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Modified structure of two-dimensional polythiophene derivatives by incorporating electron-deficient units into terthiophene-vinylene conjugated side chains and the polymer backbone: synthesis, optoelectronic and self-assembly properties, and photovoltaic application†

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Molecular engineering on the conjugated side chains of two-dimensional (2D) conjugated polymers was conducted and its effect on the optical, electronic, self-assembly and photovoltaic properties was investigated. A new monomer, **M2**, was prepared by capping (*E*)-3'-(2-(2,5-dibromothiophen-3-yl)vinyl)-4,4''-bis(2-ethylhexyl)-2,2':5',2''-terthiophene, **M1**, with two heptanoyl groups, and then coupled with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene via microwave-assisted Stille polymerization to produce a series of polythiophene derivatives with terthiophene-vinylene conjugated side chains, **TTV-PTs**. Copolymer **P2** shows a down-shifted HOMO energy level, enhanced solubility, and red-shifted absorption, as compared with **P1**; however, the bulky side chains significantly disrupt the coplanarity of thiophene rings in the polymer backbone and the ability to self-assemble into an ordered structure. The GIXRD measurements reveal that the original crystallinity of **P1** can be recovered by simply inserting a few 2,1,3-benzothiadiazole units into the polythiophene main chain in **P2** through a random copolymerization route to yield a terpolymer, **P3**, which possesses excellent crystallinity, thereby causing a three-fold increment in hole mobility. Furthermore, the **P1/PC₆₁BM**, **P2/PC₆₁BM**, and **P3/PC₆₁BM** solar devices exhibit power conversion efficiencies of 3.89%, 1.52%, and 4.17%, respectively, under AM1.5G illumination with an intensity of 100 mW cm⁻².

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Introduction

Molecular engineering of specific semiconducting conjugated polymers for use in high-performance organic electronic devices, such as field effect transistors (FETs), photo-detectors, light-emitting diodes (LEDs), and photovoltaics (PVs), requires a better understanding of the relationship between their chemical structure and optoelectronic properties.^{1–7} Several successful strategies for the structural design of conjugated polymers, such as donor–acceptor (D–A) copolymerization,^{8–10}

two-dimensional (2-D) conjugation,^{11–13} and side-chain engineering,^{14–16} have been developed to enhance their light-harvesting ability, charge mobility, self-assembling, solubility, and turning their molecular energy levels to meet the requirements of organic electronic devices.^{5,17–20} Poly(thienylene-vinylene)s (PTVs), which is one of polythiophene derivatives (PTs) containing alternating thiophene and vinylene units along the main-chains, have been intensively studied for their photoelectrical property and photovoltaic applications, due to their good charge transport property.^{2,21–25} In addition, previous literatures also have shown that polythiophene derivatives (PTs) with thienylene-vinylene conjugated side chains possess broader absorption spectra and relatively low-lying HOMO energy levels compared with their linear analogues, since the thienylene-vinylene conjugated side chains could extend the π -electron delocalization of polymer backbone.^{2,26–30} For example, chemically grafting conjugated side chains onto polymer backbone through vinylene-linkage, such as thienylene-vinylene³¹ and bi(thienylenevinylene),¹¹ is effective to extend the absorption range and down-shift the HOMO energy

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level of polythiophene. However, the steric hindrance of bulky branches frequently lowers the coplanarity of thiophene rings on the main chain, leading to weak crystallinity and low π - π^* absorption intensity.²⁸ To overcome this problem, unsubstituted thienyl moieties have been inserted into the backbone as spacer to reduce the grafting density and increase the distance between conjugated branches.³² Nevertheless, the introduction of such electron-rich spacer is accompanied by the substantial decline of solubility and the raise of HOMO level, thus complicating the fabrication process and limiting the maximum attainable open-circuit voltage (V_{oc}) of solar devices, respectively.

Recently, we established a new class of polythiophene derivatives with terthiophene-vinylene (TTV) conjugated side chains, **P1**, whose structure is illustrated in Fig. 1, by chemically attaching polythiophene backbone with branched side chains through vinylene bridge.¹³ This polymer has adequate solubility, an extended absorption spectrum, a deep HOMO level and, more importantly, retains excellent crystallinity. It has been well documented that the bandgap reduction of polymer donor in organic photovoltaics is crucial in enhancing the photocurrent and then the power conversion efficiency (PCE). One important approach toward red-shifting the absorption band is the integration of electron-rich and electron-deficient units into the polymer backbone or conjugated side chains that would enhance effectively intramolecular charge transfer (ICT) to reduce the optical bandgap. In comparison to alternative copolymerization of these monomers, the strategy of random copolymerization has advantages of further broadening the absorption region caused by multiple chromophores.^{18,28,30,33} Overall, these strategies, such as incorporating electron-withdrawing groups into polymer backbone and/or conjugated side chains, would be conducive to absorption ability of conjugated polymer.

Herein, we designed and synthesized two 2-D conjugated polymers, **P2** and **P3** (Fig. 1), by attaching two carbonyl groups to the TTV conjugated side chains and incorporating 2,1,3-benzothiadiazole (BTD) units into the polymer backbone. Because of the attachment of two carbonyl groups to the TTV conjugated side chains, **P2** displays a deeper HOMO energy level and better solubility, and its absorption band from conjugated side chain is red-shifted in comparison to **P1**. In addition, BTD, a planar and strongly electron-withdrawing unit, is widely used to build high-performance donor-acceptor copolymers.^{34,35}

Importantly, due to the randomized incorporation of steric-less BTD units into the polymer backbone of terpolymer, **P3**, its presence not only broadened the polymers absorption band but also promoted its self-assembling ability.³⁶ The best PSC devices based on **P3**/PC₆₁BM gave a PCE of 4.17% under AM1.5G illumination with an intensity of 100 mW cm⁻². The effects of molecular structure design on the optical, electrical, crystallographic, and photovoltaic properties of these copolymers were systematically investigated.

Results and discussion

The synthetic routes used to prepare the new monomer, **M2**, and the target copolymers are shown in Scheme 1. On the basis of the reactivity of **M1**, it was anticipated that Friedel-Crafts acylation would preferentially occur at the 5 and 5'' positions of the terthiophene side chain. Therefore, the new monomer **M2** was synthesized using **M1**, heptanoyl chloride, and aluminum chloride. A coupling constant of *ca.* 16.0 Hz in the ¹H NMR spectrum of **M2** (Fig. S1 in the ESI†) clearly indicates that the

Scheme 1 Synthetic routes for monomers and the corresponding polymers.

Fig. 1 Chemical structures of **P1**, **P2**, and **P3** (R = 2-ethylhexyl; R' = n-hexyl).

E-isomer is the exclusive product. Detailed characterization data for this monomer is given in the ESI.†

All polymers were polymerized under microwave-assisted conditions. Microwave-assisted Stille polymerization lends itself very well to our polymerization, because conditions can be quickly optimized and the reaction time was dramatically shortened.³⁷ We tried to simply optimize the polymerization conditions of **P1** by varying the catalyst, monomer concentration, and microwave heating conditions. The results of the polymerization experiments are listed in Table S1 (ESI†). The results show that lower catalyst content, higher monomer concentration, and longer reaction time seem to produce polymers with higher molecular weights and lower polydispersity index (PDI) in polymerization of **P1**.

The optimized polymerization conditions of **P1** were further applied in the synthesis of **P2** and **P3**. Terpolymer **P3** was polymerized with a molar feed ratio of **M2** : **M3** : **M4** of 2 : 3 : 1. It is noteworthy that the polymerization of random copolymer **P3** is highly reproducible by microwave-assisted polymerization. The raw products were precipitated into methanol and collected through a Soxhlet thimble by filtration, which was then subjected to repeated Soxhlet extraction with methanol, acetone, hexane, and methylene chloride to remove the small molecules and oligomers, and finally with chloroform to collect the target compounds.

P1 and **P2** have comparable yields of *ca.* 80% and exhibit good solubility in common solvents such as tetrahydrofuran (THF), chloroform, chlorobenzene (CB), and *o*-dichlorobenzene

(*o*DCB). Moreover, gel permeation chromatography (GPC) shows that they have very similar molecular weight characteristics with number-average molecular weights of around 27 kDa with respect to polystyrene standards, as indicated in Table 1. However, **P3** displays lower solubility in THF than the other polymers and therefore it is unavailable to obtain the molecular weight data by GPC. By using elemental analysis, the average *m/n* ratio in **P3** was calculated to be 4.4, indicating that there is *ca.* 18% BTB units into the polymer backbone in reality.

Thermal properties of all polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis, as shown Fig. S7 in the ESI.† TGA plots reveal that the temperatures with 5% weight loss of **P1**, **P2**, and **P3** are 449, 419, and 430 °C, respectively, under N₂ atmosphere at a heating rate of 10 °C min^{−1}. All compounds exhibit excellent thermal stability with degradation temperatures (*T_d*) at 5% weight loss well beyond 400 °C. DSC plots were measured up to 300 °C, **P1** exhibits an obvious phase transition at 282.1 °C which is considered its melting point. However, the other bulk samples display no apparent thermal transition.

UV-vis absorption spectra of the polymers in dilute CB solution and as spin-coated film on glass substrates are shown in Fig. 2. The corresponding absorption data of the polymers is summarized in Table 1. Comparison of the UV-vis spectra of **P2** and **P3** with control polymer **P1** reveals how the structural modifications of the side and main chains affect the optical properties of branched-type 2-D PTs. First, in dilute CB solution, **P2** displays two distinct absorption bands between 300 and 650 nm. The low-energy band

Table 1 Molecular weight, thermal, optical, and electrochemical properties of the polymers

Polymer	<i>M_n</i> ^a (kDa)	PDI ^a	<i>T_d</i> ^b (°C)	Solution, λ _{max} ^c (nm)	Film, λ _{max} ^d (nm)	Film, λ _{onset} ^d (nm)	<i>E_g</i> ^{opte} (eV)	<i>E_{HOMO}</i> ^f (eV)	<i>E_{LUMO}</i> ^g (eV)
P1	27.0	3.94	449	341, 528	355/564	654	1.90	−4.90	−3.00
P2	27.7	2.81	419	398, 510	406/557	669	1.85	−5.14	−3.29
P3	×	×	430	410, 579	407/579	743	1.67	−5.07	−3.40

^a *M_n* and PDI of the polymers were estimated by GPC using polystyrene as standards in THF. ^b 5% weight-loss temperature measured by TGA under N₂ atmosphere. ^c Measured in dilute CB solution (10^{−3} g L^{−1}). ^d Measured on glass substrates spin-coated with polymers from a CB solution (10 g L^{−1}) followed by thermal annealing (120 °C, 15 min). ^e Estimated from the onset wavelength of the absorption spectra: *E_g*^{opt} = 1240/λ_{onset}. ^f HOMO energy levels were evaluated by ultraviolet photoelectron spectroscopy (AC2 equipment) of thin polymer films on glass substrates. ^g Calculated according to the equation: *E_{LUMO}* = *E_{HOMO}* + *E_g*^{opt} (eV).

Fig. 2 UV-vis absorption spectra of polymers (a) in dilute CB solution at room temperature; (b) solid films prepared by spin-coating followed by thermal annealing at 120 °C for 15 min.

that peaks at ~ 535 nm corresponds to the π - π^* transition of the conjugated backbone, whereas the high-energy (short wavelength) band that peaks at ~ 398 nm and exhibits a distinct red-shift (of 57 nm) compared to **P1** that originates from the intramolecular charge transfer between two electron-withdrawing heptanoyl groups and the terthiophene unit in the TTV conjugated side chain. However, owing to the replacement of H-atoms by two heptanoyl groups in the TTV conjugated side chain, the conjugated side chains become more bulky to disturb the coplanarity of the polymer backbone and therefore its π - π^* transition peak is observed with a slight blue-shift (of 18 nm) and relatively weak intensity compared to **P1**. Furthermore, in comparison with **P2**, random copolymer **P3** possesses a significantly broader absorption region covering a wavelength range of 300–750 nm. **P3** also exhibits two distinct absorption bands at 407 nm and 579 nm. Because of the introduction of BTB units in the polymer backbone, the low-energy absorption band displays obvious red-shift that is mainly attributed to the ICT interaction of the BTB and BT units in the polymer backbone. Importantly, the partial bulky **M2** units were replaced by less steric BTB units that would also enhance π - π^* transition absorption due to reducing the twisting of polymer backbone. Through simple structural modifications of the side and main chains, we have successfully extended the absorption region of branched-type 2-D PTs, thereby enhancing their light-harvesting ability.

As shown in Fig. 2(b), the polymer films generally display red-shifted and broader absorption than their corresponding solutions due to interchain associations and better planarity in the solid state.³⁸ Therefore, the maximum values of the low-energy absorption peaks are red-shifted by *ca.* 36 nm, 47 nm, and 23 nm for the **P1**, **P2**, and **P3** films, respectively, in comparison with solutions. Moreover, the optical bandgaps (E_g^{opt}) of **P1**, **P2**, and **P3**, estimated from the absorption onsets of their solid films, are 1.90, 1.85, and 1.67 eV, respectively. **P3** obviously displays a lower bandgap than **P2** because of the incorporation of strong electron-withdrawing BTB units into the polymer backbone. The absorption edge of random terpolymer **P3** is red-shifted to the near-infrared region, implying that it has great potential for effective photon-harvesting and could achieve a high short-circuit current in PSCs.²⁷

Molecular structural design is important for organic materials that directly has effect on polymer orientation in thin films, leading to decide the performance of charge transport. However, it's rare to be studied in 2-D PTs' system. Herein, to further understand the influence of molecular structure designs on solid-state crystallinity and polymer self-assembly in TTV-PTs, the two-dimensional grazing incidence X-ray diffraction (2D-GIXRD) technique was used to measure the intermolecular *d*-spacing and average crystallite size in the drop-cast thin films of polymer with thermal annealing procedure for investigating the behaviors of molecular packing orientation of **P1**–**P3**, as shown in Fig. S4.† The intermolecular *d*-spacing parameter and average crystallite size were determined from the diffraction peaks using Bragg's law and Scherrer's equations.³⁹

As extracted from the out-of-plane 2D-GIXRD profile shown in Fig. 3, **P1** thin film possesses a visible (100) diffraction peak at $2\theta = 3.01^\circ$ (corresponding to an interlayer *d*-spacing of

Fig. 3 Grazing incidence X-ray diffraction patterns of polymer films prepared by drop-cast followed by thermal annealing at 120 °C for 15 min. The inset-1 and inset-2 shows the region around $2\theta = 2$ – 4° and 5 – 25° , respectively, in greater detail.

2.54 nm with an average crystallite size of 16.5 nm), indicating lamellar packing parallel to the surface normal with an edge-on (100) orientation of the conjugated plane.⁴⁰ As two hydrogen atoms were replaced by two heptanoyl substituents at 5 and 5' positions of the terthiophene side chain of **P1**, polymer **P2** thin-film displayed amorphous nature that indicating the more bulky side groups in **P2** hinder the molecular stacking. Therefore, although the additional two heptanoyl groups in TTV side chains could enhance the solubility and red-shift absorption in UV-vis region, it is destructive for polymer self-assembly and backbone coplanarity by larger side chains.

Interestingly, **P3** displays a strong (100) diffraction peak at $2\theta = 3.01^\circ$ (corresponding to a lamellar *d*-spacing of 2.54 nm with an average crystallite size of 11.3 nm). In other words, partial bulky **M2** units were replaced by less sterically hindering BTB (**M4**) units in the polymer backbone that release enough free space to reduce the steric effect on the polymer backbone and promote molecular organization. This is an important strategy to induce polymer self-assembly for 2-D polythiophene derivatives by random copolymerization with less-steric units, such as 2,1,3-benzothiadiazole. In addition, compared to **P1**, the FWHM and intensity of (100) diffraction peak for **P3** thin films is broader and stronger, respectively, indicating **P3** thin films have higher degree of crystallinity and smaller average crystalline grain.

The charge mobility of conjugated polymers exerts a significant influence on the FF value of PSC devices,⁴¹ and many studies have revealed that the hole mobility of a crystalline conjugated polymer is usually higher than that of an amorphous conjugated polymer and therefore is more comparable with the electron mobility in the active layer, where the electron mobility is dominated by fullerene.⁴² The hole mobilities of polymers were measured in a hole-only device (ITO/PEDOT:PSS/pristine polymer/Au) using the space-charge-limited current (SCLC) method. Fig. S6(a)† which is plotted as $\ln(J_{\text{dark}}L^3V^{-2})$ versus $(VL^{-1})^{0.5}$ in ESI† shows the dependence of the measured

current density on the applied voltage. The mobilities were calculated according to the following formula:⁴³

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \frac{V^2}{L^3} \exp\left(0.89 \sqrt{\frac{V}{E_0 L}}\right),$$

where J denotes the current density, ε_r is the dielectric constant of the organic molecule, ε_0 is the permittivity of free space, L is the thickness of the active layer, V is the applied voltage, and E_0 is the characteristic field. The mobility of the polymer films was deduced from the intercept value of $\ln\left(\frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0\right)$. Therefore, the hole mobility of pristine **P1**, **P2**, and **P3** were determined to be $3.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $3.8 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $1.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. It should be noted that thin film of **P1** exhibited a diffraction peak at $2\theta = 20.17^\circ$, shown in inset figure in Fig. 3, that would be classified as face-on orientation and correspond to a π - π stacking distance of 3.81 Å. Therefore, it is reasonable to explain that the pristine **P1** thin film possesses the highest hole mobility by SCLC method, because it's well known that face-on polymer orientations have been suggested to promote the charge mobility by SCLC method and PSCs;^{44,45} meanwhile, the pristine **P3** thin film takes an edge-on orientation nature on the substrate which might be caused by the bulky side groups hindering the development of π - π stacking of polymer backbone. Nevertheless, it is evident that the formation

of an ordered polymer-chain structure improved the carrier mobility of the polymer material.

The highest occupied molecular orbital (HOMO) energies were estimated from the ionization potentials of spin-coated films determined by UV photoelectron spectroscopy in air using an AC2 photoelectron spectrometer (Riken Keiki Co.).⁴⁶ Fig. S3† plots the square root of the counting rate (CR) as a function of the photon energy. The photoemission threshold energy, also called the work function, was determined from the crossing point of the background and yield lines. Therefore, the work functions of **P1**, **P2**, and **P3**, were found to be -4.90 eV , -5.14 eV , and -5.07 eV , respectively (see Table 1) and the energy-level diagrams of polymers derived from AC2 photoelectron spectroscopy and UV-vis absorption data are shown in Fig. 4. Furthermore, the lowest unoccupied molecular orbital (LUMO) energies were calculated using the optical band gap (E_g^{opt}) and the HOMO energies determined from AC2 measurement according to the following equation: $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$ (eV).

By comparing with the HOMO of **P1**, the HOMO of **P2** is 0.24 eV deeper. Because two additional electron-withdrawing heptanoyl substituents attached to the 5 and 5' positions of the terthiophene side chain that enhance its air stability in ambient conditions, **P2** possessed further down-shifted HOMO level than **P1**. Furthermore, **M2** units were partially replaced by **M4** units in the backbone of **P3** such that the lower ratio of monomers containing conjugated side chains in the polymer backbone resulted in the HOMO rising. Similar results have also been observed for other 2-D PTs random copolymers.^{27,29,47} In addition, the differences ($>0.5 \text{ eV}$) in the LUMO levels of the polymers and PC₆₁BM ($\sim 4.20 \text{ eV}$) are still adequate enough for efficient charge transfer, even for the lowest LUMO in **P3**.^{27,48} The AC2 measurements reveal that our series of 2-D conjugated polymers have lower HOMO energies than rr-P3HT (*ca.* -4.68 eV under identical condition); this will be beneficial for the fabrication of photovoltaic devices with high V_{oc} values.

The broader absorption bands and lower-lying HOMO energy levels of our polymers suggest that they might exhibit promising photovoltaic properties. Bulk heterojunction PSC devices were fabricated using **P1**, **P2**, or **P3** as the electron donor, and PC₆₁BM as the electron acceptor. The device structure is ITO/PEDOT:PSS/polymer:PC₆₁BM/Ca/Al. The cell performance was optimized by varying the polymer to PC₆₁BM

Fig. 4 Energy diagram of **P1**, **P2**, and **P3**.

Fig. 5 (a) J - V curves (b) IPCE spectra of optimized polymer/PC₆₁BM devices under AM1.5G illumination with an intensity of 100 mW cm^{-2} .

Table 2 Photovoltaic properties of polymer solar cell devices based on the polymers, **P1**, **P2**, and **P3** with optimized ratios of PC₆₁BM under AM1.5G illumination with an intensity of 100 mW cm⁻²

Polymer/fullerene	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	R_{sh} (kΩ cm ²)	R_s (Ω cm ²)
P1 /PC ₆₁ BM ^a	788 ± 4	7.24 ± 0.05	67.76 ± 0.27	3.87 ± 0.02 (3.89)	1.01 ± 0.03	9.03 ± 0.27
P2 /PC ₆₁ BM ^b	688 ± 4	5.50 ± 0.28	38.25 ± 0.44	1.44 ± 0.08 (1.52)	0.47 ± 0.03	58.94 ± 2.75
P3 /PC ₆₁ BM ^c	770 ± 0	9.25 ± 0.13	57.59 ± 0.63	4.10 ± 0.07 (4.17)	0.86 ± 0.09	11.61 ± 0.52

^a Blend ratio 10 : 8 (w/w), in CB solvent, annealing at 100 °C for 10 min. ^b Blend ratio 10 : 8 (w/w), in *o*-DCB solvent, annealing at 80 °C for 10 min.

^c Blend ratio 7 : 7 (w/w), in *o*-DCB solvent, annealing at 120 °C for 10 min.

blend ratio in the active layer and thermal annealing temperature. The J - V curves of the optimized polymer/fullerene devices under AM1.5G illumination with an intensity of 100 mW cm⁻² are plotted in Fig. 5(a) and the relevant photovoltaic characteristics are listed in Table 2. The highest PCEs (%) for each PSC device are 3.89% (**P1**/PC₆₁BM 1 : 0.8 w/w), 1.52% (**P2**/PC₆₁BM 1 : 0.8 w/w), and 4.17% (**P3**/PC₆₁BM 1 : 1 w/w).

The incident photo-to-electron conversion efficiencies (IPCE) of the optimized polymer/fullerene devices under AM1.5G illumination with an intensity of 100 mW cm⁻² are plotted in Fig. 5(b). The J_{sc} values calculated by integrating the IPCE data with the AM1.5G spectrum were 7.64, 5.86 and 9.55 mA cm⁻² for **P1**, **P2** and **P3** devices, respectively. The IPCE results not only

agree with the measured J_{sc} values, considering that an error of 3–6% commonly takes place for the IPCE measurements, but also exhibit well-matched curves with their optical absorptions.^{27,30,49} The IPCE spectra of the **P1**/PC₆₁BM (1 : 0.8 w/w) device covers a wavelength range of 350–650 nm. Moreover, the device based on **P2**/PC₆₁BM and **P3**/PC₆₁BM show higher IPCE values in the wavelength range of 400–430 nm and 370–475 nm, respectively, than **P1**/PC₆₁BM. This result reveals that two additional heptanoyl substituents attached to the TTV conjugated side chain can effectively enhance absorption bands between 350 and 480 nm as shown in Fig. 2(b) and further lead to increase photocurrent generation in the region. However, the **P2**/PC₆₁BM device shows a rather low IPCE over most of the

Fig. 6 AFM (a–c) topography images and (d–f) phase images of spin-coated films of polymer/PC₆₁BM blends. The scan sizes for all images are 2 μm × 2 μm.

response range, thus causing its lower J_{sc} and PCE. For the **P3**/PC₆₁BM device, the active region of the IPCE curve covers the broadest wavelength range from 300 to 750 nm. The existence of the two heptanoyl substituents in **P3** promote the higher IPCE values from 370 to 475 nm compared to the **P1** device; meanwhile, by incorporating BTB units into the **P3** backbone, the IPCE curve is further extended to 750 nm, thus causing this device to have the broadest IPCE region and highest J_{sc} .

The electron and hole mobilities of the blended films were determined by using the SCLC method to gain an insight into their effective charge carrier mobilities in the optimized blend weight ratio. Experimental results shown in Fig. S6(b) and (c) and Table S2† indicate that the trend in hole mobility of the blended films is the same as that for the series resistance (R_s). As a result, the hole mobility of **P2**/PC₆₁BM is approximately two orders of magnitude lower than the electron mobility, which leads to unbalanced charge carrier transport and recombination, and may be responsible for the poor photovoltaic characteristics observed.

The open-circuit voltage (V_{oc}) of PSC device is mainly related to the difference between the HOMO of the donor and LUMO of the acceptor.⁴⁸ Thus, because of the low-lying HOMO energy levels of PTs containing conjugated side chains, an average V_{oc} of 788 mV was obtained from the **P1**/PC₆₁BM devices, which substantially exceeds the commonly reported V_{oc} (~0.6 V) for devices based on P3HT/PC₆₁BM.^{50–52} However, the lowest V_{oc} value was observed for the **P2**/PC₆₁BM device which is quite poorly consistent with the position of the **P2** HOMO energy level. The non-linear trend is decided by a couple of other factors besides the HOMO levels of the polymers, such as the dark current, blend morphology of the photoactive layers, and interface resistance.^{30,34,53–55} Fig. S5 (shown in ESI†) shows dark J - V curves of polymer/PC₆₁BM devices. The dark current of the **P2**/PC₆₁BM device was obviously larger than that of the **P1**/PC₆₁BM device implying that serious recombination from dark carriers might have caused a loss of open-circuit voltage.

The morphology of photoactive layer plays a decisive role in determining the photovoltaic characteristics of PSC devices.^{56–58} Herein, atomic force microscopy (AFM) was used to investigate the morphologies of the spin-coated films of polymers/PC₆₁BM on top of ITO/PEDOT:PSS, which were prepared by using the same procedure and parameters for preparing the photoactive layers. As shown in Fig. 6, the **P2**/PC₆₁BM blend film exhibits the smoothest surface and the least degree of phase separation with a root-mean-square (RMS) roughness of 2.16 nm and a phase degree of 0.21°. However, **P2**/PC₆₁BM has the slowest hole mobility of $1.1 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is also only around one-third of that of pristine **P2**. These findings suggest that the polymer chains of **P2** form homogeneous mixture with PC₆₁BM and are unable to effectively segregate into continuous and unhindered pathways for conduction of holes to the anode. Therefore, the J_{sc} of the **P2**/PC₆₁BM solar cell is much smaller than that of both **P1**/PC₆₁BM and **P3**/PC₆₁BM devices.

Conclusions

We have successfully incorporated electron-withdrawing units, heptanoyl group and BTB moiety, into the TTV conjugated side

chains and polythiophene backbone to synthesize **TTV-PTs**, **P2** and **P3**. Compared with their parent analogue, these polymers possess apparently red-shifted absorption bands as well as down-shifted HOMO and LUMO levels that are beneficial to improve the polymer donor's light-harvesting ability and lift the V_{oc} of solar cells. However, the steric hindrance of bulky heptanoyl groups in **P2** significantly twists the polymer backbone, not only shortening the conjugation length but also lowering the crystallinity and then hole mobility. It is interesting to note that the crowding effect of oversized side groups can be completely relaxed by the insertion of 18% BTB units into the polymer main chain through a simple random copolymerization method and, therefore, the resulting terpolymer **P3** has broad absorption band, excellent crystallinity and good carrier mobility. Consequently, the bulk heterojunction solar cell fabricated from **P3**/PC₆₁BM exhibits a promised PCE of 4.17% with a V_{oc} of 770 mV, a J_{sc} of 9.3 mA cm^{-2} and an FF of 58%. A further improvement can be made by introducing larger solubilizing group onto the TTV unit to allow more BTB to be merged into the backbone. More importantly, this study offers an easy and useful strategy to design highly crystalline 2D conjugated polymers for developing high-performance polymer solar cells.

Experimental section

Materials

(*E*)-3'-(2-(2,5-Dibromothiophen-3-yl)vinyl)-4,4''-bis(2-ethylhexyl)-2,2':5',2''-terthiophene (**M1**),⁵⁹ 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**M3**),⁶⁰ 4,7-dibromo-2,1,3-benzothiadiazole (**M4**)⁶¹ were prepared *via* literature procedures. Toluene (Acros Organics, 99+%, extra pure) and *p*-xylene (Acros Organics, 99+%, extra pure) and methylene chloride (ECHO Chemical, ACS Grade, 99.5%) are dried over calcium hydride (Acros Organics, *ca.* 93%, extra pure, 10–100 mm pieces) under N₂ and stored with molecular sieves in a round-bottom flask under inert atmosphere. Flash chromatography was performed over silica gel (230–400 mesh).

(*E*)-1,1'-(3'-(2-(2,5-Dibromothiophen-3-yl)vinyl)-4,4''-bis(2-ethylhexyl)-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(heptan-1-one) (**M2**)

A solution of AlCl₃ (Acros Organics, 99%, 346.7 mg, 2.6 mmol) in anhydrous 1,2-dichloroethane (50 mL) was added to a 100 mL Schlenk flask under N₂ atmosphere. Heptanoyl chloride (Alfa Aesar, 99%, 0.4 mL, 2.6 mmol) freshly distilled was then slowly added dropwise to the solution. The mixture was stirred at room temperature for 30 min and then cooled to 0 °C. Subsequently, **M1** (960 mg, 1.3 mmol) in anhydrous 1,2-dichloroethane (10 mL) was slowly added dropwise to the solution, causing the color of the suspension to change from light yellow to deep-red. The mixture was warmed to room temperature and stirred overnight. Then 2 M hydrochloric acid (100 mL) was slowly added to quench the reaction and the resulting mixture were extracted twice with 40 mL dichloromethane, then the organic phase was combined, washed several times with saturated

sodium acetate solution and water, and dried with MgSO_4 . After removal of the solvent, the residue was purified by flash column chromatography (eluent: hexane/ CH_2Cl_2 , 1 : 1, v/v), yielding a pale-yellow oil **M2** (601.0 mg, 0.62 mmol, 48%). ^1H NMR (400 MHz, CDCl_3) δ 7.43 (s, 1H), 7.07 (d, 1H, J = 16 Hz), 7.07 (s, 1H), 7.03 (s, 1H), 6.98 (s, 1H), 6.87 (d, 1H, J = 16 Hz), 2.99–2.88 (m, 4H), 2.81–2.76 (m, 4H), 1.76–1.65 (m, 6H), 1.35–1.26 (m, 28H), 0.90–0.87 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.26, 193.21, 150.65, 150.34, 138.72, 138.57, 137.24, 137.11, 136.19, 134.78, 132.43, 131.85, 129.08, 127.13, 123.54, 123.33, 122.76, 112.32, 110.87, 42.40, 42.30, 40.19, 34.50, 32.66, 32.55, 31.60, 28.95, 28.68, 28.62, 25.74, 24.76, 24.70, 23.06, 22.49, 14.08, 14.01, 10.71 ppm; HRMS (ESI⁺): m/z calcd for $\text{C}_{48}\text{H}_{67}\text{O}_2\text{Br}_2\text{S}_4$: 963.2365 [M^+]; found: 963.2365.

Microwave-assisted polymerization procedure

Monomers were weighted into microwave tubes (G10) and then the tubes were subjected to three successive cycles of vacuum followed by refilling with nitrogen. After addition of Pd-catalyst (Alfa Aesar, tris(dibenzylideneacetone)dipalladium(0), $[\text{Pd}_2(\text{dba})_3]$, Pd 21.5% min; Acros Organics, tri-*o*-tolylphosphine, 99%; Acros Organics, tetrakis(triphenylphosphine)palladium(0), $[\text{Pd}(\text{PPh}_3)_4]$, 99%) in toluene or *p*-xylene solution (3 mol% relative to 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, **M3**), the tubes were subjected to the reaction conditions in a microwave reactor. The heating condition: raise temperature from r.t. to 200 °C as fast as possible; hold the temperature 60 min; cool down to 55 °C. Each raw product was dissolved in toluene, then precipitated into methanol and collected through a Soxhlet thimble by filtration and then subjected to consecutive Soxhlet extractions with methanol, acetone, hexane, and methylene chloride to remove the small molecules and oligomers, and finally with chloroform to collect the target compounds.

P1 is synthesized according to the procedure with **M1** (182.5 mg, 0.247 mmol) and **M3** (122.3 mg, 0.249 mmol) in 5.0 mL *p*-xylene, yielding **P1** (154.6 mg, 84.1%).

P2 is synthesized according to the procedure with **M2** (167.4 mg, 0.174 mmol) and **M3** (86.1 g, 0.175 mmol) in 3.5 mL *p*-xylene, yielding **P2** (136.5 mg, 81.0%).

P3 is synthesized according to the procedure with **M2** (203.6 mg, 0.211 mmol), **M3** (156.0 mg, 0.317 mmol) and **M4** (31.1 mg, 0.105 mmol) in 6.3 mL *p*-xylene, yielding **P3** (104.5 mg, 49.5%). Elemental analysis: found (average value): S, 20.620%; H, 7.221%; C, 68.015%; N, 0.610%.

Characterization and instrumentation

Microwave assisted polymerizations were performed in Anton Paar Monowave 300 microwave reactor. ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz on Bruker DRX-400 spectrometer. All NMR spectra were calibrated by chloroform-*d* (CDCl_3) where ^1H NMR chemical shifts of CDCl_3 is 7.23 ppm; in addition, ^{13}C NMR of CDCl_3 is 77.0 ppm. Microwave assisted polymerizations were performed in Anton Paar Monowave 300 microwave reactor. Thermal gravimetric analysis (TGA) was measured on TA Instruments Hi-Res TGA 2950 and differential scanning calorimetry (DSC) was recorded on

PerkinElmer DSC 8000 under N_2 atmosphere at a heating rate of 10 °C min^{-1} . Ultraviolet-visible absorption (UV-vis) spectra were recorded on a JASCO MD-2010 spectrometer. Gel permeation chromatography (GPC) was conducted at 40 °C using two Jordi DVB mixed-bed columns (250 × 10 mm; suitable for separating polymers with molecular weights from 3×10^3 to 5×10^6 g mol^{-1}) using THF as the eluent at a flow rate of 1.0 mL min^{-1} on a JASCO instrument that was equipped with UV-vis and refractive index (RI) detectors connected in series. 2D-GIXRD measurements were carried out on the wiggler beamline BL17A1 of the National Synchrotron Radiation Research Center (NSRRC, Taiwan), with a wavelength of 1.333 Å delivered from a superconducting wavelength-shifting magnet and a Si(111) triangular crystal monochromator (TCM). The grazing angle was large enough to probe the interior of the films and meantime small enough to increase the X-ray path length within the films by orders of magnitude.⁶² The data were recorded by a Mar3450 image plate with exposure duration 60 second. The two-dimensional diffraction pattern was converted to a one dimensional powder diffraction profile by fit-2D program. The diffraction patterns are fitted in the one dimensional powder diffraction spectra using Gauss function of OriginPro 8 to locate the peak positions and calculate the full-width at half-maximum. The work functions of materials were measured using an AC2 photoelectron spectrometer (Riken Keiki Co.). Atomic force microscopy (AFM) images were captured using tapping model in Digital Instruments Nanoscope III. The AFM samples were prepared by spin-coating the blend solution on a ITO/PEDOT:PSS substrate.

Device fabrication

The polymer solar cells (PSCs) were fabricated with a configuration of ITO/PEDOT:PSS/active layer/Ca/Al. The ITO glasses were cleaned by a sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol for 20 min. Then PEDOT:PSS was filtered through a 0.2 μm filter and spin-coated at 3500 rpm for 30 s on top of ITO electrode. Subsequently, the PEDOT:PSS film was baked at 140 °C for 10 min in the air, and then moved into a glovebox. The blend solution of PC_{61}BM and synthesized polymers in a solvent was filtered with/without a 0.45 μm filter and spin-coated at 800 rpm for 30 s on top of the PEDOT:PSS layer. These devices were thermally annealed at various temperatures for 10 min, followed by capping with Ca (~20 nm) and then Al (~60 nm) in a thermal evaporator at a base pressure of *ca.* 10^{-6} Pa. The active area of the devices is 0.06 cm^2 . The current density–voltage measurements of the devices were conducted on a computer-controlled Keithley 2400 Source Measure Unit under AM1.5G simulated solar irradiation at 100 mW cm^{-2} . The light incident intensity was calibrated by a mono-Si reference cell with a KG5 filter (PV Measurements, Inc.), which was pre-calibrated by the National Renewable Energy Laboratory. The SCLC measurements were carried out using a Keithley 2400 source meter under dark condition. The IPCE spectra were recorded under illumination by a xenon lamp and a monochromator (TRIAx 180, JOBIN YVON), and the light

intensity was calibrated by using an OPHIR 2A-SH thermopile detector.

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