Synthesis and Electronic Energy-Level Regulation of Imide-Fused Poly(thienylene vinylene) Derivatives

Xiaochen Wang,^{1,2,3*} Chen Gao,^{1*} Kai Wang,^{1,3} Xi Fan,³ Haiqiao Wang,¹ Xiaoyu Li,² Zhi-Guo Zhang,³ Yongfang Li³

¹State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China ²Key Laboratory of Carbon Fiber and Functional Polymers of Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

³CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China Correspondence to: H. Wang (E-mail: wanghaiqiao@mail.buct.edu.cn) or X. Li (E-mail: lixy@mail.buct.edu.cn) or Y. Li (E-mail: liyf@iccas.ac.cn) or Z. G. Zhang (E-mail: zgzhangwhu@iccas.ac.cn)

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ABSTRACT: A series of novel poly(thienylene vinylene) derivatives (PTVs), **P20-P24**, with imide substituents were designed and synthesized by palladium-catalyzed Stille coupling polymerization, wherein the imide substituent density was decreased gradually, which allowed us to explicitly study the effect of electron-deficient substituent on the optical, electrochemical, and photovoltaic properties of the PTVs. All of the four polymers showed broad absorption bands with optical bandgaps between1.66 and 1.78 eV. By reducing density of electron-deficient imide group, the LUMO energy levels of the polymers could be tuned gradually from -3.75 to -3.43 eV, with HOMO levels upshifted from -5.64 to -5.16 eV. Bulk heterojunction solar cells with the polymers as donor and PC₇₁BM as acceptor demonstrated very different excitons dissociation behavior. With decreasing the imide-fused unit density, the open-circuit voltage (V_{OC}) values in the devices decreased from 0.78 to 0.62 V, whereas the short-circuit currents (J_{SC}) increased from 0 to 2.26 mA cm⁻² and then decreased to 1.01 mA cm⁻². By adjusting the electron-withdrawing imide substituent density, power conversion efficiency of the PTVs-based solar cells can be increased to four times, reached 0.86%. To the best of our knowledge, this is the first systematic study of the relationship between molecular energy level and photovoltaic properties of PTVs. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 4975–4982

KEYWORDS: conjugated polymers; electrochemistry; electronic energy level; polymer solar cells; poly(thienylene; vinylene) (PTVs); synthesis; thieno[3,4-*c*]pyrrole-4,6-dione (TPD)

INTRODUCTION In recent years, low-bandgap-conjugated polymers have drawn much attention due to their better match to the solar energy spectrum for the application in polymer solar cells (PSCs).^{1–7} Poly(thienylene vinylene) derivatives (PTVs) is an important class of low-bandgap polymers.⁸⁻¹⁵ PTVs have already proven to have broad absorption spectra (bandgap ca. 1.5-1.8 eV) combining with high hole mobility (up to 0.2 cm² V⁻¹ s⁻¹),¹⁶ which makes them attractive candidates for photovoltaic applications. However, power conversion efficiency (PCE) of bulk heterojunction (BHJ) PSCs based on PTVs as donor were rather low (0.2-0.3%).¹⁷⁻²⁰ Huo et al. synthesized poly(3-carboxylated thienylenevinylene) (P3CTV)²¹ with an electronwithdrawing carboxylate substituent, which possesses lower HOMO energy level and enhanced fluorescence. The PCE of the PSCs based on P3CTV as donor reached 2.01%. Recently,

we reported a new poly(thienylene vinylene) derivative, POTBTV,²² with electron-deficient benzothiadiazole unit inserted into the backbone. PCE of solar cell based on POTBTV reached 1.53%. These results indicate that the photovoltaic performance of the PTV derivatives could be greatly improved by connecting electron-withdrawing substituents to either the main chain or side chains of PTVs molecules. However, to achieve efficient PTVs, it is necessary to further study the effect of the electron-deficient substituent on the optical, electrochemical, and photovoltaic properties.

Herein, three monomers, trans-1,2-bis(tributylstannyl)ethylene, 2,5-dibromo thiophene, and imide-fused thiophene (*N*alkylthieno[3,4-*c*]pyrrole-4,6-dione, TPD) dibromide were copolymerized using the Pd-catalyzed Stille reaction to produce a series of PTVs, **P20-P24**, with molar feed ratios of TPD to pristine thiophene unit ranging from 2:0 to 2:4, as

*Xiaochen Wang and Chen Gao contributed equally to this work. © 2013 Wiley Periodicals, Inc.





SCHEME 1 Molecular Structure of P20-P24.

shown in Scheme 1, to study the effect of the imide-fused unit density on the physicochemical and photovoltaic properties of the polymers. Imide was chosen as the electronwithdrawing substituent because the polymers based on imide-fused thiophene, TPD, have demonstrated excellent photovoltaic properties as electron donors for OPVs.²³⁻²⁶ Note here that the symmetric structures of TPD and pristine thiophene make these polymers regioisomer-free, in contrast to 3-alkyl or 3-carboxylated thienylenevinylene polymer, which made it more convenient to evaluate the effect of the electron-deficient substituent density.

The UV-vis absorption spectra of these polymers do not have a strong dependence on the electron-deficient substituent density. As can be expected, the highest occupied molecular orbital (HOMO) energy levels upshifted gradually (from -5.64 to -5.16 eV) with the decrease of the electrondeficient substituent density. As a result, photovoltaic performance of the PSCs based on the blend of the polymers as donor and PC₇₁BM as acceptor changed regularly. More importantly, the effect of electron-deficient substituent density was studied systematically to better understand the relationship between the molecular energy levels and photovoltaic properties of the PTVs.

EXPERIMENTAL

Materials

2-Octyldodecylamine $(4)^{27}$ and thieno[3,4-*c*]furan-1,3-dione $(5)^{23}$ were synthesized according to the literatures. Other reagents and solvents were commercial grade and used as received without further purification. All reactions were performed under nitrogen atmosphere.

Measurements and Characterization

The molecular weights of the polymers were measured by gel permeation chromatography (GPC) method. The GPC measurements were performed on Waters 515-2410 with polystyrenes as reference standard and tetrahydrofuran (THF) as an eluent. All new compounds were characterized by nuclear magnetic resonance spectra (NMR). The NMR was recorded on a Bruker AV 600 spectrometer at room temperature. Chemical shifts of ¹H NMR and ¹³C NMR were reported in ppm. Splitting patterns were designated as s (singlet), t (triplet), d (doublet), m (multiplet), and br (broaden). Elemental analyses were performed on a Flash EA 1112 analyzer. UV-vis absorption spectra were recorded

on a Shimadzu spectrometer model UV-3150. Absorption spectra measurements of the polymer solutions were carried out in chloroform (analytical reagent) at 25 °C. Absorption spectra measurements of the polymer films were carried out on the quartz plates with the polymer films spin-coated from the polymer solutions in chloroform (analytical reagent) at 25 °C. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e electrochemical workstation with a glassy carbon, Pt wire, and Ag/Ag⁺ electrode as the working electrode, counter electrode, and reference electrode, respectively, in a 0.1-mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. Polymer thin films were formed by drop-casting polymer solutions in chloroform on the working electrode and then dried in air.

Fabrication of Photovoltaic Devices

PSCs were fabricated with ITO glass as a positive electrode, Ca/Al as a negative electrode, and the blend film of the polymer:PCBM between them as a photosensitive layer. The ITO glass was precleaned and modified by a thin layer of PEDOT:PSS, which was spin-cast from a PEDOT:PSS aqueous solution (Clevious P VP AI 4083 H. C. Stark, Germany) on the ITO substrate, and the thickness of the PEDOT:PSS layer was about 60 nm. The photosensitive layer was prepared by spincoating a blend solution of the polymer and PC71BM in odichlorobenzene (DCB) on the ITO/PEDOT:PSS electrode. Then, the Ca/Al cathode was deposited on the polymer layer by vacuum evaporation under 3×10^{-4} Pa. The thickness of the photosensitive layer was about 80 nm, measured on an Ambios Tech XP-2 profilometer. The effective area of one cell was about 4 mm². The current-voltage (J vs. V) measurement of the devices was conducted on a computer controlled Keithlev 236 source measure unit. A xenon lamp with an AM 1.5 filter was used as the white-light source, and the optical power at the sample was 100 mW cm⁻². Atomic force microscopy (AFM) images of the thin films were obtained on a Nanoscope VAFM (Digital Instruments) operating in tapping mode.

Synthesis of the Monomer and Polymers 5-(2-Octyldodecyl)thieno[3,4-c]pyrrole-4,6-dione (6)

Thieno[3,4-*c*]furan-1,3-dione (5) (7.7 g, 50 mmol) and 2octyldodecylamine (4) (16 g, 52.5 mmol) were dissolved in toluene (300 mL) and the mixture was refluxed for 24 h. The reaction mixture was cooled down and the solvent was removed under reduced pressure. The residue solid was dissolved in thionyl chloride (250 mL) and the mixture was refluxed for 3 h. After the removal of the volatiles, the remnant was added to water (300 mL) and extracted with dichloromethane (3 × 100 mL). The extracts were combined and washed with water and brine then dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure. The residue crude product was purified by column chromatography on silica, eluting with petroleum ether/dichloromethane (from 2:0 to 2:1), to give a white solid (20 g, 92%).

¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.80 (s, 2H, Ar-H), 3.51 (d, 2H, CH₂), 1.85 (m, 1H, CH), 1.34 (m, 2H, CH₂), 1.24 (m, 30H, CH₂), 0.88 (t, 6H, CH₃). ¹³C NMR (600 MHz, CDCl₃): δ (ppm)



SCHEME 2 Synthetic route of monomer TPD.

162.90, 136.63, 125.43, 42.73, 36.85, 31.89, 31.87, 31.43, 29.95, 29.61, 29.58, 29.53, 29.32, 29.27, 26.24, 22.66, 14.09.

13-Dibromo-5-(2-octyldodecyl)thieno[3,4-c]pyrrole-4,6dione

5-(2-Octyldodecyl)thieno[3,4-*c*]pyrrole-4,6-dione **6** (4.34 g, 10 mmol) was dissolved in a mixture of sulfuric acid (20 mL) and trifluoroacetic acid (60 mL). NBS (5.37 g, 30 mmol) was added to the solution and the reaction mixture was stirred at room temperature overnight. The mixture was diluted with water (200 mL) and then extracted with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using petroleum ether/dichloromethane (from 1:0 to 1:1) to afford the title product as a white solid (4.9 g, 83%).

¹H NMR (600 MHz, CDCl₃): δ (ppm) 3.48 (d, 2H, CH₂), 1.82 (m, 1H, CH₂), 1.34 (m, 2H, CH₂), 1.25 (m, 30H, CH₂), 0.88 (t, 6H, CH₃). ¹³C NMR (600 MHz, CDCl₃): δ (ppm) 160.61, 134.73, 112.86, 43.09, 36.84, 31.90, 31.88, 31.45, 29.89, 29.62, 29.58, 29.53, 29.33, 29.27, 26.27, 22.66, 14.10.

General Procedures of Polymerization

The synthesis of the polymers were carried out using palladium-catalyzed Stille coupling between monomer 1,3dibromo-5-(2-octyldodecyl)thieno[3,4-c]pyrrole-4,6-dione (TPD), 2,5-dibromothiophene (7), and (*E*)-1,2-bis(tributylstannyl)ethane (8), as shown in Scheme 2. Under the protection of nitrogen, monomers were dissolved in chlorobenzene. The solution was flushed with nitrogen for 10 min, and then $Pd_2(dba)_3$ (2.5% in mol), (o-tol)₃P (20% in mol) was added. After being purged for 15 min, the mixture was heated at 140 °C for 48 h. After cooled to room temperature, the reaction mixture was added dropwise to 100 mL methanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with ethanol, hexane, and chloroform. The polymer recovered from chloroform solution was purified by preparative column chromatography. Then, the product was dried under vacuum for 1 day to yield the titled polymers.

P20

The feed ratio of **TPD:7:8** was 1:0:1. Yield: 72%. ¹H NMR (600 MHz, THF- d_8): δ (ppm) 9.05–6.00 (br, 2H), 2.49



SCHEME 3 Synthetic route of polymers P20-P24.

(br, 2H), 2.45 (br, 1H), 1.34 (br, 32H), 0.91 (br, 6H). Elem. Anal. Found: C: 73.18, H: 9.44, N: 3.05.

P21

The feed ratio of **TPD:7:8** was 2:1:3. Yield: 37%. ¹H NMR (600 MHz, THF- d_8): δ (ppm) 8.80–5.80 (br, 18 H), 2.49 (s, 10 H), 2.45 (s, 5 H), 1.32 (br, 160 H), 0.92 (br, 30 H). ELEM. ANAL. Found: C: 70.98, H: 7.79, N: 2.18.

P22

The feed ratio of **TPD:7:8** was 1:1:2. Yield: 71%. ¹H NMR (600 MHz, THF- d_8): δ (ppm) 9.00–5.40 (br, 29 H), 2.49 (s, 10 H), 2.45 (s, 5 H), 1.32 (br, 160 H), 0.91 (br, 30H). ELEM. ANAL. Found: C: 69.45, H: 6.61, N: 1.56.

P24

The feed ratio of **TPD:7:8** was 1:2:3. Yield: 33%. ¹H NMR (600 MHz, THF- d_8): δ (ppm) 7.80–5.80 (br, 48 H), 2.49 (s, 10 H), 2.45 (s, 5 H), 1.32 (br, 160 H), 0.92 (br, 30 H). ELEM. ANAL. Found: C: 68.14, H: 5.65, N: 1.05.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthesis routes of monomers and corresponding polymers are outlined in Schemes 2 and 3, respectively. 2-Octyldodecylamine (4) was synthesized from 2-octyl-1dodecanol as shown in Scheme 2. Polymers **P20-24** were synthesized by palladium-catalyzed Stille coupling polymerization and confirmed by ¹H NMR spectroscopy and elemental analysis. Based on the ¹H NMR spectroscopy (Fig. 1) and elemental analysis, the composition of the polymers were in well agreement with the expected results (as shown in Table 1), indicating that the synthetic approach adopted here



FIGURE 1 ¹H NMR spectra of polymer solutions in THF- d_8 .

Polymer	Feed Ratio (TPD:7)	Copolymer Composition (m:n) ^a	<i>M</i> _n (K)	<i>M</i> _w (K)	PDI
P20	2:0	2:0	32.2	100.0	3.1
P21	2:1	2:0.8	20.0	63.4	3.2
P22	2:2	2:1.9	29.6	85.7	2.9
P24	2:4	2:3.8	15.1	49.3	3.3

TABLE 1 Polymerization Results and Characterization of the Copolymers

^a Composition of the polymers were determined by elemental analyses.

enables the design and adjustment of the electron-deficient substituent density in copolymer expediently according to the demand. All the polymers can be readily dissolved in common solvents, such as chloroform, toluene, THF and chlorobenzene, and processed to form smooth and pinhole-free films upon spin-coating. Feed ratio, copolymer composition, number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) of the polymers are listed in Table 1.

Optical Properties

Figure 2 shows absorption spectra of the polymers in chloroform solution (1 mg/100 mL) and as spin-coated films on quartz substrates. Table 2 summarizes the optical data, including the absorption peak wavelengths (λ_{abs}), absorption edge wavelengths (λ_{onset}), and the optical band gap (E_g^{opt}).

All of the polymers showed broad absorption bands covering the visible region in both chloroform solutions and solid films (Fig. 2). In chloroform solutions, absorption intensity of the polymers increased gradually from P20 to P24. The absorption peak wavelength and edge wavelength were redshifted from P20 to P22, indicating the enhancement of intramolecular charge transfer (ICT) effect. Extraordinarily, P24 showed an absorption edge wavelength between P21 and P22 and an observable blue-shift of its absorption peak in both solution and film states compared to P22. This phenomenon may be due to the relative low molecular weight and low electron-deficient imide group density in P24, which can limit the ICT effect. In the film state, the absorptions peaks of all the polymers were red-shifted by 9-18 nm compared to those in solution. These bathochromic shifts were on account of the intermolecular association and π - π stacking of these polymer chains in the solid states.

Electrochemical Properties

Cyclic voltammetry had been employed and considered as an effective tool in measuring the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of conjugated oligomers and polymers.^{28,29}

Cyclic voltammograms of the polymer films are shown in Figure 3. The onset oxidation potential (E_{ox}) /onset reduction potential (E_{red}) of **P20**, **P21**, **P22**, and **P24** were 0.93/ -0.96, 0.72/-1.08, 0.60/-1.16, and 0.45/-1.28 V versus

 Ag/Ag^+ electrode, respectively. The energy levels of HOMO and LUMO of the polymers were calculated according to the equations:

$$HOMO = -IP = -e(E_{ox} + 4.71)(eV);$$
 (1)

$$LUMO = -EA = -e(E_{red} + 4.71)(eV).$$
 (2)

From the value of $E_{\rm ox}$ and $E_{\rm red}$ of the polymers, the HOMO and the LUMO were calculated and listed in Table 2. It had been well recognized that the LUMO energy level of the donor polymer must be positioned above that of the acceptor PCBM by a reasonable value (e.g., 0.3 eV)⁶ to overcome the binding energy of the excitons for efficient charge separation.^{1,4,6} By reducing density of electron-deficient



FIGURE 2 Absorption spectra of the polymers in (a) chloroform solution (concentration of 1 mg/100 mL) and (b) solid film on a quartz plate.

Polymer	λ_{abs} in CHCl ₃ (nm)	λ _{abs} in films (nm)	λ _{onset} in films (nm)	Eg ^{opt} (eV)	HOMO (eV)	LUMO (eV)	Eg ^{ec} (eV)
P20	578, 628	587, 636	696	1.78	-5.64	-3.78	1.86
P21	588	598	725	1.71	-5.43	-3.63	1.80
P22	592	606	745	1.66	-5.31	-3.55	1.76
P24	564	582	740	1.68	-5.16	-3.43	1.73

TABLE 2 Optical and Electrochemical Properties of the Polymers

imido group, the HOMO and LUMO energy levels of the polymers were upshifted gradually from **P20** to **P24**, as shown in Figure 4. The differences of LUMO energy levels between the polymers and $PC_{71}BM$ (ca. -3.91 eV)³⁰ ranged from 0.16 to 0.48 eV; thus, excitons dissociation efficiencies in their corresponding BHJ devices could be very different.

Photovoltaic Properties

To investigate the influence of electron-deficient substituent density on photovoltaic properties of the PTV derivatives, bulk heterojunction PSC devices with a configuration of ITO/ PEDOT:PSS/polymer:PC₇₁BM/Ca/Al were fabricated. Active layers of the polymer:PC₇₁BM (1:2, w/w) were spin-coated from DCB solutions. The current density-potential characteristic of PSCs based on the blends of polymer:PC₇₁BM under illumination of AM1.5G, 100 mW cm⁻² are shown in Figure 5. The open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), thickness and mobility of active layers, maximum PCE (PCE_{max}), and average PCE (PCE_{ave}) were summarized in Table 3.

The PSCs based on the imide-containing PTVs possessed higher V_{oc} than that of devices based on alkyl-substituted PTVs.^{8,21} This can be attributed to the lower HOMO levels of the polymers due to the electron-withdrawing imide substituents. The PCE (0.23%) of the PSCs based on **P24** was close to that of typical PTVs,^{17–21} indicating that one-third imide substitution of the thiophene units in **P24** influences the photovoltaic performance of the polymers very little.



FIGURE 3 Cyclic voltammograms of the polymer films on glassy carbon electrode in 0.1 mol L^{-1} Bu₄NPF₆, CH₃CN solution with a scan rate of 100 mV s⁻¹.

With the imide substitution increasing to a half of thiophene units in **P22**, the photovoltaic performance of the PTV derivative was improved dramatically, as shown in Figure 6 and Table 3. All the V_{oc} , J_{sc} , and FF of the PSC based on **P22** as donor and PC₇₁BM as acceptor improved significantly in comparison with those of the devices with **P24** as donor. PCE of the PSC based on **P22** reached 0.86%, which is about four times of that of **P24**. The strong electron-withdrawing substitution of imide could be the reason for the improved photovoltaic performance, like that for P3CTV.²¹ With further increase of imide substitution on the thiophene units in the polymers, **P21** showed poorer photovoltaic performance with a PCE of 0.12% and a lower short-circuit current of 0.39 mA cm⁻². Because LUMO energy level downshifted



FIGURE 4 Energy level diagrams for the polymers and $PC_{71}BM$.



FIGURE 5 Current density-voltage characteristics of PSCs based on polymer: $PC_{71}BM$ blends under illumination of AM1.5G, 100 mW cm⁻².

Polymer	$V_{\rm oc}$ (V)	$J_{\rm sc}~({ m mA~cm^{-2}})$	FF	PCE _{max} /PCE _{ave} (%)	Thickness (nm)	Mobility (cm ² V ⁻¹ s ⁻¹)
P20	-	-	-	-/-	106	$5.1 imes10^{-5}$
P21	0.78	0.39	0.40	0.12/0.11	117	$3.9 imes 10^{-4}$
P22	0.75	2.26	0.51	0.86/0.82	109	$5.8 imes10^{-4}$
P24	0.62	1.01	0.36	0.23/0.21	101	$1.5 imes10^{-4}$

TABLE 3 Photovoltaic Properties of the PSCs Based on the Polymers as Donor and $PC_{71}BM$ as Acceptor Under the Illumination of AM1.5G, 100 mW cm⁻²

gradually from **P22** to **P21** to **P20** with the increase of the imide substitution, the difference between the LUMO energy levels of the polymer donor and PC₇₁BM acceptor decreases from **P22** to **P21** to **P20**. For **P21**, the difference decreased to 0.28 eV, which is not large enough to overcome the binding energy of the excitons for efficient charge separation, so that the J_{sc} and PCE of the corresponding solar cell decreased remarkably. For **P20** with imide group fused to every thiophene ring in the polymer, photovoltaic response could not be observed due to too small difference between LUMO energy levels of **P20** and PC₇₁BM. In the other hand, the HOMO energy levels of the polymers also decreased with the increase of the imide substitution from **P24** to **P20**; therefore, the V_{oc} of the PSCs with the polymer as donor increased accordingly.

According to the following eq 3 proposed by Brabec et al.,⁶ the calculated V_{oc} should be 1.22, 1.10, and 0.95 V for P21, P22, and P24, respectively, which are 0.33–0.44 V higher than the experimental values. In order to reveal the reason for the deviation of the V_{oc} from the theoretical value, we studied the properties of the previously reported PTVs photovoltaic materials and summarized the relationship between HOMO and V_{oc} in Figure 7. Simple linear fit line of the collected data was also shown in Figure 7. In the case of low [HOMO(PTVs)-LUMO(PCBM)] (high HOMO), the V_{oc} of PTVs-based solar cells was coincided with eq 3. With the increase of [HOMO(PTVs)-LUMO(PCBM)], the V_{oc} of PTVs-based solar cells deviated from the line of eq 3. In another word, with the decrease of HOMO level of PTVs, the difference between



FIGURE 6 Short-circuit current of the solar cells based on the polymers with variable LUMO levels.

|HOMO(PTVs)-LUMO(PCBM)| and V_{oc} of corresponding solar cells increased. It seems that, for PTVs donor materials, the term of empirical factor (0.3) in eq 3 should not be a constant but a function of HOMO(PTVs). There might be some additional energetic loss existed in the PTVs:PCBM system.

$$V_{\rm oc} = (1/e)(|E_{\rm HOMO}^{\rm Donor}| - |E_{\rm LUMO}^{\rm PCBM}|) - 0.3 \, \rm V$$
(3)

To further study the performance of the PSCs, the morphology and hole mobilities of the photosensitive layers were measured. Figure 8 shows the AFM images of the active layer surfaces. The average surface roughness (R_a) values of the AFM topographic images were all less than 1 nm for the blends of **PTVs**:PC₇₁BM, indicating smooth surface of the active layers. The **P20**:PC₇₁BM film showed clear phase separation with a large domain size over 100 nm. The **P24**:PC₇₁BM film gave a featureless phase separation image. They were not good for exciton transportation and dissociation on the interface of polymer and PC₇₁BM. For the **P21**:PC₇₁BM and **P22**:PC₇₁BM blend films, the clear patterns of polymer/PCBM domains showed good interpenetrating networks which were beneficial to the exciton dissociation and charge carriers transport.

The hole mobilities in the photosensitive layers were measured by the space charge-limited current (SCLC) method using devices with structure of ITO/PEDOT:PSS/ polymer: $PC_{71}BM/Au$. For unipolar transport in a trap-free



FIGURE 7 Open-circuit voltage (V_{oc}) of different PTVs-based bulk-heterojunction solar cells plotted versus the difference between HOMO of the PTVs and LUMO of PC₇₁BM. The straight solid line represents a linear fit; dash line represents the eq 3.



FIGURE 8 Tapping mode AFM height images (2 \times 2 μ m²) of the polymer:PC₇₁BM blend films.

semiconductor with an ohmic injecting contact, the SCLC can be approximated by the Mott-Gurney equation³¹:

$$J \simeq \frac{9}{8} \varepsilon_{\rm r} \varepsilon_0 \mu_0 \exp\left(0.891\gamma \sqrt{\frac{V}{L}}\right) \frac{V^2}{L^3} \tag{4}$$

where *J* is the current density, $\varepsilon_{\rm r}$ is the dielectric constant of the polymer, ϵ_0 is the free-space permittivity (8.85 \times 10^{-12} F m⁻¹), μ_0 is the charge mobility at zero field, γ is a constant, L is the thickness of the blend film layer, $V = V_{appl}$ – $V_{\rm bi}$, $V_{\rm appl}$ is the applied potential, and $V_{\rm bi}$ is the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, $V_{\rm bi} = 0.2$ V). Figure 9 displayed $\ln(JL^3/V^2)$ versus $(V/L)^{0.5}$ curve for the measurement of the hole mobility of the copolymers by the SCLC method. As summarized in Table 3, the hole mobilities of the polymers calculated using eq 4 are 5.1 \times 10 $^{-5}$, 3.9 \times 10 $^{-4}$, 5.8 \times 10 $^{-4}$, and 1.5 \times 10 $^{-4}$ $cm^2V^{-1}s^{-1}$ for **P20**, **P21**, **P22**, and **P24**, respectively. Obviously, the photovoltaic performance of the polymers is not determined by their hole mobilities, but mainly influenced by the LUMO energy levels and the electron-withdrawing substitution.

CONCLUSIONS

To investigate the influence of electron-deficient substituent content on the photovoltaic properties of the PTV derivatives, we designed and synthesized a series of novel PTVs, **P20-P24**, with various content of electron-deficient imide



FIGURE 9 $\ln(JL^3/V^2)$ versus $(V/L)^{0.5}$ plots for the measurement of the hole mobility in polymer:PC₇₁BM blends by the SCLC method.

substituent, via a palladium-catalyzed Stille coupling method. The content of the imide substituent on thiophene units of the PTVs was found to have a great impact on electrochemical and photovoltaic properties of the PTV derivatives. All of the four polymers show broad absorption bands covering the visible region with optical bandgaps of 1.78, 1.71, 1.66, and 1.68, respectively. By increasing content of imide substituent from P24 to P20, the LUMO and HOMO energy levels of the polymers downshifted gradually from -3.43 to -3.75eV and from -5.16 to -5.64 eV, respectively. P24 with onethird imide substitution on thiophene units show a similar photovoltaic performance with hexyl-substituted PTV. P22 with a half imide substitution on the thiophene units possesses a suitable LUMO and HOMO energy levels, and displayed an improved photovoltaic performance with PCE increased four times to 0.86%. But further increase of the content of imide substituent in P21 and P20 results in too low LUMO energy level and decreased photovoltaic performance. This work provide a facile electronic energy-level regulation method, which allows ones to design photovoltaic polymers for better understanding the relationship between the molecular structure and photovoltaic properties of PTVs.

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