units and benzothiadiazole (BT) [14,15], benzoxadiazole (BO) [16] or diketopyrrolopyrrole (DPP) [17–19] as acceptor units have been reported with excellent charge carrier transporting properties, indicating the possibility for the substitution of amorphous silicon transistors [20,21].

Herein, two novel D–A copolymers, PTVTBT and PTVTBO, using the highly π -extended TVT as an electron-rich unit and benzodiathiazole (BT) or benzoxadiazole (BO) as an electron-deficient one, were designed and synthesized (see Scheme 1) for solution-processed high-performance PFETs. We found that BT- or BO-based conjugated polymers are ones of the most important polymer semiconductors due to their convenient preparation, excellent thermal stability, and electronic characteristic; and many efforts have been devoted to the design and synthesis of new BT/BO derivatives [22,23]. Up to now, hole mobilities of the PFETs based on BT-containing polymers have been up to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after systematic optimization [24]. Thus, it still remains a big challenge to explore new BT/BO-based polymers to gain high field-effect mobility. In this work, we introduce TVT units to BT/BO-based polymers. The incorporation of the highly π -extended TVT units adjacent to the BT or BO units in the main chain of the conjugated polymers can extend the coplanarity of the main backbone and promote intermolecular interaction. In addition, intermolecular interaction between the electron-donating TVT and electron-accepting BT or BO could further shorten the distances between the polymer main chains, which would facilitate the charge carrier transport.

2. Experimental

2.1. Materials and synthetic procedures

4,7-Bis(5-bromothiophen-2-yl)-5,6-bis(dodecyloxy)benzo-[c][1,2,5]-thiadiazole
(**M₁**) and

4,7-bis(5-bromothiophen-2-yl)-5,6-bis(dodecyloxy)benzo[c][1,2,5]oxadiazole (**M₂**)

were prepared according to the literature procedures [25,26]. Tetrahydrofuran (THF) was dried over Na/benzophenoneketyl and freshly distilled prior to use. Other chemicals and reagents were used as received from commercial sources without further purification. All reactions were performed under nitrogen atmosphere.

2.2. Synthesis of PTVTBT

To a solution of the monomer **M₁** (165.4 mg, 0.20 mmol) and *trans*-1,2-bis(tributylstannyl)ethene (121 mg, 0.20 mmol) in chlorobenzene (6 mL) purged with nitrogen for 15 min, Pd₂(dba)₃ (10 mg, 0.01 mmol) and P(*o*-tol)₃ (25 mg, 0.08 mmol) were added. After being purged for 15 min, the mixture was heated at 135 °C for 24 h. Then, the reaction mixture was cooled to room temperature and added dropwise to 200 mL methanol, and subsequently collected by filtration and washed with methanol. The crude polymer was purified by Soxhlet extraction with methanol, hexane, and chlorobenzene, successively. The chlorobenzene solution was concentrated under reduced pressure and precipitated in methanol. The precipitate was filtered and finally dried under vacuum to obtain a shiny, bronze-colored solid (129 mg, yield 93%). Molecular weight by GPC (trichlorobenzene): $M_n = 22.8$ kDa, $M_w = 66.8$ kDa, PDI = 2.93).

¹H NMR (600 MHz, CDCl₃). δ (ppm): 8.49 (br, 2H), 7.59–6.96 (br, 4H), 4.31–3.98 (br, 4H), 2.10–0.48 (m, 46H).

Elemental analysis. Calc. for $(C_{40}H_{56}N_2O_2S_3)_n$: C, 69.32; H, 8.14; N, 4.04; Found: C, 69.30; H, 8.25; N, 4.02.

2.3. Synthesis of PTVTBO

The monomer **M**₂ (165.4 mg, 0.20 mmol) and *trans*-1,2-bis(tributylstannyl)ethene (121 mg, 0.20 mmol) were dissolved in chlorobenzene (6 mL). After degassing under nitrogen for 15 min, Pd₂(dba)₃ (10 mg, 0.01 mmol) and P(*o*-tol)₃ (25 mg, 0.08 mmol) were added to the mixture. Subsequently, the reaction mixture was heated at 135 °C for 24 h. The crude polymer was precipitated with methanol and then was purified by Soxhlet extraction with methanol, hexane, and chlorobenzene, successively. The chlorobenzene solution was concentrated and precipitated in methanol. The precipitate was filtered and dried under vacuum to obtain a shiny bronze-colored solid (131.9 mg, yield 95.3%). Molecular weight by GPC (trichlorobenzene): $M_n = 27.0$ kDa, $M_w = 114.4$ kDa, PDI = 4.24).

¹H NMR (600 MHz, CDCl₃). δ (ppm): 8.41 (br, 2H), 7.74–6.95 (br, 4H), 4.35–3.96 (br, 4H), 2.24–0.13 (m, 46H).

Elemental analysis. Calc. for $(C_{40}H_{56}N_2O_3S_2)_n$: C, 70.96; H, 8.34; N, 4.14; Found: C, 70.83; H, 8.37; N, 4.09.

2.4. Measurements and characterization

Number-average (M_n) and weight-average (M_w) molecular weights of the polymers were determined by Waters 515-2410 gel permeation chromatography (GPC) with polystyrene as reference standard and trichlorobenzene as an eluent. Nuclear magnetic resonance spectra were recorded on a Bruker AV 600 spectrometer in CDCl₃ at room temperature. ¹H NMR chemical shifts were referenced to internal

tetramethylsilane (TMS, 0 ppm). Splitting patterns were designated as s (singlet), t (triplet), d (doublet), m (multiplet), and br (broad). Elemental analyses were performed with a Carlo Erba model 1160 elemental analyzer. Thermal gravimetric analysis (TGA) was measured on a Netzsch TG209C analyzer with a heating rate of 10 °C/min under inert atmosphere. UV–Vis–NIR absorption spectra were carried out on a Shimadzu UV-3150 spectrophotometer. Cyclic voltammetry (CV) measurements were conducted on a Zahner IM6e electrochemical workstation. Pt disk coated with the polymer film, Pt plate, and Ag/AgNO₃ electrode were used as working electrode, counter electrode, and reference electrode, respectively. An anhydrous solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile was used as the electrolyte. X-ray diffraction (XRD) measurements were performed in the reflection mode at 40 kV and 200 mA with Cu K α radiation using a 2 kW Rigaku X-ray diffractometer. Atomic force microscopy (AFM) images were obtained with a Nanoscope V instrument, and operated in a tapping mode.

2.5. *Fabrication of field-effect transistor devices*

The polymer FETs with a bottom-gate bottom-contact (BGBC) configuration were fabricated on highly doped silicon with thermally grown oxide (SiO₂ 300 nm). Gold source/drain electrodes were patterned by photolithography on SiO₂ substrates to manipulate the channel length (L) and channel width (W = 1400 μ m). The polymer films were deposited onto octadecyltrichlorosilane (OTS)-modified Si/SiO₂ surfaces by spin-coating a polymer solution in *o*-dichlorobenzene (5 mg/mL). The FET devices were annealed on a hot plate for 5 min in air directly and characterized by measuring the transfer and output characteristics in air with a Keithley 4200 semiconductor characterization system. The mobility of devices was calculated in the saturation

regime. The equation is listed as follows:

$$I_{DS} = (W/2L) C_i \mu (V_{GS} - V_{th})^2$$

where W/L is the channel width/length ratio, C_i is the insulator capacitance per unit area, and V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively.

3. Results and discussion

3.1. Synthesis and thermal analysis

The synthesis routes of the polymers PTVTBT and PTVTBO are showed in Scheme 1. The two polymers were synthesized by palladium-catalyzed Stille-coupling polymerization between the corresponding dibrominated monomer and *trans*-1,2-bis(tributylstannyl)ethane. Precipitation and Soxhlet extraction were used to purify the crude polymers and to remove low-weight oligomers and catalysis residues. The polymers were sequentially extracted with methanol, hexanes, and chlorobenzene. The chlorobenzene fraction was then reduced in volume, precipitated into methanol, and collected by filtration, yielding shiny, bronze-colored solids in a yield of 93–95.3%. The PTVTBT and PTVTBO can be readily dissolved in common solvents such as toluene and chlorobenzene. Moreover, the polymers exhibit good film-forming ability and high-quality pinhole-free thin films could be obtained by simple spin-coating techniques. The polymers PTVTBT and PTVTBO showed moderate number-average molecular weights ($M_n = 22.8$ KDa for PTVTBT, and $M_n = 27$ KDa for PTVTBO, see Table 1) determined by GPC in trichlorobenzene solution relative to polystyrene standards. The thermal behavior of the polymers was measured by TGA under nitrogen atmosphere at a heating rate of 10 °C/min as shown in Fig. 1.

All polymers have good thermal stability with high decomposition temperatures (5% weight loss) over 300 °C.

3.2. *Optical and electrochemical properties*

The absorption spectra of the studied polymers were measured in both solution and thin films (Fig. 2), and the correlated optical parameters are summarized in Table 2, including the absorption peak wavelengths (λ_{abs}) and the optical band gap ($E_{\text{g}}^{\text{opt}}$). The absorption spectra of both the polymers in dilute chloroform solution show two absorption peaks. The absorption at short wavelength can result from π - π^* transitions and one at long wavelength range may be attributed to the intramolecular charge transfer (ICT) between the acceptor (BT or BO) and donor (TVT) units. The two polymers exhibit different absorption peak at long wavelength range, indicating that the BT and BO units have different electron accepting ability. Compared to solution of the PTVTBT and PTVTBO in chloroform, their corresponding thin films show broadened absorption spectra. This phenomenon is common for conjugated polymers, attributing to the aggregation of the conjugated polymer main chains in solid films. Both the PTVTBT and PTVTBO thin films exhibit two well-defined peaks at longer wavelength part. The absorption edges for the PTVTBT and PTVTBO solid films locate at 733 and 727 nm, corresponding to optical band gaps of 1.69 and 1.71 eV, respectively.

Cyclic voltammetry (CV) has been employed and considered as an effective tool in investigating electrochemical properties of conjugated oligomers and polymers

[27]. Cyclic voltammograms of the polymer films are shown in Fig. 3. The energy levels of the highest occupied molecular orbits (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the polymers were calculated according to the equations [28] of $E_{\text{HOMO}} = - (E_{\text{ox}}^{\text{onset}} + 4.71) \text{ (eV)}$ and $E_{\text{LUMO}} = - (E_{\text{red}}^{\text{onset}} + 4.71) \text{ (eV)}$. From the value of onset oxidation potential ($E_{\text{ox}}^{\text{onset}}$) and reduction potential ($E_{\text{red}}^{\text{onset}}$) of the polymers, the HOMO and LUMO energy levels were calculated and listed in Table 2. The moderate onset oxidation potentials of PTVTBT and PTVTBO are determined to be 0.42 and 0.49 V vs. Ag/Ag⁺, respectively, corresponding with the HOMO energy levels to be −5.13 and −5.20 eV. These data could match well with work function of Au electrode facilitating hole injection from Au source-drain electrodes to polymeric semiconductor layer and leading to good characteristics of FET devices. Moreover, corresponding LUMO energy levels were estimated to be −3.54 and −3.55 eV for PTVTBT and PTVTBO, respectively. According to the equation of $E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \text{ (eV)}$, the electrochemical band gaps were determined to be 1.59 eV for the PTVTBT and 1.65 eV for the PTVTBO, which match well with their corresponding optical bands.

3.3. Field-effect transistor properties

Bottom-gate bottom-contact PFET devices were employed to research the carrier transporting characteristics of the copolymers PTVTBT and PTVTBO. The Au and OTS-modified SiO₂ were used as the source-drain electrodes and gate dielectric layer. The polymer thin films were prepared by spin-coating the corresponding polymer

solution in *o*-dichlorobenzene (5 mg/mL) to OTS-treated-Si/SiO₂ substrates. In order to optimize the device performance, different annealing temperature and different channel length (L) of the FET devices (L = 5, 10, 20, 30, 40, and 50 μm) were used. All devices based on polymers were annealed at 100, 140, 180, 220, and 260 $^{\circ}\text{C}$. Electronic properties of all devices were measured under ambient conditions. The device parameters of PFETs based on the copolymer PTVTBT or PTVTBO are shown in Tables 3 and S1-5. Transfer and output characteristics of the PFET devices with a channel length of 5 μm after annealing at different temperatures are shown in Figs. 4 and S1-11. Both PTVTBT and PTVTBO-based PFETs show typical hole-transporting characteristics. The mobility, on/off current ratio, and threshold voltage were estimated from the saturation regimes.

The annealing temperature of polymer thin films and channel length have a large effect on device performance. The highest mobilities were obtained in the PFETs with a channel length of 5 μm . The unannealed PTVTBT and PTVTPO-based devices with a channel length of 5 μm show a hole mobility of 0.15 and 0.2 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. The annealing temperature has a large effect on the hole mobility. After thermal annealing at 100 $^{\circ}\text{C}$, the PTVTBT-based devices with a channel length of 5 μm exhibit a highest mobility of 0.25 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ with a very high on/off current ratio of $10^6 \sim 10^7$. With the further increase of annealing temperature, the mobilities of PTVTBT become decreasing. However, the mobility of PTVTBT-based devices reached in a new peak of 0.22 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ after thermal annealing at 220 $^{\circ}\text{C}$. At annealing temperature of 260 $^{\circ}\text{C}$, the mobilities of the PTVTBT-based OFETs with a

channel length of 5 μm decrease dramatically to $0.0072\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. The PTVTBO-based FETs with a channel length of 5 μm show the highest mobility of $0.50\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ with an on/off current ratio of $10^7\sim 10^8$ after thermal annealing at 140°C for 5 min. The mobilities of the PTVTBO-based devices with a channel length of 5 μm become decreasing when the annealing temperature exceeds 140°C . The obtained hole mobilities of $0.25\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ for PTVTBT and $0.50\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ for PTVTBO are among relatively high values for BT or BO-based polymers. The above results indicated that the two polymers with BT or BO units showed different charge carrier transporting characteristics and the BO/BT units exhibit a large effects on the device performances. The polymer with BT unit shows a higher mobility than that of one with BO unit. On the other hand, both polymers PTVTBT and PTVTBO have almost same HOMO energy levels resulting in same energy barrier of hole injection from the Au source-drain electrode into polymer semiconducting layer. Therefore, different electronic performances of the PFET devices based on the polymers PTVTBT and PTVTBO should be ascribed to different morphologies and crystalline ordering in their thin films.

3.4. Thin-film morphologies and ordering structures

In order to investigate the effects of BO/BT units on the electronic characteristics of the PTVTBT and PTVTBO-based OFETs, morphologies and ordering structures of the polymer thin-films were studied by XRD and AFM. XRD patterns of the polymer thin films deposited on OTS-modified Si/SiO₂ substrates are shown in Fig. 5. For the

PTVTBT and PTVTBO thin films without annealing, no obvious diffraction peaks were observed. After the thermal annealing, both the PTVTBT and PTVTBO thin films shows obvious enhancement of crystalline ordering. For the PTVTBT thin films, after annealing at 140 °C, one diffraction peak at 3.42° emerges, which is corresponding to the polymer lamellar spacing (d_1) of 25.67 Å. Moreover, for the PTVTBO thin films with annealing treatments at 100 °C, one diffraction peak at 3.1° appears, which is corresponding to the polymer lamellar spacing (d_1) of 28.52 Å. When annealing temperature further increases to 100 °C, the diffraction peak become stronger and sharper. These XRD studies clearly manifest the enhancement of molecular ordering within the PTVTBT and PTVTBO thin films after annealing, which are in agreement with the observation that hole mobilities of devices increase with annealing.

AFM is used to further investigate the morphology of polymer films with different annealing temperatures. Fig. 6 shows the typical AFM topographical images (5 μm × 5 μm) of the PTVTBT and PTVTBO thin films without and with annealing. AFM images of the polymer thin films support the OFET results. For the PTVTBT thin films, the highly uniform intertwined polymer fibers can be observed from AFM topographical image which benefit to the charge transport and lead to high charge carrier mobilities. However, for the PTVTBO thin films, some gathered grain with larger size were clearly observed compared to the PTVTBT thin films. This nonuniform thin film should result in low mobilities of the PTVTBO thin films. Therefore, the BO/BT units display a significant effect on the morphology and

forming ability of the PTVTBT and PTVTBO thin films leading to different device performances.

4. Conclusions

In this article, two D–A copolymers with the electron-rich TVT unit and electron-deficient BT or BO one have been designed and synthesized by Pd-catalyzed Stille coupling polymerization. Good thermal stability was demonstrated by thermal gravimetric analysis. The HOMO energy levels of -5.13 and -5.22 eV were derived from cyclic voltammetry. Both polymers exhibit good solution processability and solubility in common organic solvents, and show excellent hole-transporting characteristics. The mobilities of the polymer FET devices based on PTVTBT and PTVTBO reach to 0.25 and $0.50\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, respectively. The corresponding thin-film morphologies and ordering structures have been investigated by XRD and AFM. The annealing treatment enhances the molecular ordering within PTVTBT and PTVTBO thin films.

Acknowledgement

This work was financially supported by the National Science Foundation of China (51473021, 21474116, and 51233006), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB12030100), and the Major State Basic Research Development Program (2011CB808403).

References

- [1] Wang C, Dong H, Hu W, Liu Y, Zhu D. *Chem Rev* 2012;112:2208–67.
- [2] Yan H, Chen Z, Zheng Y, Newman C, Quinn J, Kastler F, Facchetti A. *Nature* 2009;457:679–86.
- [3] Sirringhaus H, Tessler N, Friend R. *Science* 1998;280:1741–44.
- [4] Wen Y, Liu Y, Guo Y, Yu G, Hu W. *Chem Rev* 2011;111:3358–406.
- [5] Mei J, Diao Y, Appleton A, Fang L, Bao Z. *J Am Chem Soc* 2013;135:6724–46.
- [6] Chen H, Guo Y, Mao Z, Yu G, Huang J, Zhao Y, Liu Y. *Chem Mater* 2013;23:3589–96.
- [7] Shi S, Xie X, Gao C, Shi K, Chen S, Yu G, Li X, Wang H. *Macromolecules* 2014;47:616–25.
- [8] Lei T, Dou J, Cao X, Wang J, Pei J. *J Am Chem Soc* 2013;135:12168–71.
- [9] Chen H, Guo Y, Yu G, Zhao Y, Zhang J, Gao D, Liu H, Liu Y. *Adv Mater* 2012;24:4618–22.
- [10] Kang Il, Yun HJ, Chung DS, Kwon SK, Kim YH. *J Am Chem Soc* 2013;135:14896–99.
- [11] Li Y, Singh S, Sonar P. *Adv Mater* 2010;22:4862–66.
- [12] Sonar P, Singh S, Williams E, Li Y, Soh M, Dodabalapur A. *J Mater Chem* 2012;22:4425–35.
- [13] Sonar P, Singh P, Li Y, Ooi Z, Ha T, Wong I, Soh M, Dodabalapur A. *Energy Environ Sci* 2011;4:2288–96.
- [14] Cho S, Lee J, Tong M, Seo J, Yang C. *Adv Funct Mater* 2011;21:1910–6.

- [15] Kronemeijer A, Gili E, Shahid M, Rivnay J, Salleo A, Heeney M, Sirringhaus H. Adv Mater 2012;24:1558–65.
- [16] Shi S, Xie X, Jiang P, Chen S, Wang L, Wang M, Wang H, Li X, Yu G, Li Y. Macromolecules 2013;46:3358–66.
- [17] Cheng C, Yu C, Guo Y, Chen H, Fang Y, Yu G, Liu Y. Chem Commun 2013;49:1998–2000.
- [18] Zhang X, Richter L, DeLongchamp D, Kline R, Hammond M, McCulloch I, Heeney M, Ashraf R, Smith J, Anthopoulos T, Schroeder B, Geerts Y, Fischer D, Toney M. J Am Chem Soc 2011;133:15073–84.
- [19] Matthews J, Niu W, Tandia A, Wallace A, Hu J, Lee W, Giri G, Mannsfeld S, Xie Y, Cai S, Fong H, Bao Z, He M. Chem Mater 2013;25:782–9.
- [20] Li J, Zhao Y, Tan H, Guo Y, Di C, Yu G, Liu Y, Lin M, Lim S, Zhou Y, Su H, Ong B. Sci Rep 2012;2:754.
- [21] Kang I, An T, Hong J, Yun H, Kim R, Chung D, Park C, Kim Y, Kwon S. Adv Mater 2013;25:524–8.
- [22] Kronemeijer AJ, Gili E, Shahid M, Rivnay J, Salleo A, Heeney M, Sirringhaus H. Adv Mater 2012;24:1558–65.
- [23] Ong KH, Lim SL, Tan HS, Wong HK, Li J, Ma Z, Moh LCH, Lim SH, de Mello JC, Chen ZK. Adv Mater 2011;23:1409–13.
- [24] Zhang W, Smith J, Watkins SE, Gysel R, McGehee M, Salleo A, Kirkpatrick J, Ashraf S, Anthopoulos T, Heeney M, McCulloch I. J Am Chem Soc 2010;132:11437–9.

- [25] Qin R, Li W, Li C, Du C, Veit C, Schleiermacher HF, Andersson M, Bo Z, Liu Z, Inganäs O, Wuerfel U, Zhang F. *J Am Chem Soc* 2009;131:14612–3.
- [26] Bouffard J, Swager TM. *Macromolecules* 2008;41:5559–62.
- [27] Li Y, Cao Y, Gao J, Wang D, Yu G, Heeger AJ. *Synth. Met.* 1999, 99, 243–8.
- [28] Shi S, Wang X, Sun Y, Chen S, Li X, Li Y, Wang H. *Mater. Chem.* 2012, 22, 11006–8.

Graphical Abstract

Table 1. Molecular weights and thermal properties of the copolymers.

Polymer	M_n (KDa)	M_w (KDa)	PDI	T_d (°C) ^a
PTVTBT	22.8	66.8	2.93	311.6
PTVTBO	27.0	114.4	4.24	300.6

^aDetermined by TGA with the 5% weight-loss in an inert atmosphere.

Table 2. Optical and electrochemical characteristics of the copolymers.

Polymer	$\lambda_{\max}$ (nm) ^a	$\lambda_{\max}$ (nm) ^b	E_g^{opt} (eV) ^c	$E_{\text{ox}}^{\text{onset}}/E_{\text{red}}^{\text{onset}}$ (V)	$E_{\text{HOMO}}/E_{\text{LUMO}}$ (eV)
PTVTBT	399,587	418,630,673	1.69	0.42/−1.17	−5.13/−3.54
PTVTBO	390,614	399,625,671	1.71	0.49/−1.19	−5.20/−3.52

^aObtained in solution. ^bMeasured in thin film. ^cDetermined by onset of optical absorption of thin film.

Table 3. Electrical parameters of field-effect transistors at different annealing temperatures **with a channel length of 5 μm .**

Polymer	Annealing temperature	μ_{h} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	$I_{\text{on}}/I_{\text{off}}$	V_{th} (V)
PTVTBT	25	0.15	10^4 – 10^5	–17
	100	0.25	10^6 – 10^7	–25
	140	0.19	10^7 – 10^8	–23
	180	0.15	10^6 – 10^7	–29
	220	0.23	10^6 – 10^7	–33
	260	0.0072	10^5 – 10^6	–27
PTVTBO	25	0.20	10^3 – 10^4	+17
	100	0.34	10^3 – 10^4	+22
	140	0.50	10^7 – 10^8	+18
	180	0.37	10^7 – 10^8	+14
	220	0.14	10^3 – 10^4	–20
	260	0.0058	10^3 – 10^4	–32

Figure Captions

Scheme 1 Synthetic route of the copolymers

Fig. 1. TGA plots of the polymers with a heating rate of 10 °C/min under an inert atmosphere.

Fig. 2. UV–Vis absorption spectra of the copolymers in (a) CHCl₃ solution and (b) thin films.

Fig. 3. Cyclic voltammograms of the PTVTBT and PTVTBO thin films on a platinum electrode in 0.1 M Bu₄NPF₆ acetonitrile solution at a scan rate of 100 mV s⁻¹.

Fig. 4. Transfer (left) and output (right) characteristics of the polymer FETs with a channel length of 5 μm and a channel width of 1400 μm: (a, b) PTVTBT-based devices with annealing at 100 °C for 5 min; (c, d) PTVTBO-based devices with annealing at 140 °C for 5 min.

Fig. 5. X-ray diffraction patterns of the (a) PTVTBT and (b) PTVTO thin films after thermal treatment at different temperatures.

Fig. 6. AFM images (5 μm × 5 μm) of the PTVTBT and PTVTBO thin films after thermal treatment at different temperatures. For PTVTBO films: (a) room temperature, (b) 100 °C, (c) 140 °C, (d) 180 °C, (e) 220 °C, (f) 260 °C; and for PTVTBT film: (g) room temperature, (h) 100 °C, (i) 140 °C, (j) 180 °C, (k) 220 °C, (l) 260 °C

Scheme 1

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6