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New Poly(Selenophene-Thiophene) Bearing π -Conjugating Spacers for Polymer Field-Effect Transistors and Photovoltaic Cells[†]

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Five new poly(selenophene-thiophene), including PSe4TV, PSe4TT, PSe4TTT, and **P2Se4TTT**, were synthesized via Stille coupling polymerization enable various π -conjugated spacers of vinylene (V), thiophene (T), bithiophene (2T), and thieno[3,2-b]thiophene (TT). Tuneable polymer structural, optical, and electrochemical properties were observed because different π -conjugated building blocks in the polymer main chain, affecting the conformation of polymer backbone. Details of polymer morphologies were investigated using transmission electron microscopy (TEM), atomic force microscopy (AFM), and grazing incidence X-ray diffraction (GIXD) systematically. P2Se4TTT possessed smallest energy band gap, densest molecular packing structure as well as firbrillar-like nanostructures among the studied polymers since the TT moiety could enhance the coplanrity of polymer backbone, and the inserted biselenophene reduce the hindrance of thiophene side chains. Hence, highest field-effect mobility of this set of polymers was explored to be 0.27 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ from **P2Se4TTT**-based field-effect transistor device with a high on/off ratio over 10^5 . The power conversion efficiencies (PCEs) of the photovoltaic cells based on polymer/PCBM blends were in the range of 0.43-1.18 % for our synthesized polymers. Among them, P2Se4TTT-based device could achieve the best PCE of 2.29 % using o-dichlorobenzene/1,8diiodoctane (98:2 v/v) mixture as processing solvent. The enhancement of active layer uniformity responded to the increment of efficiency. The above results demonstrated that the new-designed polymers could serve as a promising candidate for polymer optoelectronic device applications.

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Introduction

Polymeric semiconductors have received extensive scientific interest for organic optoelectronic devices in recent years because of their potential advantages, such as low cost, solution processability, good flexibility and stretchability, over inorganic or organic small-molecular semiconductors.¹ For these reasons, semiconducting polymers offer the opportunities to impact current industrial technologies and develop the next-generation organic electronics, as demonstrated for polymer photovoltaic cells (PVs),²⁻⁹ field-effect transistors (FETs),¹⁰⁻¹⁶ and memories¹⁷⁻²⁰ in research field now.

Side chains are act as a crucial component in the design of novel conjugated polymers.²¹ They not only directly relate to the solubility but also affect the molecular packing motifs and thin film morphologies. Alkyl side chains with different branching structure²² or functionalized groups²³ have been already investigated. On the other hand, side chains including conjugated moieties are also exhibited, which can further enhance the absorption range and the charge carrier mobility

for device applications. Li et al. have evaluated variant conjugated side chains, e.g. bi(thienylenevinylene),²⁴ phenothiazinevinylene,²⁵ or bi(phenylenevinylene),²⁶ into thiophene backbone to facilitate the extension of π -electron delocalization and broad absorption. Moreover, our group have discovered a series of biaxially extended conjugated thiophene-based polymers²⁷⁻³¹ possess high carrier mobility (up to 0.61 cm² V⁻¹ s⁻¹)³⁰ and solar cell efficiency (up to 4.04 %).²⁸

In addition, high performance polymer FET and PV devices have been explored using selenophene rings to replace thiophene rings recently.9-14,32,33 The incorporation of selenophene provides the chance to enhance the chain interaction and the carrier transport ability since selenium generally exhibits a stronger heteroaromatic interaction than sulfur.³⁴ Park et al. reported that poly(5,5'-bis(3dodecylthiophene-2-yl)-2,2'-biselenophene) exhibited much better carrier mobility and power conversion efficiency thiophene-based poly(3,3"-didodecyl compared to quaterthiophene).³⁵ Also, one of the highest hole mobility



Scheme 1. The synthetic route on preparing Se4T- and 2Se4T-based conjugated polymers.

(higher than 10 cm² V⁻¹ s⁻¹) in conjugated polymer community was observed in the selenophene-containing polymer, explored by Kim and his coworkers.³⁶ Thus, combine the advantages of selenium atom in polymer backbone and conjugated thiophene units on polymer side chain, materials with strong intermolecular interaction, broad absorption, good charge carrier mobility, and high power conversion efficiency may obtained.

In this paper, new conjugated materials enable selenophenecontaining main chain and conjugated thiophene side chains, Se4T and 2Se4T, were developed. After copolymerized with different π -conjugating spacers, including vinylene (V), thiophene (T), bithiophene (2T), and thieno[3,2-b]thiophene (TT), using Stille coupling reaction under microwave heating. Five semiconducting polymers of Poly((E)-5-dodecyl-2'-(5-(5dodecyl-[2,3'-bithiophen]-2'-yl)selenophen-2-yl)-5'-(prop-1-en-1-yl)-2,3'-bithiophene) (PSe4TV), Poly(5"-dodecyl-5'-(5-(5dodecyl-[2,3'-bithiophen]-2'-yl)selenophen-2-yl)-2,2':4',2"terthiophene) (PSe4TT), Poly(5"-dodecyl-5"-(5-(5-dodecyl-[2,3'-bithiophen]-2'-yl)selenophen-2-yl)-2,2':5',2":4",2"'quaterthiophene) (PSe4T2T), Poly(2- (5-dodecyl-2'-(5-(5dodecyl-[2,3'-bithiophen]-2'-yl)selenophen-2-yl)-[2,3'bithiophen]-5'-yl)thieno[3,2-b]thiophene) (PSe4TTT). and Poly(2-(5-dodecyl-2'-(5'-(5-dodecyl-[2,3'-bithiophen]-2'-yl)-[2,2'-biselenophen]-5-yl)-[2,3'-bithiophen]-5'-yl)thieno[3,2b]thiophene) (P2Se4TTT), were explored (Scheme 1). The synthesis, optical, electrochemical, and optoelectronic device

synthesis, optical, electrochemical, and optoelectronic device characteristics were explored. The film morphology, additionally, was investigated using transmission electron microscopy (TEM), atomic force microscopy (AFM), and grazing incidence X-ray diffraction (GIXD). The charge carrier transport ability of the studied polymers was obtained by using the top-contact/bottom-gate FETs. Moreover, polymer PV cells

were fabricated with sandwiched ITO/PEDOT:PSS/polymer:PCBM/Ca/Al device configuration. The effects of selenium atom in polymer chain, conjugated thiophene rings on side chains, and various spacer moieties on the performance of FETs and PVs were discussed systematically.

Experimental

Materials

3-bromothiophene, 2-bromothiophene, selenophene, trimethyl(thiophen-2-yl)stannane, (E)-1,2bis(tributylstannyl)ethene (V), tri(o-tolyl)phosphine, and tris(dibenzylideneacetone)dipalladium(0) were purchased from Aldrich (Missouri, USA) and used without further purification. Tetrakis(triphenylphosphine)palladium(0) was purchased from TCI (Tokyo, Japan) and used as received. Common organic solvents (tetrahydrofuran, toluene, and dimethylformamide) for synthesis and anhydrous solvents (such as chloroform, chlorobenzene and o-dichlorobenzene) for device applications were purchased from Aldrich (Missouri, USA). Monomers, including 2,5-bis(trimethylstannyl)thiophene (T),^{37,38} 5,5'-(2T),³⁹ bis(trimethylstannyl)-2,2'-dithiophene 2,5-(TT).⁴⁰ 2.5bis(trimethylstannyl)-thieno[3,2-b]thiophene (Se),³⁸ bis(trimethylstannyl)-selenophene 5,5'-(2Se),^{34,41} bis(trimethylstannyl)-2,2'-biselenophene were synthesized according to the procedures in literatures. The synthetic steps of newly designed selenophenequarterthiophene (Se4T) and biselenophene-quarterthiophene (2Se4T) compounds are shown in Scheme S1 and summarized (Figs. S1-S8). A surface treatment agent of in ESI † octadecyltrichlorosilane (ODTS) was purchased from Acros (Geel, Belgium) for field-effect transistor characterization.

[6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) and 1,8diiodoctane (DIO) was purchased from Solenne BV (Groningen, The Netherlands) and Alfa Aesar (Massachusetts, USA), respectively, for photovoltaic cell applications.

General Procedures for Polymerization

The general procedure of synthesizing Se4T- and 2Se4T-based conjugated copolymers (PSe4TV, PSe4TT, PSe4T2T, PSe4TTT, P2Se4TTT) is depicted in Scheme 1. Dibromo monomers (Se4T or 2Se4T), ditin monomers (V, T, 2T or TT), tri(o-tolyl)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 5 ml chlorobenzene under nitrogen atmosphere. The vessel was then sealed with a snap cap, and the polymer was polymerized under microwave heating at 160 °C for 30-60 min. After end-capped with 2-(tributylstynnyl)-thiophene and 2-bromothiophene (both 1.1 equiv. with respect to ditin monomer and under microwave heating at 170 °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 in vacuum at 40 °C.

Poly((E)-5-dodecyl-2'-(5-(5-dodecyl-[2,3'-bithiophen]-2'yl)selenophen-2-yl)-5'-(prop-1-en-1-yl)-2,3'-bithiophene) (PSe4TV)

Amounts of 288 mg (0.302 mmol) Se4T, 183 mg (0.302 mmol) V, and 5 ml chlorobenzene were used to afford a maroon solid (yield: 180 mg, 70 %). ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.24–6.75 (m, br, Ar–H and Vin-H, 10H), 2.81–2.77 (t, Ar–CH₂, 4H), 1.68–1.11 (br, –CH and –CH₂, 34H), 0.88–0.84 (br, –CH₃, 12H). Anal. Calcd. for [C₄₈H₆₆S₄Se]: C, 67.80; H, 7.82; S, 15.08. Found: C, 67.34; H, 7.70; S, 15.50. The weight average molecular weight (M_w) and polydispersity index (PDI) estimated from GPC are 33241 g mol⁻¹ and 2.09, respectively.

Poly(5''-dodecyl-5'-(5-(5-dodecyl-[2,3'-bithiophen]-2'yl)selenophen-2-yl)-2,2':4',2''-terthiophene) (PSe4TT)

Amounts of 322 mg (0.34 mmol) Se4T, 138 mg (0.34 mmol) T, and 5 ml chlorobenzene were used to afford a vermilion solid (yield: 193 mg, 65 %). ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.69–6.88 (m, br, Ar–H, 10H), 2.82–2.61 (br, Ar–CH₂, 4H), 1.82–1.11 (br, –CH and –CH₂, 34H), 0.89–0.71 (br, –CH₃, 12H). Anal. Calcd. for [C₅₀H₆₆S₅Se]: C, 66.26; H, 7.34; S, 17.69. Found: C, 66.32; H, 6.99; S, 18.02. The weight average molecular weight (M_w) and polydispersity index (PDI) estimated from GPC are 22335 g mol⁻¹ and 1.71, respectively.

Poly(5^{'''}-dodecyl-5^{''}-(5-(5-dodecyl-[2,3'-bithiophen]-2'yl)selenophen-2-yl)-2,2':5',2'':4'',2'''-quaterthiophene) (PSe4T2T)

Amounts of 342 mg (0.36 mmol) Se4T, 176 mg (0.36 mmol) 2T, and 5 ml chlorobenzene were used to afford a maroon solid (yield: 207 mg, 61 %). ¹H-NMR (400 MHz, CDCl₃), δ (ppm):

7.12–6.47 (m, br, Ar–H, 12H), 2.84–2.71 (br, Ar–CH₂, 4H), 1.79–1.11 (br, –CH and –CH₂, 34H), 0.91–0.75 (br, –CH₃, 12H). Anal. Calcd. for $[C_{54}H_{68}S_6Se]$: C, 65.61; H, 6.93; S, 19.46. Found: C, 65.62; H, 6.48; S, 19.25. The weight average molecular weight (M_w) and polydispersity index (PDI) estimated from GPC are 28493 g mol⁻¹ and 1.80, respectively.

Poly(2-(5-dodecyl-2'-(5-(5-dodecyl-[2,3'-bithiophen]-2'yl)selenophen-2-yl)-[2,3'-bithiophen]-5'-yl)thieno[3,2*b*]thiophene) (PSe4TTT)

Amounts of 309 mg (0.32 mmol) Se4T, 151 mg (0.32 mmol) TT, and 5 ml chlorobenzene were used to afford a maroon solid (yield: 218 mg, 70 %) ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.46–6.54 (m, br, Ar–H, 10H), 2.91–2.62 (br, Ar–CH₂, 4H), 1.79–1.05 (br, –CH and –CH₂, 34H), 0.94–0.76 (br, –CH₃, 12H). Anal. Calcd. for [C₅₂H₆₆S₆Se]: C, 64.89; H, 6.91; S, 19.99. Found: C, 65.28; H, 6.59; S, 19.89. The weight average molecular weight (M_w) and polydispersity index (PDI) estimated from GPC are 67507 g mol⁻¹ and 2.08, respectively.

Poly(2-(5-dodecyl-2'-(5'-(5-dodecyl-[2,3'-bithiophen]-2'-yl)-[2,2'-biselenophen]-5-yl)-[2,3'-bithiophen]-5'-yl)thieno[3,2*b*]thiophene) (P2Se4TTT)

Amounts of 326 mg (0.30 mmol) 2Se4T, 140 mg (0.30 mmol) TT, and 5 ml chlorobenzene were used to afford a maroon solid (yield: 266 mg, 81 %) ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.19–6.59 (m, br, Ar–H, 12H), 2.94–2.69 (br, Ar–CH₂, 4H), 1.78–1.07 (br, –CH and –CH₂, 34H), 0.95–0.73 (br, –CH₃, 12H). Anal. Calcd. for [C₅₅H₆₆S₆Se₂]: C, 61.31; H, 6.17; S, 17.86. Found: C, 61.68; H, 5.98; S, 17.38. The weight average molecular weight (M_w) and polydispersity index (PDI) estimated from GPC are 69483 g mol⁻¹ and 1.57, respectively.

Characterization

Microwave polymerization was carried out using a Biotage microwave reactor in sealed vessels. ¹H-NMR spectra was recorded with a Bruker Avance 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. 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 BL-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. UV-Vis absorption spectrum was explored using a Hitachi U-4100 spectrophotometer. For the thin film spectra, polymers were first

dissolved in o-dichlorobenzene (12 mg ml⁻¹), followed with filtering through a 0.45 µm 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 Μ 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. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1230 instrument operating at a voltage of 200 keV with a Gatam dual vision CCD camera. Note that the preparation of polymer thin film samples were the same as that of the device fabrications for the measurements of GIXD, UV, AFM, and TEM.

Fabrication and Characterization of Field-Effect Transistors

The field-effect transistors (FETs) were fabricated from the studied copolymers with a 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. Α silane coupling agent, octadecyltrichlorosilane (ODTS), was modified onto the SiO₂ layer by the following preparation procedures: the cleaned wafers were immersed into a 10 mM solution of ODTS in anhydrous toluene at room temperature overnight, then the substrates were rinsed with toluene, acetone, isopropyl alcohol, and dried with a steam of nitrogen. The polymer semiconductors (e.g. PSe4TV, PSe4TT, PSe4T2T, PSe4TTT, and **P2Se4TTT**) were firstly dissolved in o-dichlorobenzene (12 mg ml⁻¹) at 100 °C for at least 5 h, then the polymer solutions were filtered through 0.22 µm pore size of PTFE membrane syringe filters. Afterward, polymer thin films were deposited on ODTS-modified SiO₂/Si substrates by spincoating method at a spin rate of 800 rpm for 60 s. In addition, annealing process (140 °C under nitrogen atmosphere for 1 h) was introduced to enhance the FET performance. The topcontact source/drain electrodes were defined by 100-nm-thick gold through a regular shadow mask, and the channel length (L) and width (W) were 50 and 1000 µm, respectively. Electrical characteristics of FET were recorded in a N2-filled glove box using a Keithley 4200 semiconductor parametric analyzer (Keithley Instruments Inc., Cleveland, OH, USA).

Fabrication and Characterization of Polymer Photovoltaic Cells

All the bulk-heterojunction photovoltaic cells were fabricated by the following procedures: the glass–indium tin oxide (ITO) substrates (obtained from Lumtec (Taiwan), 5 Ω sq⁻¹) were first patterned by lithograph, then cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried by a hot plate at 120 °C for 5 min. Afterward, the substrates were treated with oxygen plasma for Poly(3,4-ethylenedioxy-thiophene):poly(styrene-10 min. sulfonate) (PEDOT:PSS, Baytron P VP AI4083) was filtered through a 0.45 µm pore size PTFE membrane syringe filter and deposited on ITO by spin-coated at 3800-4000 rpm in air, then dried at 150 °C for 15 min under vacuum. The polymer/PCBM blend (with the polymer concentration of 12-15 mg ml⁻¹) was prepared by dissolving the components in anhydrous odichlorobenzene or o-dichlorobenzene/DIO in a nitrogen-filled glove box. The active layer was then spin-coated on the top of the PEDOT:PSS layer at 1000 rpm for 60 s, and annealed at 140 °C for 10 min in glove box. Subsequently, the device was thermally evaporated a Ca (30 nm)/Al (100 nm) electrode under high vacuum ($<10^{-6}$ torr). The active area of the device was defined as 4 mm² and encapsulated with UV-curing glue. The current-voltage (J-V) characteristic of the polymer photovoltaic cells were conducted by using a computercontrolled Keithley 2400 (Keithley Instruments Inc., Cleveland, OH, USA) source measurement unit (SMU) with a Peccell solar simulator under the illumination of AM 1.5 G, 100 mW cm⁻². The illumination intensity was calibrated by a standard Si photodiode detector with KG-5 filter.



Fig. 1. ¹H-NMR Spectrum of P2Se4TTT in CDCl₃. (x: CDCl₃)

Results and Discussion

Polymer Characterization

New selenophene-containing molecules with conjugated thiophene side chains, Se4T and 2Se4T, are successfully designed and synthesized. The synthetic route and synthesis details are list in Supplementary Information. The monomers are linked with different π -conjugating spacers, including vinylene (V), thiophene (T), bithiophene (2T), and thieno[3,2-*b*]thiophene (TT), creating five polymers with tunable optical and electrical properties. The chemical structures of the studied

 Table 1 Molecular weight, optical, and electrochemical characteristics of the synthesized polymers.

	Molecular Weight		UV-vis absorption spectra			Cyclic voltammetry	
Polymers	${\mathbf M_w}^a$	PDI ^a	$\lambda_{max}^{sol b}$	$\lambda_{max}^{\qquad \ film \ b}$	Eg opt c	E ^{ox} onset/HOMO	LUMO ^d
	$(g \text{ mol}^{-1})$		(nm)	(nm)	(eV)	(V/eV)	(eV)
PSe4TV	33241	2.09	500	244, 304, 515	1.87	0.71/-5.03	-3.16
PSe4TT	22335	1.71	496	248, 521	1.90	0.75/-5.07	-3.17
PSe4T2T	28493	1.80	497	245, 519	1.91	0.77/-5.09	-3.18
PSe4TTT	67507	2.08	507	245, 315, 553	1.87	0.70/-5.02	-3.15
P2Se4TTT	69483	1.57	529	244, 306, 577	1.78	0.58/-4.90	-3.12

^a Determined by GPC using polystyrene standard in THF at 40 °C. ^b *o*-dichlorobenzene as the processing solvent. ^c Estimated from the onset of UV-vis absorption. ^d LUMO = HOMO + E_g^{opt} .

polymers and monomers are confirmed by ¹H-NMR and elemental analysis. Fig. 1 shows the ¹H-NMR spectrum of **P2Se4TTT** in CDCl₃ solution. Signals between 6.6 and 7.2 ppm are assigned to the protons on the aromatic rings, which are assigned to the protons on the selenophene and thiophene rings of polymer main chain and the protons on the side chain thiophene rings. Moreover, the peaks at 2.75 ppm (thiophene-CH₂, peak f) and $1.75 \sim 0.75$ ppm (-CH₂ and -CH₃, peak g) are attributed to the dodecyl group in the 2Se4T unit. The numbers of aliphatic and aromatic protons are estimated from the integration value of peaks, which are consistent with the proposed polymer structures. The ¹H-NMR spectra of other studied polymers also exhibited a good agreement with the proposed polymer structures, as shown in Fig. S9 (ESI⁺). Additionally, the elemental analyses of the carbon, hydrogen, nitrogen, and sulfur contents illustrate a good agreement with the theoretical content. This set of polymers have weightaveraged molecular weights in the range of 22 ~ 69 kDa with polydispersity of 1.6 ~ 2.1 from GPC measurement, as summarized in Table 1. The relatively low molecular weights of PSe4TV, PSe4TT, and PSe4T2T are related to their solubility (Table S1 (ESI[†])), which are only partially dissolved in tetrahydrofuran and chloroform. Thus, the GPC would only count the small molecular weights portion. All the synthesized polymers, generally, are soluble in o-dichlorobenzene (o-DCB), providing the solution-processable thin films for transistors and photovoltaic applications.

Thermal Properties

Thermogravimetric analysis (TGA) was used to determine the thermal stability of our designed polymers, as shown in Fig. 2(a). The thermal decomposition temperature (T_d , 5 % weight loss) of **PSe4TV**, **PSe4TT**, **PSe4T2T**, **PSe4TTT**, and **P2Se4TTT** is 389, 395, 407, 405, and 410 °C, respectively, indicating these polymers possess good thermal stability for optoelectronic device applications. Differential scanning

calorimetry (DSC) was also evaluated to explore the thermal transition of the studied polymer (Fig. S10 in ESI \dagger). For the Se4T- and 2Se4T-based polymers, however, no obvious thermal transition in the bulk sample was observed as the heating temperature up to 250 °C, which is not uncommon in conjugated polymer system.

Optical Properties

The normalized UV-vis absorption of the studied polymers in dilute o-DCB solution and spin-coated thin films are depicted in Fig. S11 (ESI †) and Fig. 2(b), respectively. The corresponding maximum absorption wavelength of the polymers in solution (λ_{max}^{sol}) or film state (λ_{max}^{film}) and optical band gaps (E_g^{opt}) are summarized in Table 1. The absorption signal near 245 nm in solid state of all studied polymers was attributed to the π - π * transition of thiophene side chains,⁴² while the absorption peak in visible region was belonged to the electronic transition of conjugated backbone. The visible absorption maximum of PSe4TV, PSe4TT, PSe4T2T, PSe4TTT, and P2Se4TTT in dilute o-DCB solution and film state $(\lambda_{max}^{sol}, \lambda_{max}^{film})$ is (500, 515), (496, 521), (497, 519), (507, 553), and (529, 577), respectively. A significant spectral redshift ($\Delta\lambda$) of approximately 46 and 48 nm was observed on PSe4TTT and P2Se4TTT, respectively, from solution to solid state, indicating the strong interchain association and aggregation inside the polymer thin film.43 The larger redshifting of PSe4TTT and P2Se4TTT in film state implies that the incorporated TT moiety can efficiently enhance the intermolecular stacking and electronic coupling between neighboring polymer backbones in the film state,⁴⁴ compared to other studied materials (**PSe4TV** ($\Delta\lambda = 15$ nm), **PSe4TT** ($\Delta\lambda =$ 25 nm), and **PSe4T2T** ($\Delta\lambda = 22$ nm)). In addition, **P2Se4TTT** thin film possesses an observed absorption shoulder (ca. 650 nm), indicating the higher structural organization and ordered



Fig. 2. (a) TGA curves, (b) UV-Vis absorption spectra of thin film, and (c) cyclic voltammograms of the studied polymers. The polymer thin films for UV-Vis measurement were annealed at 140 °C under vacuum for 1 h.

packing, which is effective for the electronic device applications.

The optical band gap (E_g^{opt}), estimated from the onset of thin film UV-vis absorption by employing the empirical equation ($E_g^{opt} = 1240 \lambda_{onset}^{-1}$, eV), of the studied polymers are in the following order: **P2Se4TTT** (1.78) < **PSe4TTT** (1.86) < **PSe4TV** (1.87) < **PSe4T2T** (1.91) < **PSe4TTT** (1.92). The

difference of E_g^{opt} between these polymers are mainly attributed to the variant chemical structure of π -conjugated spacers. Among all synthesized polymers, the presence of large E_g^{opt} of **PSe4TT** and **PSe4T2T** is probably due to conformational distortions of polymer backbone. Especially of **PSe4TT**, the largest E_g^{opt} is obtained because the hindrance between conjugated side chains cannot be reduced effectively using single thiophene moiety as spacer. As vinylene (**PSe4TV**) and



Fig. 3. TEM and AFM phase images of (a) **PSe4T2T**, (b) **PSe4TTT**, and (c) **P2Se4TTT** thin film surfaces. All the polymer films were anneal at 140 °C under vacuum for 1 h. Note that nanofirbrillar morphology could be observed on **PSe4TTT** and **P2Se4TTT** surface.



Fig. 4. Representative 2D GIXD pattern of (a) PSe4T2T, (b) PSe4TTT, and (c) P2Se4TTT thin films annealed at 140 °C for 1 h under vacuum.

thieno[3,2-*b*]thiophene (**PSe4TTT**) spacers incorporated into the polymer system, an antisymmetric chemical structure is induced, leading to stronger intermolecular interactions as well as lower energy gaps. Moreover, smallest E_g^{opt} is exhibited on **P2Se4TTT**. The inserting of biselenophene group can further lower the conformation hindrance of thiophene side chains, and increase the intermolecular interactions in thin films since the selenium atom has a larger atomic radius and is more polarizable than the sulfur atom.⁴⁵ Note that the thieno[3,2*b*]thiophene spacer in this new polymer system (**PSe4TTT** and **P2Se4TTT**) can efficiently enhance the planarity of polymer backbone and level down the energy band gaps, compared to P4TSe and P4T2Se polymers in our pervious study.²⁹

Electrochemical Properties

To understand the effect of different conjugated spacers on the energy levels within Se4T- and 2Se4T-based polymers, electrochemistry measurement of polymer films was explored (Fig. 2(c)). Cyclic voltammetry (CV) curves of the studied polymers using thin films in dry acetonitrile at a potential scan rate of 100 mV s⁻¹. The highest occupied molecular orbital (HOMO) levels were estimated from onset oxidation potentials (E_{onset}^{ox}) , which based on the equations: HOMO = $-[E_{onset}^{ox}]$ $E^{\text{ferrocene}}_{1/2}$ + 4.8] eV; while the lowest unoccupied molecular orbital (LUMO) levels were determined on the difference between HOMO and optical band gap. Note that the measured potentials are referred to an Ag/AgCl reference electrode. The corresponding HOMO energy level of PSe4TV, PSe4TT, PSe4T2T, PSe4TTT, and P2Se4TTT is -5.03, -5.07, -5.09, -5.02, and -4.90 eV, respectively, while their LUMO energy levels are similar, in a range of -3.12 ~ -3.18 eV. All calculation results are listed in Table 1. PSe4TT (-5.07 eV) and PSe4T2T (-5.09 eV) exhibited deeper HOMO level than other studied polymers, which is mainly due to the conformational distortion on polymer chains. The single thiophene spacer cannot diminish the hindrance between conjugated side chains and the bithiophene may induce an additional torsion between two thiophene rings, then reduce the conjugation length of polymer. This result is also related to the large energy band gap of these

two polymers. Similarly, chemical structures with the higher planarity of polymer main chain would be obtained using vinylene and thieno[3,2-*b*]thiophene spacers, leading to slightly higher HOMO levels of **PSe4TV**, **PSe4TTT**, and **P2Se4TTT**. In addition, as compared to the HOMO/LUMO energy levels of **PSe4TTT** (-5.02/-3.15 eV), **P2Se4TTT** (-4.90/-3.12 eV) exhibit a higher HOMO level and a lower LUMO level due to the stronger intermolecular interaction of biselenophene ring than single selenophene ring. This strong intermolecular interaction of **P2Se4TTT** would induce the self-organization properties inside polymer thin film, which is effective for optoelectronic device applications.

Morphological Characterizations

The thin film morphologies of PSe4TV, PSe4TT, PSe4T2T, PSe4TTT, and P2Se4TTT were explored using atomic force microscopy (AFM), transmission electron microscopy (TEM), and grazing incidence X-ray diffraction (GIXD) analyses. AFM topographies (Fig. S12 in ESI⁺) exhibited that PSe4TV and PSe4TT possess large aggregates as well as high roughness on the film surfaces; while uniform and smooth surfaces (roughness < 1 nm) were observed for the other three polymers. The rough film morphology of **PSe4TV** and **PSe4TT** is mainly owing to their relative poor solubility and large conformational distortions on polymer side chain, as the small size of spacer may not reduce the hindrance thiophene side chains. The polymer thin films of PSe4T2T, PSe4TTT, and P2Se4TTT were further investigated by TEM, as shown in Fig. 3. Nanofibrillar-like structure can be observed on PSe4TTT and P2Se4TTT films, indicating the inserted fused thiophene spacer successfully enhance the planarity of polymer backbone, which could induce the self-organized packing structure. Compared to those nanofibrillar structures, no significant morphology was explored on PSe4T2T surface.

Moreover, GIXD measurement (Figs. 4 and S14 (ESI[†])) was used to understand the molecular packing structures in polymer thin films of these studied polymers. Among them, **PSe4T2T**, **PSe4TTT**, and **P2Se4TTT** exhibited distinguishable diffraction signals in q_z direction, and their primary diffraction

	As cast			Annealed at 140 °C		
	Mobility	1.00	V _t	Mobility	1.55	V _t
	$(cm^2V^{-1}s^{-1})$	on/off	(V)	$(cm^2V^{-1}s^{-1})$	on/off	(V)
PSe4TV	$(4.8\pm0.9)\times10^{-4}$	3.1×10 ⁵	-12±1	$(3.2\pm0.6)\times10^{-3}$	1.4×10^{5}	-14±2
PSe4TT	(8.1±0.1)×10 ⁻⁵	2.6×10 ³	4±1	(8.6±0.1)×10 ⁻⁴	2.8×10 ⁴	-3±1
PSe4T2T	(1.0±0.1)×10 ⁻³	4.3×10 ³	-8±2	(1.0±0.1)×10 ⁻²	1.4×10^{3}	-26±1
PSe4TTT	(5.4±0.4)×10 ⁻³	1.4×10^4	-5±2	(6.0±0.2)×10 ⁻²	2.9×10 ⁴	-13±3
P2Se4TTT	(5.7±0.4)×10 ⁻²	1.6×10^4	-5±2	(2.5±0.2)×10 ⁻¹	1.3×10 ⁵	-22±4

Table 2 FET characteristics of the studied polymers^a

^a All the electrical properties are averaged from at least 10 devices of 2 batches.



Fig. 5. FET characteristics of the studied polymers. (a) Output curves of **P2Se4TTT**. (b) Transfer curves of five Se4T- and 2Se4T-based polymers (the source/drain voltage was set as -100 V).

(100) peaks are observed at 2.64° , 2.67° , and 2.91° , respectively, corresponding to the *d*-spacing of 28.6, 28.3, and 26.1 Å. Note that the *d*-spacing of these three polymers is slightly larger than the polymers in our previous studies (17~25 Å)²⁷⁻³⁰ due to the longer alkyl side chain (dodecyl group) on thiophene rings. The diffraction intensity of PSe4TTT and P2Se4TTT is markedly stronger than PSe4T2T, and the secondary diffraction (200) signals are found around 5.57° and 6.04°, respectively, which is consistent with the appearance of orderly nanofirbrillar morphology in the TEM images. Besides, there are no significant signals on the GIXD pattern of PSe4TV (Fig. S14(a)) and **PSe4TT** (Fig. S14(b)), indicating the amorphous nature of these two polymers. P2Se4TTT possesses smallest packing distance among these five studied polymers, resulting in a densest interdigitation of polymer backbones. From the AFM, TEM, and GIXD results, the ordering nanofirbrillar crystalline packing structure of P2Se4TTT film with the interconnected networks of the polymer chains may provide the formation of highly efficient pathways for charge carrier transport.46

Polymer Field-Effect Transistor (FET) Characteristics

The influences of different conjugated spacers in the polymeric semiconductors were investigated by FET techniques using *o*-DCB as processing solvent. The electrical characteristics of the studied polymers casted on the ODTS-modified SiO₂/Si substrates are summarized in Table 2. These polymers exhibit typical p-type FET behaviors, 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). The correlation between the I_{ds} and other parameters are using the following equation:⁴⁷

$$I_{ds} = 0.5 W C_i \mu L^{-1} (V_g - V_t)^2$$
(1)

where I_{ds} is the drain-to-source current in the saturated region, W is the channel width, L is the channel length, μ is the hole mobility, C_i is the capacitance per unit area of the insulation

Table 3 Photovoltaic characteristics of	f P2Se4TTT/PC71BM-based devices
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			$V_{\rm oc}$	$J_{ m sc}$	FF	PCE ^a
P2Se41	"ГТ/РС ₇₁ ВМ	Solvent	(V)	$(mA cm^{-2})$	(-)	(%)
	1:1	o-DCB	0.65	4.49	0.305	0.78
	1:2	o-DCB	0.58	6.53	0.465	1.76
	1:3	o-DCB	0.63	4.67	0.364	1.07
	1:2	o-DCB+1% DIO	0.59	6.18	0.450	1.62
	1:2	o-DCB+2% DIO	0.74	6.79	0.455	2.29
	1:2	o-DCB+3% DIO	0.66	6.76	0.466	2.08
	1:2	o-DCB+4% DIO	0.62	6.44	0.420	1.67

^a The average value of PCE is calculated from at least 5 devices.

layer (300 nm SiO₂, $C_i = 10 \text{ nF cm}^{-2}$), V_g and V_t are the gate and threshold voltages, respectively. Fig. 5(a) and Fig. S15 (ESI⁺) show the p-type output characteristics of P2Se4TTT and other polymers, good current modulation and well-defined linear and saturation regions are explored. Furthermore, the transfer curves are depicted in Fig. 5(b), the higher drain current corresponds to higher charge carrier mobility. The average pchannel mobilities of PSe4TV-, PSe4TT-, PSe4T2T-, PSe4TTT-, and P2Se4TTT-based as-cast devices are 4.8×10⁻⁴, 8.1×10^{-5} , 1.0×10^{-3} , 5.4×10^{-3} and 5.7×10^{-2} cm²V⁻¹s⁻¹, respectively. As the FETs are annealed at 140 °C for 1 h under vacuum, the hole mobilities of PSe4TV, PSe4TT, PSe4T2T, **PSe4TTT**, and **P2Se4TTT** are increased to 3.2×10^{-3} , 8.6×10^{-4} , 1.0×10^{-2} , 6.0×10^{-2} and $2.5 \times 10^{-1} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. Note that the on/off ratios are in a range of $10^3 \sim 10^5$ for all devices. The annealing process successfully enhance the mobility of the studied materials for at least an order magnitude, due to the improved polymer chain packing as well as charge transport ability during thermal treatment.

The transistor performance of the Se4T- and 2Se4T-based polymers is largely affected by the variant conjugated spacers. With only single thiophene or double bond linkage as spacer, **PSe4TT** and **PSe4TV** exhibit low mobilities of 8.6×10^{-4} and 3.2×10^{-3} cm²V⁻¹s⁻¹, respectively. This may attribute to their amorphous structural nature and poor thin film quality on

ODTS-modified substrate, since the spacers cannot reduce the steric hindrance of thiophene side chains. Hence, the polymer chains tend to form large aggregates on the surface (Fig. S12), and the grain boundaries would disturb the charge transporting. The polymer with an additional unsubstituted thiophene ring as spacer, **PSe4T2T**, showed a higher mobility (0.01 cm²V⁻¹s⁻¹) than PSe4TT and PSe4TV after annealing owing to the bithiophene moiety provides more appropriate space to enhance the inter-digitations between polymer chains. Moreover, PSe4TTT possesses stronger charge transport ability (0.06 $cm^2V^{-1}s^{-1}$) than **PSe4T2T** because the fused-ring spacer (TT) can promote self-organization and minimize the steric interactions, thus induce crystalline packing structure and enhance the charge transport, as evidenced from morphological analyses. Highest mobility among all studied polymers is observed on **P2Se4TTT**-based device $(0.25 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1})$. The incorporated biselenophene moiety can efficiently assist in intermolecular π - π stacking due to the strong intermolecular interaction of the selenium atom, and the dense molecular packing architecture as well as nanofirbrillar polymer network are induced through TT spacer, facilitating unhindered charge transporting channel. In addition, the highest molecular weight of P2Se4TTT may also influence on thin-film microstructure, crystallinity, or domain size, leading to the best charge transport characteristics.48



Fig. 6. PV characteristics of **P2Se4TTT**/PC₇₁BM blends under the illumination with AM 1.5G solar simulated light (100 mW cm^{-2}).

Polymer Photovoltaic (PV) Cell Characteristics

The bulk heterojunction photovoltaic cell were fabricated with sandwich configuration а of ITO/PEDOT:PSS/Polymer:PCBM/Ca (30 nm)/Al (100 nm). The active layers of the studied polymers were prepared through optimal annealing temperature at 140 °C for 10 min. The J-V curves of polymer/PC₆₁BM blends were measured in air after encapsulation with UV-curing glue, as shown in Fig. S16 in ESI[†]. The detailed PV properties including short-circuit current (J_{sc}) , open-circuit voltage (V_{oc}) , fill factor (FF), and power conversion efficiency (PCE) of polymer/PC61BM blends are summarized in Table S2 (ESI⁺). The highest PCEs of PSe4TV, PSe4T2T, PSe4TTT, and P2Se4TTT are 0.43, 0.42, 0.61, and 1.18 %, respectively, which are based on the same polymer/PC₆₁BM blend ratio. The PV cell based on PSe4TT could not detect typical J-V characteristics due to its poor film quality and charge transport ability. P2Se4TTT achieves the highest PCE among this set of polymers owing to the high J_{sc} value, which is supported from its highest p-type mobility and broadest absorption as well as smallest band gap. Moreover, the J_{sc} of **P2Se4TTT** can be further enhanced (from 4.19 to 6.53 mA cm⁻²) using PC₇₁BM as acceptor (Fig. 6) because this stronger acceptor (PC71BM) can increase the photocurrent as well as absorption coefficient in the visible region, compared to PC₆₁BM.⁴⁹ The optimal efficiency of 1.76 % is obtained as the blend ratio of **P2Se4TTT**/PC₇₁BM at 1:2 (w/w) (Table 3).

It has been reported that adding additives (e.g. 1,8diiodoctane) into polymer/fullerene blends can successfully tune the bulk heterojunction morphology of solar cells, leading to better exciton dissociation efficiency and transport of the separated charge carriers to the respective electrode.^{50,51} Hence, **P2Se4TTT**-based PV cells are further investigated by using 1,8-diiodoctane (DIO) as additives with *o*-DCB in preparing active layers. The *J-V* characteristics of the devices were shown in Fig. 6 and summarized in Table 3. Different amounts of DIO (1~4% adding ratio by weight) were investigated in **P2Se4TTT**/PC₇₁BM (1:2 w/w) system, and the optimized PCE, 2.29 %, could be obtained as 2 wt% of DIO was added. The present of DIO significantly improve the J_{sc} and V_{oc} value of PVs from 6.53 to 6.79 mA cm⁻² and 0.58 to 0.74 V, respectively, compared to that of **P2Se4TTT**/PC₇₁BM PV cells without DIO. The enhancements of those PV factors should be mainly judged by the morphology of the **P2Se4TTT**/PC₇₁BM aggregations are clearly reduced as DIO introduced, leading to better thin film uniformity as well as higher PCE.

Conclusions

In conclusion, five new Se4T- and 2Se4T-based polymers (PSe4TV, PSe4TT, PSe4T2T, PSe4TTT, and P2Se4TTT) were successfully designed and synthesized using palladium(0)catalyzed Stille polymerization. The optical and electrochemical properties of this set of polymers were highly depended on their chemical structures, which incorporated different π -conjugated spacers. Smallest band gap (1.78 eV) could be observed on P2Se4TTT among the studied polymers due to the inserting of biselenophene and thieno[3,2b]thiophene moieties can further lower the conformation hindrance of thiophene side chains, and increase main chain coplanarity as well as the intermolecular interactions in thin films. The field-effect mobilities of these polymers could be as high as 0.25 cm²V⁻¹s⁻¹ with a large on/off ratio above 10⁵ (P2Se4TTT). This high mobility result was attributed to the dense molecular packing structure and nanofirbrillar morphology of P2Se4TTT thin film, as demonstrated by AFM, TEM, and GIXD. The solar cell efficiency of the polymer/PC₆₁BM blends were in the range of 0.43 ~ 1.18 % under the illumination of AM 1.5G (100 mW cm⁻²). In particular, **P2Se4TTT** showed the highest PCE of 2.29 % (J_{sc} = 6.79 mA cm⁻², $V_{oc} = 0.74$ V, and FF = 0.455) using the additive of 2 % DIO, which was mainly due to its high p-type mobility, broad absorption (small band gap), and uniform polymer/PC71BM blending morphology. The above results indicated that the design of polymer with selenophenecontaining main chain with conjugated thiophene side chain and connect with variant π -conjugated spacers could successfully tuned the optoelectronic characteristics, leading to the potential to use for future polymer devices applications.

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