

Synthesis of New Thiadiazole-Containing Polythiophene Derivatives and Their Application to Organic Solar Cells

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New thiadiazole-containing π -conjugated polymers have been successfully synthesized by the Stille coupling reaction of 2,5-bis(5'-bromo-3',4'-dihexylthien-2'-yl)-1,3,4-thiadiazole (**1**) with various distannyl compounds as acceptor and donor monomer units, respectively. Most of polymers showed lower highest occupied molecular orbital (HOMO) energy level than poly(3-hexylthiophene) (P3HT). It was found that the bulky side chains of donor units tend to prevent the arrangements of main chains. The polymer comprised of thienothiophene donor units without side chains displayed relatively high solar cell performance with a power conversion efficiency (PCE) of 2.8% under the illumination of AM 1.5, 100 mW/cm².

Keywords: thiadiazole, polythiophene, organic solar cell, conjugated polymer

1. Introduction

Bulk-heterojunction (BHJ) polymer solar cells (PSCs), in which the photoactive layer consists of an interpenetrating network of a donor (D) of π -conjugated polymer and an acceptor (A) of soluble fullerene, have attracted much attention because of their easy processability, low material cost, high efficiency, and mechanical flexibility [1-14]. One of the most successful system until now utilizes a blend of P3HT and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as the active layer, normally giving PCEs in the range of 4-5% [2,6,7]. However, the HOMO energy level of P3HT is too high (ca. -4.76 eV[15]) that limits the open circuit voltage (V_{oc}) values of the PSCs to ca. 0.6 V. It is well-known that the modulation of the HOMO/lowest unoccupied molecular orbital (LUMO) energy levels for the polymers is essential to realize a high V_{oc} value without sacrificing the broad light harvesting and efficient charge separation, which correspond to a J_{sc} value [16]. Donor-acceptor (D-A) polymers are attractive as *p*-type materials for PSCs due to the facile tunability of the HOMO/LUMO energy levels by properly choosing the D and A moieties.

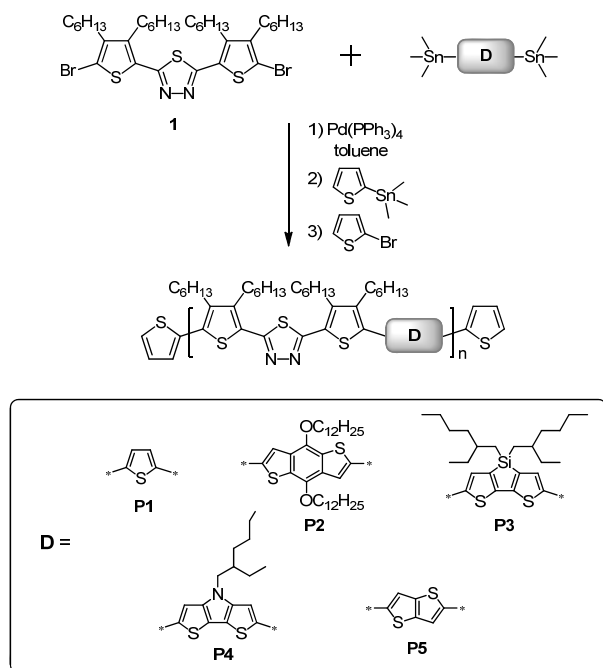
1,3,4-Thiadiazole (TD) is an electron-deficient unit containing two electron-withdrawing imine groups (C=N) and can be used as an A unit. For

instance, a structure similar to the benzothiadiazole units have frequently been utilized as an A unit in D-A polymers to achieve high PCEs [17-22]. However, a few reports have described the PSCs using D-A type polymers bearing TD units [23,24], regardless of its electron-withdrawing nature as well as the more compact structure without hydrogen atom at 3- and 4-positions, compared to the benzothiadiazole units, which would be preferable for more densely packed structures for the polymer films to induce a high charge mobility.

Previously, we synthesized D-A type polythiophene derivatives carrying TD units (**P1**) based on the Stille coupling reaction [25] of 2,5-bis(trimethylstannyl)thiophene and the corresponding monomers of 2,5-bis(5'-bromo-3',4'-dihexylthien-2'-yl)-1,3,4-thiadiazole (**1**) (see Scheme 1) [26]. The polymer **P1** showed low-lying HOMO levels of -5.33 eV, as expected. In addition, the BHJ PSC based on **P1**:PCBM=1:1 (w/w) exhibited PCEs up to 3.0% with the high V_{oc} value of 0.80 V under the illumination of AM 1.5, 100 mW/cm². However, more efficient light-harvesting of the TD-based conjugated polymer was required to further improve the PSC performance, because **P1** could not absorb the sunlight well over 600 nm.

Herein, we report the synthesis and PSC characterization of an array of TD-containing

polythiophene derivatives using various donor units (Scheme 1), aiming at more efficient light absorption especially for visible-near infrared region.



Scheme 1. Synthesis of TD-containing polythiophene derivatives.

2. Method

2-1. Materials

All chemicals were purchased from Aldrich, Japan and used as received unless noted. **1** [26], 2,6-bis(trimethylstannyl)-4,8-didodecyloxybenzo[1,2-*b*;3,4-*b*]dithiophene [27], 4,4'-bis(2-ethylhexyl)-5,5'-bis(trimethylstannyl)dithieno[3,2-*b*:2',3'-*d*]silole [28], *N*-(2-ethylhexyl)-2,6-bis(trimethylstannyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole [29,30], and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene [31,32] were synthesized according to the previous reports. 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene was recrystallized before use.

2-2. Synthesis of Polymers

*Poly(4,8-didodecyloxybenzo[1,2-*b*;3,4-*b*]dithiophene-*alt*-5',5'-(2'',5''-bis(3',4'-dihexylthien-2'-yl)-1'',3'',4''-thiadiazole) (P2)*

To **1** (0.263 g, 0.353 mmol) and 2,6-bis(trimethylstannyl)-4,8-didodecyloxybenzo[1,2-*b*;3,4-*b*]dithiophene (0.312 g, 0.353 mmol), was added a Pd(PPh₃)₄ (62.5 mg, 0.0541 mmol) solution in toluene (15.0 mL), which was

deoxidized by bubbling with N₂ for 15 min. The solution was refluxed under argon for 2 days, followed by end-capping with tributyl(2-thienyl)stannane (25.0 μL, 0.0786 mmol) and 2-bromothiophene (10.0 μL, 0.104 mmol), successively, reacting for 2 h each. After quenching the reaction mixture by hydrochloric acid, the solution was neutralized with sodium bicarbonate. The product was extracted with chloroform, washed with potassium fluoride aqueous solution, followed by precipitation in methanol/water (1/1, v/v). After filtration, the crude product was purified by soxhlet extraction with methanol, acetone, hexanes, and chloroform. Flush column chromatography eluting with chloroform, followed by freeze-drying from absolute benzene solution afforded **P2** as red solid. Yield; 0.333 g (83%). SEC: *M*_n = 26,500 g/mol; PDI = 1.68. ¹H NMR (300 MHz, CDCl₃, δ, ppm, 25 °C): 7.59 (s, 2H), 4.34 (s, 4H), 3.15–2.56 (m, 8H), 1.94 (quint, *J* = 7.00 Hz, 4H), 1.86–1.09 (m, 68H), 1.08–0.76 (m, 18H). IR, ν (cm⁻¹): 1558 (C=N stretching), 1267 (C–O–C symmetry), 1061 (C–O–C asymmetry).

Other polymers were synthesized according to the similar procedure as **P2**.

*Poly(4,4'-bis(2-ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]silole-*alt*-5',5'-(2'',5''-bis(3',4'-dihexylthien-2'-yl)-1'',3'',4''-thiadiazole) (P3)*

Yield; 0.216 g (80%). SEC: *M*_n = 9,470 g/mol; PDI = 1.74. ¹H NMR (300 MHz, CDCl₃, δ, ppm, 25 °C): 7.22 (s, 2H), 2.93 (s, 4H), 2.78 (s, 4H) 1.84–1.09 (m, 48H), 1.86–1.09 (m, 48H), 1.09–0.48 (m, 28H). IR, ν (cm⁻¹): 1558 (C=N stretching).

*Poly(N-(2-ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole-*alt*-5',5'-(2'',5''-bis(3',4'-dihexylthien-2'-yl)-1'',3'',4''-thiadiazole) (P4)*

Yield; 0.205 g (70%). SEC: *M*_n = 17,400 g/mol; PDI = 1.72. ¹H NMR (300 MHz, CDCl₃, δ, ppm, 25 °C): 7.13 (s, 2H), 4.08 (s, 2H), 2.88 (m, 8H), 1.98 (s, 1H), 1.84–1.20 (m, 40H), 1.06–0.80 (m, 18H). IR, ν (cm⁻¹): 1560 (C=N stretching).

*Poly(thieno[3,2-*b*]thiophene-*alt*-5',5'-(2'',5''-bis(3',4'-dihexylthien-2'-yl)-1'',3'',4''-thiadiazole) (P5)*

o-Dichlorobenzene was used in place of chloroform for soxhlet extraction and column

chromatography due to low solubility of **P5**.

Yield; 0.089 g (42%). SEC: $M_n = 19,000$ g/mol; PDI = 1.70. ^1H NMR (300 MHz, *o*-dichlorobenzene- d_4 , δ , ppm, 80 °C): 7.39 (s, 2H), 3.04 (s, 4H), 2.88 (s, 4H), 1.71 (s, 8H), 1.56–1.47 (m, 8H), 1.43–1.15 (m, 16H), 0.96–0.80 (m, 12H). IR, ν (cm^{-1}): 1558 (C=N stretching).

2-3. PSC Fabrication

All the BHJ PSCs were fabricated using the same procedures as follows: The patterned glass-indium tin oxide (ITO) substrates (obtained from Lumtec, ltd. (7 Ω/sq)) were cleaned with detergent, and ultrasonicated in acetone and isopropyl alcohol, and subsequently dried on a hot plate at 120 °C for 5 min, and finally treated with oxygen plasma for 10 min. Poly(3,4-ethylenedioxy-thiophene):poly(styrene-sulfonate) (PEDOT:PSS, Baytron P VP AI4083) was passed through a 0.45 μm filter before being deposited on ITO with a thickness around 30 nm by spin coating at 4500 rpm in the air and dried at 140 °C for 20 min outside a glovebox and then for 10 min inside. The blended film of the polymer/PCBM (1:1, by wt.) was prepared by dissolving them in anhydrous chlorobenzene or *o*-dichlorobenzene (10 mg/mL), followed by spin-coating on the top of PEDOT:PSS layer at the speed rate of 600 rpm for 60 s. Subsequently, the devices were completed by thermal evaporation of Ca (30 nm) and Al (100 nm) under high vacuum condition ($<10^{-6}$ Torr). The active area of the device is 4 mm^2 . The current density–voltage (J – V) measurement of the PSC was conducted by a computer-controlled Keithley 2400 source measurement unit with a Oriel solar simulator under the illumination of AM 1.5G, 100 mW/cm^2 . The illumination intensity was calibrated by a standard Si photodiode detector with KG-5 filter.

2-4. Measurements

Molecular weights and polydispersity indices (PDIs) were measured by SEC on a Jasco GULLIVER 1500 equipped with a pump, an absorbance detector (UV, $\lambda = 254$ nm), and three polystyrene gel columns based on a conventional calibration curve using polystyrene standards. CHCl_3 (40 °C), THF (40 °C), or *o*-dichlorobenzene (135 °C) was used as a carrier solvent at a flow rate of 1.0 mL/min. ^1H and ^{13}C NMR spectra were

recorded on a Bruker DPX (300 MHz) in chloroform- d or *o*-dichlorobenzene- d_4 calibrated to tetramethylsilane as an internal standard (δH 0.00). FT-IR spectra were measured on a Horiba FT-720 spectrometer. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and a TA instruments Q-100 connected to a cooling system at a heating rate of 10 °C/min for differential scanning calorimetry (DSC). UV-visible absorption spectra were recorded using a Hitachi U-4100 spectrophotometer. CV was performed with the use of a three-electrode cell in which ITO was used as a working electrode, and the polymer film was coated on it in 0.5×0.7 cm^2 . A platinum wire was used as an auxiliary electrode. All cell potentials were taken in a 0.1 mol/L acetonitrile solution of tetrabutylammonium perchlorate at a scan rate of 0.1 V/s.

3. Results and Discussion

3-1. Synthesis of TD-Containing Polymers

P2-P5 were synthesized based on the Stille coupling reaction [25] of TD-containing dibromide monomer **1** and four kinds of distannyl compounds in the presence of $\text{Pd}(\text{PPh}_3)_4$ as a catalyst (Scheme 1). The molecular weights of the polymers are reasonably high (> 10 K) except for **P3**. These results are summarized in Table 1. **P2-P4** are well soluble in common organic solvents such as toluene, THF, and chloroform; however **P5** is only soluble in *o*-dichlorobenzene.

3-2. Thermal Property

The thermal stability of **P2-P5** was examined by TG/DTA. The $T_{d,5\%}$ values of all polymers exceed 330 °C, so that their thermal stability is good enough for device fabrication. The DSC curves for **P2** and **P3** did not show any melting or glass transition behaviors before degradation. In contrast, **P4** and **P5** exhibited clear melting peaks at 222 and 289 °C, respectively, during a heating scan (Fig. 1). There is one T_c peak of **P5** at 262 °C during a cooling scan, while two T_c peaks (158 and 194 °C) were observed for **P4**, which could be attributed to alkyl side chain and main chain, respectively.

Taking the higher T_c value of **P5** than that of **P4** into consideration, it can be mentioned that the

Table 1. Molecular weights and thermal properties of **P2-P5**

polymers	M_n (g/mol)	PDI	$T_{d,5\%}$ (°C) ^d	T_m (°C) ^e	T_c (°C) ^e
P2	26,500 ^a	1.68 ^a	337	—	—
P3	9,470 ^a	1.74 ^a	358	—	—
P4	17,400 ^b	1.72 ^b	387	222	158, 194
P5	19,000 ^c	1.70 ^c	391	289	262

^aDetermined by SEC using polystyrene standards in CHCl₃. ^bDetermined by SEC using polystyrene standards in THF. ^cDetermined by SEC using polystyrene standards in *o*-dichlorobenzene at 135 °C. ^dThe 5 % weight-loss temperatures under inert atmosphere. ^eThe T_m and T_c values were determined by DSC.

introduction of fused ring without side chains such as thienothiophene unit efficiently enhances the packing structure of main chains.

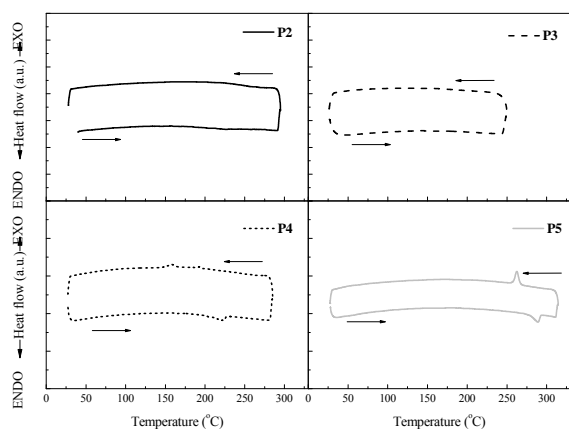


Fig. 1. DSC thermograms of **P2-P5** at the heating rate of 10 °C/min under a nitrogen atmosphere.

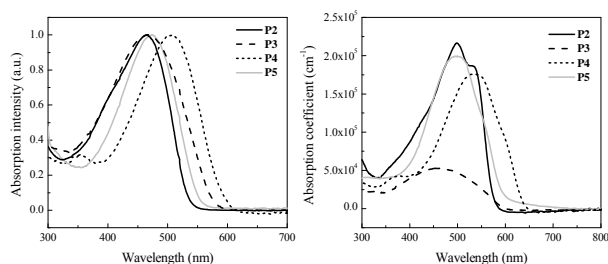


Fig. 2. UV-vis absorption spectra of (a) **P2-P4** (chloroform) and **P5** (*o*-dichlorobenzene) in solution state and (b) **P2-P5** in film state.

Table 2. Optical properties and energy levels of **P2-P5**

polymers	λ_{\max}^a (nm)		$E_g^{\text{opt},b}$	HOMO ^c (eV)	LUMO ^d (eV)
	soln.	film			
P2	465	498	2.15	-5.52	-3.37
P3	468	463	2.06	-5.42	-3.36
P4	509	535	1.93	-5.11	-3.18
P5	475	500	2.06	-5.29	-3.23

^aAbsorption maxima. ^bOptical band gap estimated from the onset of absorption spectra in solid film. ^cDetermined from the onset oxidation based on the reference energy level. ^dCalculated by the equation; LUMO = HOMO + E_g^{opt} (eV).

3-3. Optical Property

Fig. 2 showed UV-vis absorption spectra of **P2-P5** in solution and film states. The λ_{\max} values were found at 465 (**P2**), 468 (**P3**), 509 (**P4**), and 475 nm (**P5**). **P2**, **P3**, and **P5** showed similar λ_{\max} values as **P1**, despite of the introduction of fused rings which generally have more coplaner structures. **P4**, which had the lowest bandgap due to the relatively high HOMO energy level, showed the red-shift in the absorbance. In the film state, **P2**, **P4**, and **P5** displayed large bathochromic shift compared to the solution states. In addition, a shoulder could be observed, which is indicative of intermolecular packing structure. **P3** did not show the bathochromic shift probably due to the two bulky 2-ethylhexyl substituents in donor units so that the molecular interaction could be weakened.

3-4. Electronic Property

In order to evaluate the HOMO energy levels of **P2-P5**, cyclic voltammetry was performed (Fig. 3). The HOMO energy values were calculated by the equation;

$$\text{HOMO} = -(E_{\text{onset}}^{\text{ox}} - E_{\text{ferrocene}}^{1/2} + 4.8) \text{ (eV)}$$

As can be seen in Table 2, **P2**, **P3**, and **P5** showed much lower HOMO energy levels than P3HT (-4.88 eV), due to the highly effective acceptor unit of thiadiazole. Even in the case of **P4** which has the highest HOMO energy level caused by the strong donor unit of dithienopyrrole, the value is still below -5.0 eV. Therefore, the high V_{oc} values would be expected for all the polymers.

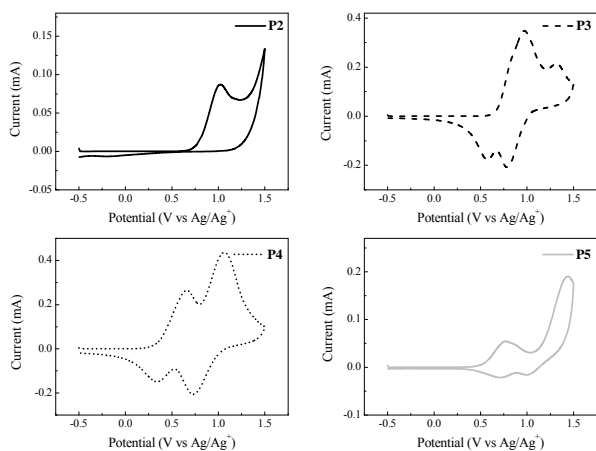


Fig. 3. Cyclic voltammograms of the **P2-P5** films on ITO electrodes in 0.1 mol/L tetrabutylammonium perchlorate CH₃CN solutions at a scan rate of 0.1 V/s.

3-5. Polymer Solar Cell Performance

BHJ PSC devices were fabricated with the sandwich structure of ITO/PEDOT:PSS/**P2-P5**:PCBM(1:1, w:w)/Ca/Al. The results were summarized in Table 3 and *I-V* curves are shown in Fig. 4. The devices were characterized with or without annealing after encapsulation inside glovebox under the illumination of AM 1.5G (100 mW/cm²). The device using **P2**:PCBM showed high *V*_{oc} values affected by low HOMO energy level; however, *J*_{sc} values are very low, resulting in the poor PSC performance (PCE < 1%) (Table 3). This is because of amorphous nature and large bandgap of **P2**. The **P3**:PCBM PSC device also suffered from the low PSC performance probably due to low *FF* values derived from amorphous nature and thus low charge mobility. The annealing treatment in the both system did not enhance the performance at all.

In sharp contrast, the **P4**:PCBM PSC device achieved 1.7% without annealing when *o*-dichlorobenzene was used as a cast solvent. The *J*_{sc} value was much improved compared to **P2** and **P3**, probably caused by the crystalline structure as well as low bandgap of **P4**. However, the *V*_{oc} value of the **P4**:PCBM PSC device was somewhat sacrificed by relatively high HOMO energy level of **P4**. The highest performance among all the polymers comes from the **P5**:PCBM system which shows a *V*_{oc} value of 0.870 V, a *J*_{sc} value of 6.35 mA/cm², a *FF* value of 0.461, achieving a PCE of

Table 3. PSC characteristics of polymer/PCBM (1:1, w:w) under the illumination of AM 1.5, 100 mW cm⁻²

poly mers	Solv. ^a	anneal.	<i>V</i> _{oc} (V)	<i>J</i> _{sc} (mA/ cm ²)	<i>FF</i>	PCE ^b (%)
P2	DCB	Non	0.852	2.03	0.409	0.71
P2		100 °C, 10 min	0.848	1.89	0.413	0.67
P3	CB	Non	0.555	1.43	0.300	0.24
P3		100 °C, 10 min	0.356	1.06	0.313	0.12
P4	DCB	Non	0.754	4.59	0.476	1.7
P4		100 °C, 10 min	0.762	3.60	0.421	1.2
P5	DCB	Non	0.870	6.35	0.461	2.8
P5		100 °C, 10 min	0.850	4.76	0.353	1.4

^aCB and DCB mean chlorobenzene and *o*-dichlorobenzene, respectively. ^bThe average value of PCE was calculated from 3 or 4 pixels in the device.

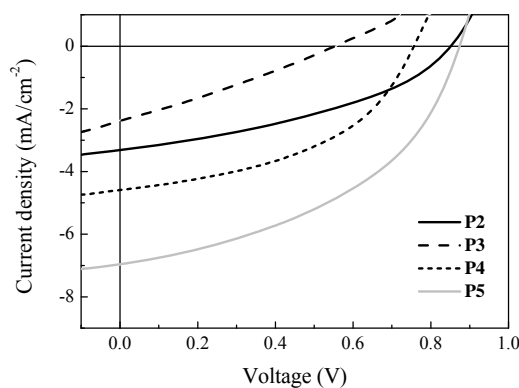


Fig. 4. *J-V* curves of the PSC devices based on polymer/PCBM (1:1, w:w) under the illumination of AM 1.5, 100 mW/cm².

2.8%. The high *V*_{oc} and *J*_{sc} values correspond to low lying HOMO energy level and high crystallinity (high charge mobility), respectively. After optimization of the **P5**:PCBM system, the more higher PCE can be expected, although the annealing process leads worse performance at the present time.

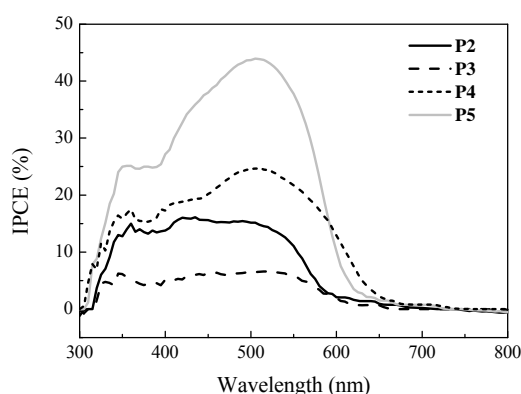


Fig. 5. Photocurrent action spectra of the PSC devices based on **P2-P5**/PCBM (1:1, w/w).

Fig. 5 shows the photocurrent action spectra of the ITO/PEDOT:PSS/**P2-P5**:PCBM(1:1, w:w)/Ca/Al devices. All the devices exhibited a photoresponse in the range of 300-600 nm (**P2** and **P3**), 300-630 nm (**P5**), and 300-650 nm (**P4**), indicating that the absorption of the polymer:PCBM blends reflects the photocurrents in these wavelength regions. The devices based on **P2** and **P3** show significantly low maximum incident photon-to-current conversion efficiency (IPCE) values of 17% and 7%, respectively, which is coincident with the low J_{sc} value for the photovoltaic performance of the **P2**:PCBM and **P3**:PCBM devices, as mentioned above. In contrast, the device based on **P4** exhibits higher maximum IPCE value of 25% and that of **P5** does the highest values of 44% among the four devices. Such a high photoconversion efficiency agrees well with the highest J_{sc} and PCE values of the **P5**:PCBM PSC device.

4. Conclusions

A series of thiadiazole-containing π -conjugated polymers has been successfully synthesized based on the Stille coupling reaction between **1** and varied distannyl compounds as acceptor and donor monomer units, respectively. The low HOMO energy levels were realized by introducing the efficient acceptor unit of **1** in the range of -5.11~ -5.52 eV, resulting in high V_{oc} values up to 0.87 V (**P5**). While, the introduction of bulky side chains of donor units was ineffective for chain packing to reduce the J_{sc} values. The best solar cell performance has been achieved by the **P5**:PCBM device, showing the PCE of 2.8%, due to high V_{oc}

value of 0.870 V as well as relatively high J_{sc} value of 6.35 mA/cm², derived from the high planarity of the unsubstituted thienothiophene donor unit.

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References

1. G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science* **270** (1995) 1789.
2. Y. J. Cheng, S. H. Yang and C. S. Hsu, *Chem. Rev.* **109** (2009) 5868.
3. J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. C. Bazan, *Nat. Mater.* **6** (2007) 497.
4. J. H. Tsai, C. C. Chueh, M. H. Lai, C. F. Wang, W. C. Chen, B. T. Ko and C. Ting, *Macromolecules* **42** (2009) 1897.
5. J. Peet, A. J. Heeger and G. C. Bazan, *Acc. Chem. Res.* **42** (2009) 1700.
6. G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.* **4**, (2005) 864.
7. X. N. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels and R. A. J. Janssen, *Nano Lett.* **5** (2005) 579.
8. C. C. Chueh, T. Higashihara, J. H. Tsai, M. Ueda and W. C. Chen, *Org. Electron.* **10** (2009) 1541.
9. N. Blouin, A. Michaud and M. Leclerc, *Adv. Mater.* **19** (2007) 2295.
10. Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C. S. Ha and M. Ree, *Nat. Mater.* **5** (2006) 197.
11. Y. F. Li and Y. P. Zou, *Adv. Mater.* **20** (2008) 2952.
12. Y. T. Chang, S. L. Hsu, G. Y. Chen, M. H. Su, T. A. Singh, E. W. G. Diau and K. H. Wei, *Adv. Funct. Mater.* **18** (2008) 2356.
13. H. Xin, F. S. Kim and S. A. Jenekhe, *J. Am. Chem. Soc.* **130** (2008) 5424.

14. Y. Y. Liang, Y. Wu, D. Q. Feng, S. T. Tsai, H. J. Son, G. Li and L. P. Yu, *J. Am. Chem. Soc.* **131** (2009) 56.
15. J. H. Hou, Z. A. Tan, Y. Yan, Y. J. He, C. H. Yang and Y. F. Li, *J. Am. Chem. Soc.* **128** (2006) 4911.
16. M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.* **18** (2006) 789.
17. Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.* **22** (2010) E135.
18. T. Y. Chu, J. Lu, S. Beaupré, Y. Zhang, J. R. Pouliot, S. Wakim, J. Zhou, M. Leclerc, Z. Li, J. Ding and Y. Tao, *J. Am. Chem. Soc.* **133** (2011) 4250.
19. H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, *Angew. Chem., Int. Ed.* **50** (2011) 2995.
20. C. M. Amb, S. Chen, K. R. Graham, J. Subbiah, C. E. Small, F. So and J. R. Reynolds, *J. Am. Chem. Soc.* **133** (2011) 10062.
21. Z. He, C. Zhong, X. Huang, W. Y. Wong, H. Wu, L. Chen, S. Su and Y. Cao, *Adv. Mater.* **23** (2011) 4636.
22. R. F. Service, *Science* **332** (2011) 293.
23. T. Umeyama, E. Douvogianni and H. Imahori, *Chem. Lett.* **41** (2012) 354.
24. P. S. Patil, N. S. Haram, R. R. Pal, N. Periasamy, P. P. Wadgaonkar and M. M. Salunkhe, *J. Appl. Polym. Sci.* **125** (2012) 1882.
25. B. Carsten, F. He, H. J. Son, T. Xu and L. Yu, *Chem. Rev.* **111** (2011) 1493.
26. T. Higashihara, H. C. Wu, T. Mizobe, C. Lu, M. Ueda and W. C. Chen, *Macromolecules* **45** (2012) 9046.
27. J. Hou, M. H. Park, S. Zhang, Y. Yao, L. M. Chen, J. H. Li and Y. Yang, *Macromolecules* **41** (2008) 6012.
28. B. C. Popere, A. M. Della-Pelle, A. Poe, G. Balaji and S. Thayumanavan, *Chem. Sci.* **3** (2012) 3093.
29. S. J. Evenson, T. M. Pappenfus, M. C. R. Delgado, K. R. Radke-Wohlens and J. T. L. Navarrete, S. C. Rasmussen, *Phys. Chem. Chem. Phys.* **14** (2012) 6101.
30. L. S. Fuller, B. Iddon and K. A. Smith, *J. Chem. Soc., Perkin Trans.* **1** (1997) 3465.
31. G. Zhang, Y. Fu, Z. Xie and Q. Zhang, *Sol. Energy Mater. Sol. Cells* **95** (2011) 1168.
32. L. Huo, J. Hou, H. Y. Chen, S. Zhang, Y. Jiang, T. L. Chen and Y. Yang, *Macromolecules* **42** (2009) 6564.