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Biaxially Extended Conjugated Polymers with Thieno[3,2-b]thiophene Building Block for High Performance Field-**Effect Transistor Applications**

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Supporting Information

ABSTRACT: Biaxially thiophene side chain extended thieno [3,2b]thiophene (TT2T)-based polymers, PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T, were synthesized by Stille coupling polymerization with different conjugated moieties of thiophene (T), bithiophene (2T), thieno[3,2-b]thiophene (TT), and thiophenevinylene-thiophene (TVT), respectively. The electronic properties of the prepared polymers could be effectively tuned because the variant π conjugated building block affected the backbone conformation and the resulted morphology. The morphology of the thin films characterized by atomic force microscopy and grazing incidence X-ray diffraction showed that P2TTT2T and PTVTTT2T thin films possessed a better molecular packing with a nanofiber structure owing to their coplanar backbone. The average field-effect mobilities of PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T were 6.7 \times 10⁻⁶, 0.36, 2.2 \times 10⁻³, and



0.64 cm² V⁻¹ s⁻¹ (maximum 0.71), respectively, attributed to the coplanarity of polymer skeleton. In addition, the fabricated FET devices showed a high on/off ratio over 10^7 under ambient for over 3 months, suggesting the excellent environmental stability. The above results demonstrated that the biaxially extended fused thiophene based conjugated polymers could serve as a potential candidate for organic electronic device applications.

INTRODUCTION

Conjugated polymers have attracted extensive scientific interest for flexible electronic and optoelectronic device applications, such as field-effect transistors (FETs), $^{1-13}$ photovoltaic cells, $^{14-18}$ and digital data storage devices, $^{19-22}$ due to the advantages of low cost, light weight, solution processability, and tunable physical properties.²³ Conjugated polymers with biaxially extended conjugated side chains not only facilitated ordered molecular packing but also provided multiple pathways for charge transport, leading to the enhanced field-effect mobility for transistor device.²⁴⁻³⁵ In addition, such polymers usually possess a good air stability because the side chains can freely rotate, resulting in decreased conjugation length of polymer backbone and low-lying highest occupied molecular orbital (HOMO) level. Thiophene-based side chains, including single thiophene,²⁸ bithiophene,^{24,34} and thienothiophene,³ have been synthesized onto the conjugated backbone, showing improved charge transfer ability and stable electronic device characteristics. Our group also reported biaxially extended conjugated thiophene-based polymers using bithiophene building block on polymer main chain, $^{28-33}$ exhibiting a high carrier mobility (up to 0.61 cm² V⁻¹ s⁻¹ with dithienthiophene spacer)³⁰ with a low-lying HOMO level (-5.04 to -5.62 eV).

Conjugated polymers containing fused thiophene building block could self-organize into ordered structures for enhancing device performance, including thienothiophene, dithienothiophene, and benzodithiophene.^{24,36,37} The sulfur atoms induce multiple sulfur-sulfur intermolecular interactions, increasing the effective dimensionality of the electronic states of semiconducting materials. Also, the fused structure possesses a high degree of conjugation and rigidity, which can induce strong $\pi - \pi$ stacking interaction in solid state, leading to the efficient charge transport between polymer chains.³⁶ Indeed, an enhanced charge carrier mobility over 1 $\mbox{cm}^2\ \mbox{V}^{-1}\ \mbox{s}^{-1}$ was obtained, which was comparable with that of amorphous silicon.³⁸ However, biaxially conjugated polymers using the fused thiophene ring as the building block have not been fully explored yet.

In this study, new biaxially extended conjugated polymers with the building block of fused thiophene, 3,6-bis(5-dodecylthiophen-2-yl)-thieno[3,2-b]thiophene (TT2T), was designed and synthesized. Four conjugated polymers, PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T, consisting of TT2T and different π -conjugating spacers, including thiophene (T), bithiophene (2T), thieno[3,2-b]thiophene (TT), and thiophene-vinylene-thiophene (TVT), respectively, were synthesized using the Stille coupling reaction under microwave heating (Scheme 2). The synthesis, optical, and electrochemical

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Received: June 8, 2015
Revised:
           August 5, 2015
Published: August 13, 2015
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Scheme 1. Synthetic Route on Synthesizing TT2T Monomers



Scheme 2. Synthetic Route on Preparing TT2T-Based Polymers



characteristics of polymers were explored systematically. In addition, the morphology of polymer thin films was characterized by atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXD). Top contact FET was used to investigate the charge carrier transport characteristics of the studied polymers. The FET mobility of the TT2T-based conjugated polymers could be as high as 0.7 cm² V⁻¹ s⁻¹, suggesting their promising applications for high performance organic electronic devices.

EXPERIMENTAL SECTION

Materials. Thiophene, 1-bromododecane, trimethyltin chloride, Nbromosuccinimide, tri(o-tolyl)phosphine, and tris(dibenzylideneacetone)dipalladium(0), organic solvents (tetrahydrofuran, toluene, and dimethylformamide), and anhydrous solvents (i.e., chloroform and chlorobenzene) were purchased from Aldrich (St. Louis, MO) and used without further purification. Tetrakis(triphenylphosphine)palladium(0) and 3,6-dibromothieno[3,2-b]thiophene were purchased from TCI (Tokyo, Japan) and used as received. Monomers including 2,5-bis(trimethylstannyl)thiophene (T),³⁹ 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (2T),⁴⁰ 2,5-bis(trimethylstannyl)-thieno[3,2-*b*]thiophene (TT),⁴¹ and (E)-1,2-bis(5 -(trimethylstannyl)thiophen-2yl)ethene (TVT)⁴² were synthesized according to the reported method. The synthetic steps of biaxially thiophene side chain extended thieno[3,2-b]thiophene-based quarterthiophene (TT2T) monomers are shown in Scheme 1, and the ¹H NMR spectra are summarized in the Supporting Information (Figures S1).

Synthesis of TT2T Monomers. 2-Dodecylthiophene (1).³³ *n*-Butyllithium (2.5 M in hexanes, 88 mL, 220 mmol) was added dropwise to a solution of thiophene (16.8 g, 200 mmol) in anhydrous THF (200 mL) at -78 °C under nitrogen, and then the reaction mixture was brought to room temperature. After the mixture was stirred for 1.5 h, 1-bromododecane (64.7 g, 260 mmol) was added in one portion, and the solution was stirred at room temperature overnight. The solution was added into deionized water and extracted with hexanes twice. The organic extract was dried over MgSO₄ to remove water and purified by vacuum distillation to obtain 25.6 g (yield: 50.7%) of yellow viscous liquid. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.08 (d, 1H), 6.89 (t, 1H), 6.75 (d, 1H), 2.77–2.81 (t, 2H), 1.71–1.65 (m, 2H), 1.39–1.24 (m, 18H), 0.87–0.84 (t, 3H).

(5-Dodecylthiophen-2-yl)trimethylstannane (2).³³ Compound 1 (5 g, 20 mmol) was dissolved in anhydrous THF (100 mL) at -78 °C under nitrogen, and then *n*-butyllithium (2.5 M in hexanes, 9.5 mL, 24 mmol) was added dropwise. The mixture was stirred for 4 h, and then trimethyltin chloride (5.5 g, 28 mmol) in 5 mL of THF was added. After reacting at room temperature overnight, the solution was poured into deionized water and extracted with hexanes. The organic extract was dried over MgSO₄ to remove water and evaporated to remove solvent. A yellow viscous liquid was obtained. (6.85 g, yield: 83.3%). ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 6.98 (d, 1H), 6.89 (d, 1H), 2.84–2.77 (t, 2H), 1.67–1.64 (m, 2H), 1.31–1.24 (m, 18H), 0.88–0.84 (t, 3H), 0.38–0.24 (t, 9H).

3,6-Bis(5-dodecylthiophen-2-yl)thieno[3,2-b]thiophene (TT2T). A solution of compound 2 (3.48 g, 8.39 mmol), 3,6-dibromothieno[3,2-b]thiophene (1 g, 3.36 mmol), and Pd(PPh₃)₄ (0.12 g, 0.1 mmol) in DMF (80 mL) and toluene (20 mL) was mixed in a one-neck flask.

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After five freeze-thaw cycles, the mixtures was heated up to 120 °C and stirred for 48 h under a nitrogen atmosphere. After cooling to room temperature, deionized water was added, and then the aqueous phase was extracted with chloroform. The organic extract was dried over MgSO₄ to remove water, and the solvent was evaporated under vacuum. The crude product was purified by silica gel column using hexane and chloroform as eluent to give a light yellow solid (1.79 g, yield: 83%). ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.47 (s, 2H), 7.20 (d, 2H), 6.79 (d, 2H), 2.85–2.81 (t, 4H), 1.76–1.65 (m, 4H), 1.45–1.25 (m, 36H), 0.86–0.84 (t, 6H).

2,5-Dibromo-3,6-bis(5-dodecylthiophen-2-yl)thieno[3,2-b]thiophene (TT2T-Br₂). TT2T (1 g, 1.56 mmol) was dissolved in a mixed solvent of chloroform (60 mL) and glacial acetic acid (60 mL) at 0 °C in the dark under a nitrogen atmosphere. After stirring for 30 min, *N*-bromosuccinimide (0.61 g, 3.43 mmol) was added to the reaction mixture and reacted for 5 h. The solution was poured into deionized water and extracted with chloroform. The organic extract was dried over MgSO₄ and evaporated to remove solvent. The crude product was washed with hexane several times to give a light pink solid (1.2 g, yield: 96.3%). ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.41 (d, 2H), 6.87 (d, 2H), 2.89–2.85 (t, 4H), 1.81–1.65 (m, 4H), 1.51–1.27 (m, 36H), 0.89–0.86 (t, 6H).

General Procedures for Polymerization. The general procedure of synthesizing TT2T-based polymers (PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T) is shown in Scheme 2 and carried out using a Biotage microwave reactor in sealed vessels. Dibromo monomers (TT2T-Br₂), ditin monomers (T, 2T, TT, or TVT), tri(otolyl)phosphine (16 mol % with respect to ditin monomer), and tris(dibenzylideneacetone)dipalladium(0) (2 mol % with respect to ditin monomer) were dissolved in a microwave vessel using chlorobenzene (5 mL) under a nitrogen atmosphere. The vessel was then sealed with a snap cap, and the material was polymerized by Stille coupling reaction under microwave heating at 170 °C for 60 min. After end-capped with 2-(tributylstannyl)thiophene and 2-bromothiophene (both 1.1 equiv with respect to ditin monomer and under microwave heating at 180 °C for 10 min on the end-capping), the mixture was cooled and poured into methanol to form a crude polymer. The crude polymer was purified using a Soxhlet apparatus with methanol, acetone, and hexane to remove oligomers and catalyst residues. The final product was obtained after drying under vacuum at 40 °C.

PTTT2T. Amounts of 240 mg (0.3 mmol) of TT2T-Br₂, 123 mg (0.3 mmol) of T, and 5 mL of chlorobenzene were used to afford an orange solid (yield, 92%). ¹H NMR (CD₂Cl₂), δ (ppm): 7.91–7.75 (br, Ar–H, 4H),7.21–7.05 (br, Ar–H, 2H), 2.89–2.79 (br, Ar–CH₂, 4H), 1.79–1.65 (br, –CH₂, 4H), 1.55–1.20 (br, –CH₂, 36H), 0.91–0.81 (br, –CH₃, 6H). Anal. Calcd for [C₄₂H₅₆S₅]: C, 69.75; H,8.08; S, 22.17. Found: C, 70.12; H, 7.82; S, 22.05. Weight-average molecular weight (M_w) and polydispersity index (PDI) estimated from GPC are 26 100 g mol⁻¹ and 1.8, respectively.

P2TT72T. Amounts of 240 mg (0.3 mmol) of TT2T-Br₂, 148 mg (0.3 mmol) of 2T, and 5 mL of chlorobenzene were used to afford a dark red solid (yield, 83%). ¹H NMR (CD₂Cl₂), δ (ppm): 7.18–6.92 (br, Ar–H, 6H), 6.88–6.77 (br, Ar–H, 2H), 2.981–2.81 (br, Ar–CH₂, 4H), 1.79–1.65 (br, $-CH_2$, 4H), 1.55–1.20 (br, $-CH_2$, 36H), 0.79–0.91 (br, $-CH_3$, 6H). Anal. Calcd for [C₄₆H₅₈S₆]: C, 68.60; H, 7.51; S, 23.89. Found: C, 68.81; H, 7.65; S, 23.60. Weight-average molecular weight (M_w) and polydispersity index (PDI) estimated from GPC are 14 850 g mol⁻¹ and 1.4, respectively.

PTTTT2T. Amounts of 240 mg (0.3 mmol) of TT2T-Br₂, 140 mg (0.3 mmol) of TT, and 5 mL of chlorobenzene were used to afford a dark red solid (yield, 51%). ¹H NMR (CD₂Cl₂), δ (ppm): 7.39–7.29 (br, Ar–H, 2H), 7.13–7.07 (br, Ar–H, 2H), 6.82–6.73 (br, Ar–H, 2H), 2.81–2.91 (br, Ar–CH₂, 4H), 1.79–1.65 (br, –CH₂, 4H), 1.55–1.22 (br, –CH₂, 36H), 0.78–0.92 (br, –CH₃, 6H). Anal. Calcd for [C₄₄H₅₆S₆]: C, 67.81; H, 7.50; S, 24.69. Found: C, 68.07; H, 7.74; S, 24.19. Weight-average molecular weight (M_w) and polydispersity index (PDI) estimated from GPC are 10 432 g mol⁻¹ and 1.5, respectively.

PTVTTT2T. Amounts of 320 mg (0.4 mmol) of TT2T-Br₂, 208 mg (0.4 mmol) of TVT, and 5 mL of chlorobenzene were used to afford a dark red solid (yield: 300 mg, 90%) ¹H NMR (400 MHz, CD₂Cl₂), δ

(ppm): 7.18–6.15 (br, Ar–H and Vin-H, 10H), 2.81–2.91 (br, Ar– CH₂, 4H), 1.79–1.65 (br, -CH₂, 4H), 1.55–1.22 (br, -CH₂, 36H), 0.78–0.92 (br, -CH₃, 6H). Anal. Calcd for [C₄₈H₆₂S₆]: C, 69.34; H, 7.52; S, 23.14. Found: C, 69.44; H, 6.96; S, 22.82. Weight-average molecular weight (M_w) and polydispersity index (PDI) estimated from GPC are 39 050 g mol⁻¹ and 1.5, respectively.

Characterization. ¹H NMR spectra were recorded with a Bruker Advance DRX-400 MHz spectrometer. Gel permeation chromatographic (GPC) analysis was performed on a Lab Alliance RI2000 instrument (two column, MIXED-C and D from Polymer Laboratories) connected with one refractive index detector from Schambeck SFD GmbH. All GPC analyses were performed on polymer/THF solution at a flow rate of 1 mL min⁻¹ under 40 °C and then calibrated with polystyrene standards. Elemental analysis was performed by elementary Vario EL cube (for NCSH, Germany) with sulfanilic acid as standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ using the TA Instruments (Q-50 and Q-100), respectively.

Grazing incidence X-ray diffraction (GIXD) measurements were carried out on beamline 17A1 in the National Synchrotron Radiation Research Center (NSRRC), Taiwan. An X-ray wavelength of 1.321 Å was used, and the incident angle was 0.12° . The scattering intensities are reported as intensity versus Q, where $Q = (4\pi/\lambda) \sin(\theta/2)$; λ is the wavelength of incident X-rays, and θ is the scattering angle.

The UV-vis absorption spectrum was explored using a Hitachi U-4100 spectrophotometer. For the thin film spectra, polymers were first dissolved in chloroform $(5-8 \text{ mg mL}^{-1})$, followed with filtering through a 0.45 μ m pore size PTFE membrane syringe filter, and then spin-coated at a speed rate of 800 rpm for 60 s onto quartz substrate. Cyclic voltammetry (CV) was performed on a CHI 611B electrochemical analyzer using a three-electrode cell in which ITO (polymer films area were about 0.5×0.7 cm²) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl(sat.) reference electrode. The electrochemical properties of the polymer films were detected under 0.1 M dry acetonitrile solution containing tetrabutylammonium perchlorate as the electrolyte. The morphology of polymer film surface was obtained with a Nanoscope 3D Controller atomic force microscopy (AFM, Digital Instruments, Santa Barbara, CA) operated in the tapping mode at room temperature. Commercial silicon cantilevers with typical spring constants of 21-78 N m⁻¹ were used. Note that the preparation of polymer thin film samples were the same as that of the device fabrications for the measurements of GIXD, UV, and AFM.

Computational Methodology. Theoretical molecular simulation of the studied polymers was calculated through Gaussian 03 program package.⁴³ The density functional theory (DFT) method, using Becke's three-parameter functional with the Lee, Yang, and Parr correlation functional method (B3LYP) with 6-31G(d), was used for the optimization of ground-state molecular geometry.

Fabrication and Characterization of Field-Effect Transistors. The field-effect transistors (FETs) were fabricated from the studied polymers with a bottom-gate/top-contact configuration. A 300 nm SiO_2 layer (capacitance per unit area = 10 nF cm⁻²) as a gate dielectric was thermally grown onto the highly n-type doped Si (100) substrates. The substrates were cleaned with nitrogen stream and washed with toluene, acetone, and isopropanol, in that order. The cleaned Si substrates were then modified with an octadecyltrimethoxysilane (OTS) self-assembled monolayer according to the reported procedure.⁴⁴ The polymer semiconductors (i.e., PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T) were first dissolved in chloroform or chloroform/chlorobenzene mixing solvent (5–8 mg mL $^{-1})$ at 60 $^\circ C$ for at least 2 h. Afterward, polymer thin films were deposited on OTSmodified SiO₂/Si substrates by the spin-coating method at a spin rate of 800 rpm for 60 s. In addition, annealing process (160 °C under vacuum for 1 h) was introduced to enhance the FET performance. The top-contact source/drain contacts were defined by 100 nm thick gold through a regular shadow mask, and the channel length (L) and width (W) were 50 and 1000 μ m, respectively. Electrical characteristics

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of FETs were recorded in a N_2 -filled glovebox using a Keithley 4200 semiconductor parametric analyzer (Keithley Instruments Inc., Cleveland, OH).

RESULTS AND DISCUSSION

Polymer Characterization. The molecular weights of the prepared TT2T-based polymers (PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T) are in the range of 11–39 kDa with polydispersity of 1.5–1.8 from the GPC measurement using THF as the eluent. All studied polymers possessed a good solubility in common organic solvents (i.e., tetrahydrofuran, chloroform, and chlorobenzene). The chemical structures of the TT2T-based polymers and monomers were confirmed by ¹H NMR and elemental analysis. The ¹H NMR spectrum of TT2T and PTTT2T in CD₂Cl₂ solution is shown in Figure 1.



The signals in the range of 6.7 and 7.2 ppm (peaks a, b, and c) are assigned to the protons on the aromatic rings, including the thiophene rings on polymer main chain and side chain. Moreover, the peaks at 2.8 ppm (thiophene– CH_2 , peak d) and 1.8–0.8 ppm (– CH_2 and – CH_3 , peak e) are attributed to the dodecyl group of the TT2T moiety. The numbers of aliphatic and aromatic protons are estimated from the integration value of peaks, which are consistent with the proposed polymer structures. Detailed analyses of other studied polymers are shown in Figure S2 (Supporting Information). In addition, the elemental analyses of the carbon, hydrogen, nitrogen, and sulfur contents are in a good agreement with the theoretical content. The above results suggest the successful preparation of the target polymers.

Thermogravimetric analysis (TGA; Figure 2a) and differential scanning calorimetry (DSC; Figure S3 in Supporting Information) were used to probe the thermal behaviors of the TT2T-based polymers. The thermal decomposition temper-



Figure 2. (a) TGA curves and (b) solid state UV-vis absorption spectra of the studied polymers.

ature (T_d , 5% weight loss) of PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T is 415, 422, 403, and 408 °C, respectively, indicating the good thermal stability for electronic device applications. These studied polymers did not exhibit obvious thermal transition in the bulk sample as the heating temperature up to 280 °C, which is common for the reported conjugated polymer in the research field recently.¹³ However, the polymers have the ordered structure in the microdomain, as discussed later.

Optical Properties. The normalized UV–vis absorption spectra of the studied polymer thin films are shown in Figure 2b, and their corresponding maximum absorption wavelengths (λ_{max}) and optical band gaps (E_g^{opt}) are summarized in Table 1. The visible absorption maximum of PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T in thin film state is 430, 540, 514,

Table 1. Optical	and Electroc	hemical	Properties	of the
Prepared TT2T	-Based Polym	ers		

	UV—vis absorption spectra		cyclic voltammetry		
polymers	$\lambda_{\max}^{\text{film} a}$ (nm)	$E_{g}^{opt \ b}$ (eV)	E _{onset} /HOMO (V/eV)	LUMO ^c (eV)	
PTTT2T	430	2.10	0.95/-5.27	-3.17	
P2TTT2T	540, 584	1.94	0.86/-5.18	-3.24	
PTTTT2T	513	1.93	1.00/-5.32	-3.39	
PTVTTT2T	512, 547	1.95	0.68/-5.00	-3.05	

^{*a*}Chloroform as the processing solvent. ^{*b*}Estimated from the onset of UV–vis absorption. ^{*c*}LUMO = HOMO + E_{o}^{opt} .



Figure 3. (a) Schematic structure of the TT2T-based polymers and optimized structural geometry of (b) PTTT2T, (c) P2TTT2T, (d) PTTTT2T, and (e) PTVTTT2T in dimer. All the dodecyl side chains were replaced with the methyl groups to simplify the calculation.

and 512 nm, respectively. In addition, an absorption shoulder is observed on P2TTT2T (ca. 584 nm) and PTVTTT2T (ca. 547 nm) thin film spectra. It indicates that such polymer films possess higher structural organization and ordered packing, which may be effective for the charge carrier transport.⁴⁵

The optical band gap (E_g^{opt}) is estimated from the onset of thin film UV-vis absorption by employing the empirical equation ($E_g^{opt} = 1240\lambda_{onset}^{-1}$, eV), and the corresponding E_g^{opt} of PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T is 2.10, 1.94, 1.93, and 1.95, respectively. The E_{α}^{opt} changes between the studied polymers are mainly attributed to the difference between the chemical structures of π -conjugated spacers. Among them, PTTT2T exhibits the largest optical band gap, which is mainly owing to conformational distortions of polymer backbone and the hindrance between thiophene side chains cannot be reduced effectively using single thiophene moiety as the spacer. As the thiophene spacer is enlarged using bithiophene (P2TTT2T), thieno[3,2-b]thiophene (PTTTT2T), or thiophene-vinylene-thiophene (PTVT-TT2T), the E_{g}^{opt} is then leveled down because of the reduced hindrance between polymer side chains, as evidenced by molecular simulations using the DFT method discussed later.

Electrochemical Properties. The electrochemical behaviors as well as the energy levels of the TT2T-based polymers were investigated using cyclic voltammetry (CV), as shown in Figure S4 (Supporting Information) and summarized in Table 1. The CV measured potentials are referred to an Ag/AgCl reference electrode, and the highest occupied molecular orbital (HOMO) levels were determined from the onset oxidation potentials (E_{onset}^{ox}), which based on the equations of HOMO = $-[E_{onset}^{ox} - E_{1/2}^{ferrocene} + 4.8]$ eV, while the lowest unoccupied molecular orbital (LUMO) levels were calculated by the difference between HOMO and optical band gap. The obtained HOMO energy levels are -5.27, -5.18, -5.32, and -5.00 eV for PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T, respectively, while their LUMO energy levels are -3.17, -3.24, -3.39, and -3.05 eV, respectively. The energy level

differences between the studied polymers are mainly attributed to the conformational distortion on polymer main chain. The distortions between TT2T moiety and unsubstituted spacers (T, 2T, TT, or TVT) on the polymer backbone would reduce the conjugation length. Generally, as the larger torsional angle is on polymer chain, the lower HOMO energy level is observed. Note that the HOMO levels of the studied polymers are generally lower than -5.0 eV, which may lead to stable device characteristics under ambient.^{28,30,32}

Morphological Characterizations. The thin film morphologies and molecular packing structures of TT2T-based polymers were explored using atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXD) analyses, respectively. Figure 4 shows the AFM phase images of the studied polymers. No significant structure is observed on the PTTT2T surface, which is probably owing to the small size of spacer and inefficient molecular stacking between polymer chains. As the length of spacer increased, the thin film surface starts to exhibit orderly aggregations and packing morphologies. Nanofibrillar-like structures can be observed on the P2TTT2T and PTVTTT2T films, indicating the inserted 2T and TVT spacers successfully enhance the planarity of polymer backbone and induce the self-organized packing structure.

To further investigate the molecular packing structures in polymer thin films of these studied polymers, grazing-incidence X-ray diffraction (GIXD) measurement was explored (see Figure 5). All TT2T-based polymers show distinguishable diffraction signals in the Q_z direction, and their primary diffraction (100) peaks are observed in a range of 0.22–0.33 Å⁻¹, corresponding to the *d*-spacing of 19–29 Å. The detailed crystallographic parameters of each studied polymer are listed in Table S2 (Supporting Information). The *d*-spacing of these TT2T-based polymers is similar to the 4T-based polymers in our previous studies (17–25 Å),^{28–33} and the longer alkyl side chain (dodecyl group) on thiophene side chain slightly enlarges the *d*-spacing. PTTT2T possesses the smallest *d*-spacing among the studied polymers, which is probably due to its nonsym-



Figure 4. AFM phase images of (a) PTTT2T, (b) P2TTT2T, (c) PTTTT2T, and (d) PTVTTT2T thin film surfaces. All the polymer films were annealed at 160 $^{\circ}$ C under vacuum for 1 h.



Figure 5. (a) Schematic representation of GIXD experiment. 2D GIXD pattern of (b) PTTT2T, (c) P2TTT2T, (d) PTTTT2T, and (e) PTVTTT2T thin films annealed at 160 °C for 1 h under vacuum.

metrical side chain arrangement. The longer distance between the neighbor repeating nonsymmetrical thiophene side chains may provide more space for the side chain interdigitation, leading to a smaller *d*-spacing value. The diffraction intensity of P2TTT2T is markedly stronger than other polymers, and the high-order diffraction signals (up to (400)) is observed. It indicates the P2TTT2T thin film possesses the higher extent of molecular layering among the TT2T-based polymers. In addition, the packing orientation of the polymer thin film would influence the transport ability of charge carrier through the polymer chain. Among the studied materials, PTVTTT2T shows a significantly concentrative orientation distribution (i.e., intensive azimuthal (100) signal in the Q_z direction) of the crystalline domains with respect to the substrate surface. Moreover, (010) diffraction signals are explored on P2TTT2T and PTVTTT2T with corresponding $\pi - \pi$ stacking distance of 3.91 and 4.27 Å, respectively. The (010) signal of P2TTT2T mainly presents in the Q_{ν} direction, indicating an edge-on packing structure, while an arc-like signal in the Q_z direction is observed on PTVTTT2T thin film, which may possess both face-on and edge-on packing structures. The observation of $\pi-\pi$ stacking structure of P2TTT2T and PTVTTT2T is probably owing to their better backbone coplanarity than other studied polymers. It facilitates the nanofibrillar crystalline packing structure with the interconnected networks of the polymer chains for efficient charge transporting,⁴⁶ which is consistent with Gaussian calculation and AFM results.

Molecular Simulations. To understand how the molecular conformation affects the polymer properties, theoretical simulation of the TT2T-based polymers was explored through the Gaussian 03 package program. The optimized molecular geometry on the dimers of the TT2T-based polymers is depicted in Figure 3, which is calculated at the B3LYP/6-31G(d) level. The torsional angles in the polymer main chain $(\theta_{\alpha} \text{ and } \theta_{\gamma})$ and side chain (θ_{β}) are defined (Figure 3a) and listed in the Supporting Information (Table S1). With the incorporation of different thiophene ring spacers (i.e., T, 2T, TT, and TVT), the main chain torsional angles (θ_{α}) between the TT2T moiety and the spacer units are 34°, 20°, 35°, and 15° for PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T, respectively. Spacers enabling rotatable chemical bonding (i.e., 2T and TVT) can release the conformation distortion on the polymer backbone, facilitating better polymer main chain coplanarity of P2TTT2T and PTVTTT2T, compared to the polymers with single or fused thiophene spacers (i.e., PTTT2T and PTTTT2T). Note that polymers with smaller torsional angles on polymer main chain, e.g. P2TTT2T and PTVTTT2T, possess a better structural organization and ordered packing properties, as related to their shoulder signals in UV-vis spectra. On the other hand, the side chain torsional angles (θ_{β}) of the studied polymers are explored in the range of $45^{\circ}-58^{\circ}$, which is similar to that of 4T-based polymers in our previous studies.²⁸⁻³³ The distortion between thiophene side chain and polymer backbone is mainly attributed to the intramolecular repulsion between sulfur atoms of the side chain thiophene and the main chain spacer rings.⁴⁷ Generally, the θ_{β} becomes larger with an increased number of ring spacers. From above results, polymers with 2T and TVT moieties also possess a higher backbone coplanarity than that with T or TT spacers. P2TTT2T and PTVTTT2T, hence, may facilitate better selforganization between polymer chains in solid state.

Polymer Field-Effect Transistor (FET) Characteristics. The influences of processing solvents, thermal annealing process, and chemical structures on charge carrier transport in the polymeric semiconductors were investigated by the

Table 2. FET Characteristics of the Studied Polymers⁴

		without annealing			with annealing at 160 $^\circ C$		
polymer	solvent ^b	mobility $(cm^2 V^{-1} s^{-1})$	on/off	$V_{\rm t}$ (V)	mobility (cm ² V ⁻¹ s ⁻¹)	on/off	$V_{\rm t}$ (V)
PTTT2T	CF	4.6×10^{-7}	1.4×10^{2}	-19	8.7×10^{-7}	1.2×10^{3}	-35
	CF/CB	2.9×10^{-6}	6.1×10^{3}	-31	6.7×10^{-6}	4.1×10^{2}	-19
P2TTT2T	CF	1.1×10^{-2}	2.9×10^{4}	-23	2.6×10^{-2}	5.9×10^{3}	-17
	CF/CB	1.2×10^{-2}	2.7×10^{4}	-27	3.6×10^{-1}	7.1×10^{6}	-14
PTTTT2T	CF	1.5×10^{-4}	3.0×10^{3}	-36	8.1×10^{-4}	3.9×10^{4}	-33
	CF/CB	2.0×10^{-3}	2.0×10^{3}	-35	2.2×10^{-3}	5.8×10^{4}	-30
PTVTTT2T	CF	9.2×10^{-3}	1.3×10^{5}	-32	2.9×10^{-1}	1.0×10^{7}	-32
	CF/CB	2.5×10^{-2}	3.0×10^{6}	-31	$6.4 \times 10^{-1} (7.1 \times 10^{-1})^c$	1.3×10^{7}	-39

^aAll the electrical properties are averaged from at least 10 devices of two batches. ^bCF: chloroform; CF/CB: chloroform/chlorobenzene (90/10, v/v). ^cMaximum field-effect mobility.



Figure 6. FET characteristics of the studied polymers. (a) Transfer curves of five TT2T-based polymers (the source/drain voltage was set as -100 V). Output curves (b) P2TTT2T and (c) PTVTTT2T.

fabricated FET devices. The electrical characteristics of the studied polymers spin-coated on the OTS-modified SiO₂/Si substrates are summarized in Table 2. Typical p-channel FET characteristics were explored on the TT2T-based polymers, and the saturation-regime mobility was calculated from the slope of the plot of drain/source current $(I_{ds}^{-0.5})$ as a function of the gate voltage (V_g) .⁴⁸ Figure 6a shows the typical p-type transfer characteristics of the studied polymers; the higher drain current corresponds to higher field-effect mobility. Moreover, good current modulation and well-defined linear and saturation regions are observed in the output curves of TT2T-based polymers, as shown in Figure 6 and Figure S5. The charge carrier mobilities of as-cast (i.e., without annealing) devices using CF as processing solvent are 4.6×10^{-7} (PTTT2T), 1.1 $\times 10^{-2}$ (P2TTT2T), 1.5 $\times 10^{-4}$ (PTTTT2T), and 9.2 $\times 10^{-3}$ $\rm cm^2~V^{-1}~s^{-1}$ (PTVTTT2T). As such FETs are annealed at 160 °C for 1 h under vacuum, the hole mobilities of PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T, are increased to 8.7 \times 10⁻⁷, 2.6 \times 10⁻², 8.1 \times 10⁻⁴, and 2.9 \times 10⁻¹ cm² V⁻¹ s⁻¹, respectively, with the on/off ratio of 10^3-10^7 . The results demonstrate that the annealing process successfully enhances the mobility of the TT2T-based polymers because of the improved polymer chain packing as well as charge transport ability during thermal treatment. To further improve the FET performance, mixed solvent of 90:10 (v/v) CF/CB was employed to induce the organization of polymer chain, and the corresponding charge carrier mobility is also listed in Table 2. Note that if we only use chlorobenzene (high-boiling-point solvent) as the processing solvent, a poor thin film quality would be obtained on the OTS-modified surface. In the mixed

solvent system, the high-boiling-point chlorobenzene fraction could lower the solvent evaporation rate and facilitate the organization of polymer crystallites; the mobility of all studied polymer based FET devices shows a moderate enhancement. Among them, highest mobility of 0.71 cm² V⁻¹ s⁻¹ is explored on the PTVTTT2T thin film.

The FET performances of TT2T-based polymers are largely affected by the variant conjugated spacers. With only single thiophene as spacer, PTTT2T exhibits a low mobility of $6.7 \times$ 10^{-6} cm² V⁻¹ s⁻¹. This may attribute to the small size of spacers cannot reduce the steric hindrance of thiophene side chains, disturbing the charge transporting. The polymer with an additional unsubstituted thiophene ring as spacer, P2TTT2T, showed a much higher mobility of 0.36 $\mbox{cm}^2\ \mbox{V}^{-1}\ \mbox{s}^{-1}$ than PTTT2T and PVTT2T after annealing owing to the 2T moiety provides a more appropriate space to decrease the conformation distortions of the polymer main chain. As the 2T spacer is replaced by the fused TT moiety (PTTTT2T), however, the mobility of is reduced to 2.2×10^{-3} cm² V⁻¹ s⁻¹ because the torsional angle is increased within the polymer backbone. On the other hand, with the insertion of the vinylene linkage between bithiophene, the TVT unit could improve the backbone planarity of polymer main chain. PTVTTT2T exhibits maximum mobility up to 0.71 cm² V⁻¹ s⁻¹, which is the highest value among TT2T-based polymers. Such high mobility may be attributed to the small conformation distortion on polymer backbone, good molecular packing orientation, and high molecular weight. Note that the highest molecular weight of PTVTTT2T may induce better thin-film microstructure or The air stability of the FET devices based on two polymers with a higher mobility among this TT2T series, P2TTT2T and PTVTTT2T, is investigated by measuring hole mobility (μ), on/off ratio, and threshold voltage (V_t) as a function of time, as depicted in Figure 7. The FET devices show a good air stability,



Figure 7. Air-stability testing of FET performance in the dark for the P2TTT2T (black) and PTVTTT2T (red) thin films, including, hole mobility (μ), on/off current ratio, and threshold voltage ($V_{\rm th}$). Relative humidity ranges from 50 to 65% in air.

which the average mobilities of 0.19 (P2TTT2T) and 0.32 (PTVTTT2T) cm² V⁻¹ s⁻¹ are observed under ambient as the FETs are stored in air for over 3 months (relative humidity ~50–65%). Although such values are slightly lower than that of mobilities characterized under a nitrogen atmosphere, stable on/off ratio and mobility trace can be still monitored for both P2TTT2T- and PTVTTT2T-based devices. The stable FET behaviors of P2TTT2T and PTVTTT2T in air may mainly attribute to the design of biaxially extended thiophene side chains, which can lower the HOMO level (<-5.0 eV) because of the decreased conjugation length of polymer backbone, similar to our previous works.^{28–33}

In this biaxially extended TT2T-based polymer system, the fused thiophene building block is designed to improve the charge carrier transporting. Compare P2TTT2T with P4T2T with the bithiophene spacer, the mobility of P2TTT2T (0.36 cm² V⁻¹ s⁻¹) is 20 times higher than P4T2T (0.015 cm² V⁻¹ s⁻¹)²⁹ due to the TT moiety probably induce stronger self-organization and molecular packing ability of polymer chain.³⁷ In addition, the incorporation of suitable conjugated spacer in the molecular design can further enhance the transistor performance. The maximum mobility among this newly designed polymer system, thus, can be boosted up to 0.71 cm² V⁻¹ s⁻¹ using the TVT unit as spacer, showing the potential for high performance organic FET device applications.

CONCLUSION

We have successfully prepared four biaxially extended conjugated polymers using the fused thiophene core, including PTTT2T, P2TTT2T, PTTTT2T, and PTVTTT2T, using palladium(0)-catalyzed Stille polymerization under microwave heating. The incorporation of fused thieno[3,2-*b*]thiophene building block improved the degree of polymer interchain selforganization and molecular packing, compared to the previous reported biaxially extended polymers. Ordered nanofibrillar morphology then could be obtained on P2TTT2T and PTVTTT2T thin films owing to the planar main chain conformation of polymer skeleton, as characterized by molecular simulation, AFM, and GIXD. Among this set of polymeric semiconductors, PTVTTT2T exhibited highest field-effect mobility of 0.71 cm² V⁻¹ s⁻¹ with an on/off ratio over 10⁷ using mixed solution of 90:10 (v/v) CF/CB as processing solvent. In addition, such devices showed good air stability for a 3 months testing under ambient. The results demonstrated that conjugated polymers with superior main chain coplanarity and charge transport ability could be achieved using the fused thiophene block incorporated into the biaxially extended polymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.5b01243.

Synthetic route and ¹H NMR spectrum of TT2T-Br₂; ¹H NMR spectrum, DSC traces, CV curves, and FET output characteristics of TT2T-based polymers and their thin films (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors highly appreciate the financial support from Ministry of Science and Technology of Taiwan under Contract MOST 102-2221-E-002-222-MY3. The authors also acknowledge NSRRC, Taiwan, for facilitating the GIXD experiments.

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