ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/polymers

Journal Name

ARTICLE

Random terpolymer with a cost-effective monomer and comparable efficiency to PTB7-Th for bulk-heterojunction polymer solar cells

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Tao Jiang,[a+] Jie Yang,[ab+] Youtian Tao,*[a] Cong Fan,[a] Lingwei Xue,[b] Zhiguo Zhang,*[b] Hai Li,[a] Yongfang Li,[b] and Wei Huang*[ac]

A new random terpolymer PTB7-Th-T2 has been designed and synthesized by incorporating a significantly lower cost monomer 2,2'-bithiophen for the application as donor material in polymer solar cells (PSCs). Replacing 25 mol% of extremely expensive 3-fluorothieno[3,4-b]thiophene-2-carboxylate monomer in the famous PTB7-Th by a > 30-times lower cost bithiophene, the new terpolymer PTB7-Th-T2 shows comparable HOMO energy level and increased absorption intensity in the wide wavelength range of 400-700 nm. In addition, in polymer/PC$_{71}$BM blended film, the hole mobility has improved from 1.67×10^{-4} of PTB7-Th to 2.49×10^{-4} cm^2 V^{-1} s^{-1} of PTB7-Th-T2. Power conversion efficiency (PCE) of 7.05% has been achieved in polymer bulk heterojunction photovoltaic device with the structure of ITO/PEDOT:PSS/PTB7-Th-T2:PC$_{71}$BM (1:1.5, w/w)/Ca/Al by using 3% of 1,8-diiodooctane (DIO) as solvent additive. Through introducing an amino-substituted perylene diimide (PDIN) as the cathode interlayer, a high fill factor (FF) of 67.38% and PCE of 8.19% has further been obtained, these values are higher than the control polymer PTB7-Th of 63.26% and 7.93%, respectively at the same device condition.

1. Introduction

Organic polymer solar cells (PSCs) with bulk heterojunction (BHJ) structure have attracted intense attention as the potential technology to efficiently harvest electrical energy from the sunlight due to the merits of simple fabrication by solution processing and capable of large-scale flexibility et al.[1-7] In the active layer of bulk heterojunction PSCs, electron donor materials (low band-gap conjugated polymers) are normally physically blended with electron acceptor materials (typically *n*-type fullerene derivatives), like [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (PC$_{71}$BM), providing efficient charge separation of the photo-generated excitons as well as favorable charge transport at the donor/acceptor interfaces.[8-10] Over the past decades, tremendous efforts have been made and power conversion efficiencies (PCEs) of ~10% for single-junction structure[11-16] and ~12% for multi-junction structure[17,18] in the BHJ PSCs have been successfully achieved.

The conjugated donor polymers played intrinsic importance for realizing high power conversion efficiencies in PSCs.[3,19-22] i) To realize high short circuit current density (J_{sc}), the donor polymers need to possess low bandgaps (E_g) by simultaneously embedding donor-acceptor moieties together in the backbone; ii) To obtain high open circuit voltage (V_{oc}), which is directly proportional to the energy gaps (E_g) between the HOMO (highest occupied molecular orbital) levels of donor polymers and the LUMO (lowest unoccupied molecular orbital) levels of fullerene derivatives, the donor polymers need to exhibit deep HOMO levels while still remain low bandgap; iii) To facilitate the transport of carriers and charge separation, strong interchain π-π interaction of polymers and proper interface with the fullerene derivatives should be controlled.[23] However, the trade-off between the deep HOMO and low bandgap of polymers leads to the difficulties of materials design.

Low bandgap conjugated polymers based on benzo[1,2-b:4,5-b]dithiophene (BDT) and thieno[3,4-b]thiophene (TT) units (PBDT-TTs) have been extensively studied, since they displayed satisfactory photovoltaic performance which could be attributed from their broad absorption spectra, suitable energy levels and high hole mobility et al.[24-29] For example, one

---

[a] *Key Lab for Flexible Electronics & Institute of Advanced Materials, Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University, 30 South Puzhu Road, Nanjing, 211816 (P. R. China). E-mail: iamyttao@njtech.edu.cn; iamwhuang@njtech.edu.cn.*

[b] *Beijing National Laboratory of Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190 (P. R. China). E-mail : zgzhangwhu@iccas.ac.cn.*

[c] *Key Laboratory for Organic Electronics and Information Displays and Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, 9 Wenyuan Road, Nanjing 210046 (P. R. China).*

[+] *The two authors contributed equally to this work.*

† Footnotes relating to the title and/or authors should appear here.

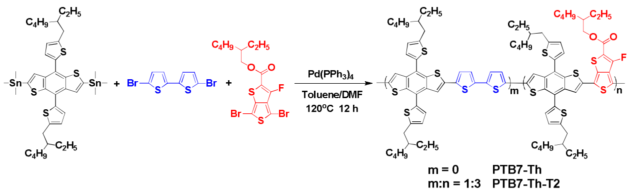
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x of the representative champion polymer PTB7 exhibited a small optical band gap (E_g) of ~1.6 eV and HOMO of *ca*. -5.15 eV,[26] and PCEs > 8% have been achieved by many research groups for the PTB7-based PSCs with optimized device architecture.[30-42] Afterwards, chemical modifications through 2-dimensional (2D) structure in conjugated polymers based on PTB7 have been made to further improve photovoltaic performance,[43-47] such as the attaching of conjugated thiophene in PTB7-Th or introducing phenoxy in PBT-OP to take place of the alkoxy substitution group on the BDT unit of PTB7.[21,48,49] The 2D-conjugated polymers have the advantages of red-shifted absorption, lower-lying HOMO levels and stronger interchain π-π interaction, which ultimately improved the photovoltaic properties.[50,51] For example, Zhan and Hou et al. reported PSCs with peak PCE values of 7.52% or 9.0% in the conventional structure of ITO/PEDOT:PSS/PTB7-Th:$PC_{71}BM$/PDIN or Ca/Al, respectively.[52,53] Moreover, Chen et al. reported high PCE of 9.35% in the inverted structure of ITO/ZnO-C60/PTB7-Th:$PC_{71}BM/MoO_3/Ag$.[21]

In spite of aforementioned success, further improvements by chemical procedures seem to face the bottleneck, not only because the chemical sites for modification are number-limited, but also the involvements of the multi-step synthetic steps may lead to the higher costs for purification which are not beneficial for large-scale production. Recently, another strategy of random terpolymers has been found to be the promising candidates for designing new donor polymers, which consist of three different monomer units in the main chain of the polymers.[54-67] Compared to the conventional two-component donor polymers, the newly involved third component embedded into the backbone could finely tune the polymer optoelectronic properties such as energy levels and carrier mobilities et al..[65] Up to date, only a few random terpolymers have been reported and PCE values over 8% have been successfully obtained by the incorporation of Zinc porphyrins or Iridium complexes.[68,69] Pure organic random terpolymers exhibiting high power conversion efficiencies have still been scarcely reported. In this work, a new terpolymer was synthesized by simply incorporating the cost-effective 2,2'-bithiophene to the typical material PTB7-Th to take place of 25 mol% of particularly expensive 3-fluorothieno[3,4-b]thiophene-2-carboxylate (TTF) monomer through random copolymerization. PSCs based on active layer of PTB7-Th-T2:$PC_{71}BM$ with DIO (1,8-diiodooctane) additive displayed satisfactory PCE value of 7.05%. By further using organic PDIN as the cathode interlayer, the PCE of the PTB7-Th-T2-based device could be improved to 8.19%, compared to the 7.89% for the PTB7-Th-based device under the same conditions. To the best of our knowledge, the PCE is among the highest values ever reported for the random terpolymers in the literature.[65-67]

2. Results and discussion

2.1. Synthesis and Characterization

As shown in Scheme 1, the polymer PBT7-Th-T2 was feasibly synthesized through the random Stille-coupling reaction among the three monomer compounds. And the control polymer PTB7-Th was prepared under the same polymerization conditions. The molecular weight of the two polymers was estimated by gel-permeation chromatography (GPC) and the number-average molecular weight (M_n) of PTB7-Th and PTB7-Th-T2 was detected to be 45 and 59 kg/mol with polydispersity index (PDI) of 2.09 and 1.58, respectively. Thermogravimetric analysis (TGA) measurement was carried out to evaluate the thermal stability of PTB7-Th-T2 (Figure 1), which exhibited high decomposition temperature (T_d, 5% weight loss) of ~350°C, which is slightly lower than that of reported PTB7-Th (383°C).[45]



Scheme 1. Synthetic route for the polymers PTB7-Th and PTB7-Th-T2.

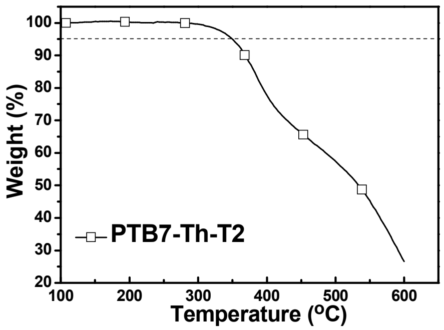


Figure 1. TGA curve of the terpolymer PTB7-Th-T2 under nitrogen atmosphere.

2.2 Optical Properties

The UV-Vis absorption spectra of PTB7-Th-T2 in dilute $CHCl_3$ solution and neat film state were shown in Figure 2. In solution, PTB7-Th-T2 displayed two distinct absorption bands, which can be attributed to the π-π* transitions from BDT to 2,2'-bithiophene segment (short wavelength region of 300–400 nm) and intra-molecular charge-transfer (ICT) interactions between the BDT donor moiety and electron accepting TTF unit (long wavelength region of 400-750 nm).[65] However, compared to PTB7-Th, the absorption band of PTB7-Th-T2 was slightly blue-shifted due to the enrichment of the electron-rich 2,2'-bithiophene segment in the backbone, which was consistent with previous reports on related polymers.[70] The same trend was also observed in the absorptions of the neat film. And consequently, the optical bandgap of PTB7-Th-T2 (1.61 eV) calculated from the onset of the absorption spectra in neat film was slightly larger than 1.59 eV of PTB7-Th. It should be noted that the absorption intensity in the wide wavelength range of 400-650 nm in solution and 400-700 nm in film state for the terpolymer PTB7-Th-T2 was distinctly higher than the control PTB7-Th, indicating the stronger light harvesting ability in the photovoltaic device.

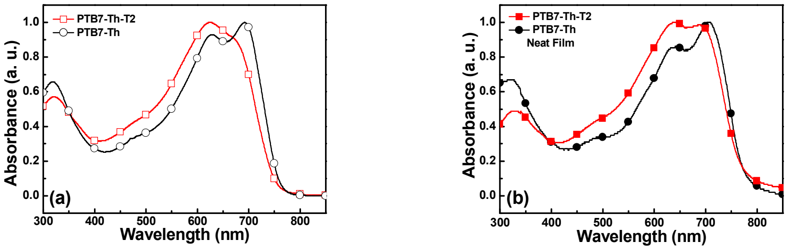


Figure 2. Normalized UV-Vis absorption spectra of PTB7-Th and PTB7-Th-T2 in dilute $CHCl_3$ solution (a) and neat film (b).

2.3 Electrochemical Property and Hole Mobility

The electrochemical behavior of PTB7-Th-T2 was examined by the cyclic voltammetry (CV) in acetonitrile solution. As shown in Figure 3, PTB7-Th-T2 exhibited quasi-reversible oxidation behavior and non-detectable reduction process. Calculated from the onset potential of the oxidation curves, the HOMO energy level for PTB7-Th-T2 was estimated to be -5.28 eV (relative to vacuum energy level). The introduction of 2,2'-bithiophene moiety slightly rises the HOMO level of PTB7-Th-T2 compared to -5.30 eV of PTB7-Th due to the replacement of electron-withdrawing TTF by the electron-donating 2,2'-bithiophene unit. Deduced from the HOMO and optical bandgap (E_g) [LUMO = –(HOMO + E_g)], the lowest occupied molecular orbital (LUMO) energy level for PTB7-Th-T2 was determined to be -3.67 eV. All the data were summarized in Table 1.

The hole mobility of the $PC_{71}BM$ blended films for PTB7-Th-T2 and PTB7-Th were measured by the method of space-charge-limited current (SCLC) with the device structure of ITO/PEDOT:PSS/polymers:$PC_{71}BM$/Au. As shown in Figure 4, it is unexpected that PTB7-Th-T2 exhibited even higher hole mobility (2.49×10^{-4} cm^2 V^{-1} s^{-1}) than that of PTB7-Th (1.67×10^{-4} cm^2 V^{-1} s^{-1}). Compared with the famous dononr polymer PTB7-Th, the comparable HOMO energy levels, the introducing of lower cost monomers, much stronger wide range absorption intensity as well as the higher charge transport ability suggested the potential application of the new terpolymer PTB7-Th-T2 in polymer solar cells.

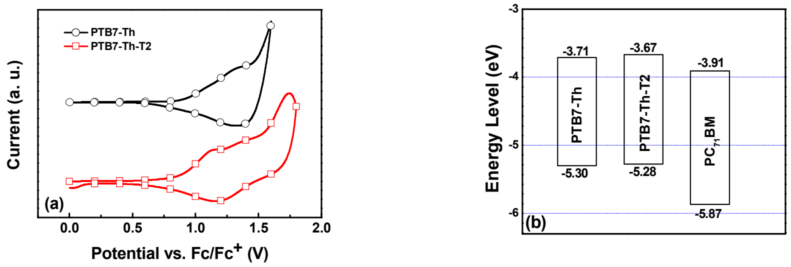


Figure 3. Cyclic voltammograms of the oxidation curves (a) and HOMO and LUMO energy level diagrams of PTB7-Th-T2, PTB7-Th and $PC_{71}BM^{45}$ (b).

Table 1. Characteristics of PTB7-Th-T2 and PTB7-Th.

Polymer	M_n/M_w (kDa)	$\lambda_{abs,max}$ (nm)^a	λ_{onset} (nm)^b	E_g (eV)^c	HOMO (eV)^d	LUMO (eV)^e
PTB7-Th-T2	59/93	625 (688)	768	1.61	-5.28	-3.67
PTB7-Th	45/94	692 (707)	780	1.59	-5.30	-3.71

^{a} Measured in dilute $CHCl_3$ solution and thin neat film (parentheses); ^{b} Measured at film state. ^{c} E_g was calculated from the onsets of UV-Vis spectra in neat film, E_g = 1240/λ_{onset}; ^{d} HOMO was measured by cyclic voltammograms; ^{e} Calculated from LUMO = HOMO + E_g.

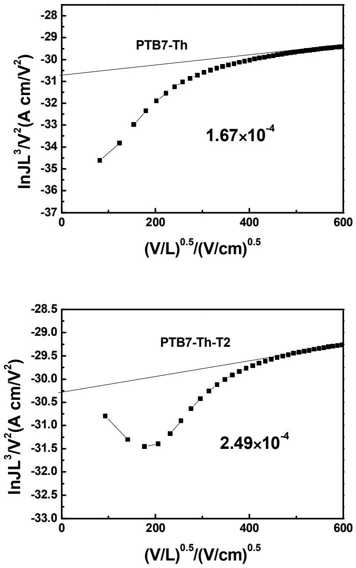


Figure 4. Space-charge-limited current (SCLC) plots of the blended films of donor polymers PTB7-Th-T2 or PTB7-Th with $PC_{71}BM$.

2.4 Photovoltaic performance

To evaluate the photovoltaic performance of PTB7-Th-T2, we initially fabricated device A with the following conventional structure of ITO/PEDOT:PSS/PTB7-Th-T2:$PC_{71}BM$/Ca/Al. For comparison, device B with PTB7-Th as donor polymer material was also fabricated. The representative current density-voltage and external quantum efficiency curves were shown in Figure 5. Device A based on PTB7-Th-T2 exhibited satisfactory maximum PCE of 6.89%, which is comparable to 6.84% in device B. However, as shown in the AFM image of Figure 6 (a) and (b), it is noted that the blended film for the active layer of device A was too smooth, with the root-meat square roughness (RMS) as low as ~0.68 nm, which was unfavourable for charge separation and charge transport.[1,4] Thus, optimized device A-I with 3% (v/v) of DIO (1,8-diiodooctane) additive was then fabricated, since DIO is widely used to improve the miscibility between donor polymers and fullerene derivatives. The interpenetrating "bicontinuous" network between the donor polymer and $PC_{71}BM$ was significantly improved, as evidenced by the larger roughness of 1.06 nm and more obvious nano-scale phase separation (Figure 6c and d). Consequently, the PCE value in device A-I increased to 7.05%, with V_{oc} = 0.75 V, J_{sc} = 14.85 mA cm^{-2} and FF = 63.46%.

It was noticeable that the PCE value of 7.05% in device A-I was only comparable to most previously reported results based on PTB7-Th, and the superior device performance of PTB7-Th-T2 has not been reflected.[45,52] It is suspected that the efficiencies was not fully exploited in the aforementioned device structure, because the hole mobility of PTB7-Th-T2 (2.49×10^{-4} cm^2 V^{-1} s^{-1}) was somewhat enhanced compared to PTB7-Th (1.67×10^{-4} cm^2 V^{-1} s^{-1}) after the involvement of the electron-rich 2,2'-bithiophene segment in the backbone. So the new balance of hole and electron transportation as well as the charge separation in the modified device configuration should be paid more attention.[71] One of the applicable strategies to solve the problems is to insert a functionalized interlayer between the active layer and metal cathode, which play the roles by simultaneously lowering the work function of the metal cathode for more feasible electron-collecting efficiency and blocking the hole carriers into metal cathode.[21,30,42] Metal oxides (e.g., ZnO, TiO_2 and $CsCO_3$) are extensively used as the interlayer.[21,72-74] However, the potential risk of using the inorganic interlayer might bring in the poor interfacial contact with the organic active layers. Thus, the organic interlayer materials (e.g., PDIN) was found to be the good alternatives.[42] Thus, optimized device A-II (3% DIO) with the configuration of ITO/PEDOT:PSS/PTB7-Th-T2:$PC_{71}BM$/PDIN/Al was further investigated, where PDIN

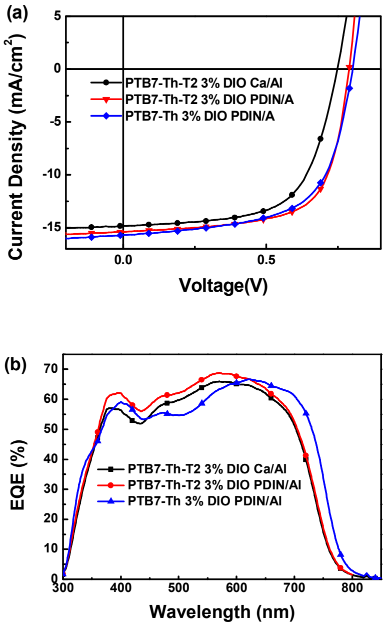


Figure 5. *J–V* curves (a) and external quantum efficiency (EQE) (b) of the representative polymer solar cell devices based on PTB7-Th-T2 and PTB7-Th under the illumination of AM 1.5G, 100 mW cm^{-2}.

Table 2. Summary of the device performance under the structure of ITO/PEDOT:PSS/Donor polymers:$PC_{71}BM$/Cathode without or with 3% DIO as the solvent additive.

Device	Donor	DIO (%)	Cathode	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE$_{max}$ (ave^a) (%)
A	PTB7-Th-T2	0	Ca/Al	0.79	14.30	60.92	6.89 (6.75)
B	PTB7-Th	0	Ca/Al	0.78	14.13	61.77	6.84 (6.72)
A-I	PTB7-Th-T2	3	Ca/Al	0.75	14.85	63.46	7.05 (6.93)
B-I	PTB7-Th	3	Ca/Al	0.76	15.29	61.15	7.15 (7.02)
A-II	PTB7-Th-T2	3	PDIN/Al	0.79	15.40	67.38	8.19 (8.05)
B-II	PTB7-Th	3	PDIN/Al	0.80	15.70	62.71	7.89 (7.81)

[a] The average PCE was obtained from over 6 devices.

(amino-substituted perylene diimide)[42] was employed as the organic interlayer material between the active layer and Al cathode. PDIN exhibits high conductivity and good contact with the metal cathode, in addition, the device performance shows little dependence on its film thickness.[42] In consequence, the PCE value was significantly enhanced to 8.19%, along with all the improved V_{oc} = 0.79 V, J_{sc} = 15.40 mA cm^{-2} and FF = 67.38%. More importantly, device A-II demonstrated better efficiencies than the fabricated control device B-II based on PTB7-Th (maximum PCE of 7.89%) under the identical conditions. Furthermore, the average PCE value obtained from over six devices was 8.05%, also higher than that of 7.81% for the PTB7-Th containing devices at the same fabrication conditions. All the key device data were summarized in Table 2. The slight superior FF and PCE, while lower J_{sc} of PTB7-Th-T2 device could be comprehensively influenced by its higher hole mobility,[66] stronger absorption intensity in the range of 450-600 nm whereas lower light-harvesting ability at longer wavelength over 700 nm (both from UV-Vis absorption and EQE curves) compared with PTB7-Th comprising device.

3. Conclusion

In summary, we have synthesized a new random terpolymer PTB7-Th-T2 by incorporating a lower cost 2,2'-bithiophene monomer to the skeleton of PTB7-Th. PTB7-Th-T2 exhibited similar optoelectronic properties with PTB7-Th whereas both blue-shifted and stronger UV-Vis absorption capability ranging from 400-700 nm. In addition, slightly higher HOMO level as well as higher hole mobility in the polymer/$PC_{71}BM$ blended film has been achieved in PTB7-Th-T2 compared to the control PTB7-Th due to the introduction of electron-rich 2,2'-bithiophene segment. Through structural modification on the famous donor polymer of PTB7-Th with lower cost monomer, the new terpolymer PTB7-Th-T2 have exhibited a comparable or even better photovoltaic performance at different cathode interlayer device structures, with PCE of 8.19% for PTB7-Th-T2 *versus* 7.89% of PTB7-Th based device. To the best of our knowledge, the PCE of 8.19% is among the highest value for the random terpolymers in the literature. Our results indicated that the strategy involved in this work afford a potential cost-effective molecular design of polymer photovoltaic materials for large-scale production of polymer solar cells.

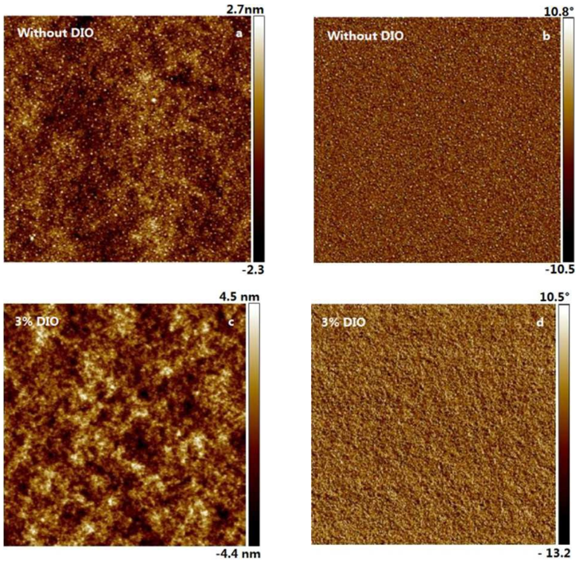


Figure 6. AFM images height image (a, c) and phase image (b, d) of PTB7-Th-T2:$PC_{71}BM$ blended films: without (a, b) and with (c, d) 3% DIO, (scale bar: 5×5 μm^2).

4. Experimental section

4.1 Characterization

^{1}H NMR spectra was measured on a Bruker DMX-400 spectrometer in d-chloroform using tetramethylsilane as the internal reference. The molecular weight of the polymers was estimated by gel-permeation chromatography (GPC) using *o*-dichlorobenzene as the eluent at 120^{o}C with polystyrenes as the internal standards. UV-visible absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Elemental analyses were carried out on a flash EA 1112 elemental analyzer. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument under dry nitrogen at a heating rate of 10 ^{o}C/min. The electrochemical cyclic voltammetry was conducted on a CHI voltammetric analyzer in acetonitrile solution at a potential scan rate of 100 mV s^{-1}, PTB7-Th-T2 or PTB7-Th film was coated on the working electrode from chloroform solution. Tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6, 0.1 mol L^{-1}) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl wire pseudo-reference electrode with ferrocene/ferrocenium (Fc/Fc$^+$) as the internal standard. The onset potential of a ferrocene/ferrocenium (Fc/Fc$^+$) redox couple is found to be 0.40 eV relative to the Ag/AgCl reference electrode in our measurement system, and the energy level of Fc/Fc+ was assumed to be at −4.8 eV under vacuum. Thus, the highest occupied molecular orbital (HOMO) was calculated from the equation of $E_{\mathrm{HOMO}} = -(E_{(\mathrm{ox})}{}^{\mathrm{onset}} - E_{(\mathrm{ferrocene})}{}^{\mathrm{onset}} + 4.8)$ eV. All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to the electrochemical measurements.

4.2 Materials and Synthesis

The monomers of 2,6-Bis(trimethyltin)-4,8-bis(5-ethylhexyl-2-thienyl)-benzo[1,2-b:4,5-b']dithiophene (M1, ~ 340 USD/g) and 2-Ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (M2) were purchased from Suna Tech Inc., the monomer 5,5'-dibromo-2,2'-bithiophen (M3) was synthesized according to a previously reported method with a cost of less than 10 USD/g.[75] The catalyst $Pd(PPh_3)_4$ was purchased from stream Inc. The other materials were common commercial level and used as received.

Synthesis of PTB7-Th-T2

Compounds M1 (2,6-Bis(trimethyltin)-4,8-bis(5-ethylhexyl-2-thienyl)-benzo[1,2-b:4,5-b']dithiophene) (181 mg, 0.2 mmol), M2 (2-Ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate) (70.8 mg, 0.15 mmol) and M3 (5,5'-dibromo-2,2'-bithiophen) (16.2 mg, 0.05 mmol) were weighed into a dry 50-mL Schlenk tube equipped with a magnetic stirrer. After 10 mg of $Pd(PPh_3)_4$ was added, the mixture was degassed three times, and then 8 mL of toluene and 2 mL of DMF were added. The reaction mixture was stirred for 12 h under nitrogen at 120^{o}C. After cooling down to room temperature, the highly viscous black gel was added to 200 mL of methanol and then stirred. The resulting polymer was collected by filtration and washed with methanol. The precipitate was further purified via Soxhlet extraction sequentially with methanol, acetone, hexane and chloroform. The polymer in the chloroform fraction was concentrated under reduced pressure and precipitated into cold methanol. The polymer was dried under vacuum. Yield: 139 mg (80%). GPC: M_n = 59 kDa, M_w = 93 kDa, PDI = 1.58. Anal. Calcd: C, 66.54; H, 6.41; Found: C, 66.35; H, 6.37%.

Synthesis of PTB7-Th

The polymer PTB7-Th was synthesized under the identical conditions with ratio of M1/M2 = 1/1. Yield: 126 mg (71%). GPC: M_n = 45 kDa, M_w = 94 kDa, PDI = 2.09. Anal. Calcd: C, 66.02; H, 6.67; Found: C, 65.47; H, 6.50%.

4.3 Fabrication and characterization of PSCs

The PSCs were fabricated with a configuration of ITO/PEDOT:PSS (30 nm)/active layer/Ca or PDIN/Al, where ITO is indium tin oxide and PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate). Ca or PDIN severs as a cathode interlayer and can lower the work function of the electrode, allowing higher-work-function metals (such as Al) to act as the cathode. A thin layer of PEDOT:PSS was deposited through spin-coating on pre-cleaned ITO-coated glass with a PEDOT:PSS aqueous solution (Baytron PVP AI 4083 from H. C. Starck) at 4000 rpm and dried subsequently at 150^{o}C for 15 min in air, then the device was transferred to a nitrogen glove box, where the active blend layer of the polymer and fullerene derivative was spin-coated onto the PEDOT:PSS layer with the ratio of 1: 1.5 (w/w) in *o*-dichlorobenzene. For PTB7-Th-T2/$PC_{71}BM$ PSCs, the active layer was formed by spin coating with *o*-DCB solution containing 10 mg mL^{-1} PTB7-Th-T2 and 15 mg mL^{-1} $PC_{71}BM$. 1,8-Diiodooctane (DIO) with a 3% volume ratio was added to the *o*-DCB solutions and stirred before use. A solution (total of 25 mg mL^{-1}) of PTB7-Th-T2/$PC_{71}BM$ blend was subsequently spin-coated (1000 rpm) on the PEDOT:PSS layer to form a photosensitive layer (ca. 100 nm thick). The thickness of the photosensitive layer was measured using a Proflometer (Ambios Tech. XP-2). The methanol solution (0.2% acetic acid) of PDIN at a concentration of 1.5 mg mL^{-1} was deposited on the active layer at 3000 rpm for 30 s, giving a PDIN layer ca. 14 nm thick. An aluminum (ca. 80 nm) layer was subsequently evaporated onto the surface of the PDIN layer under vacuum (ca. 10^{-5} Pa) to form the negative electrode. The active area of the device was 5 mm^2. The current density–voltage (J–V) characteristics were measured on a computer-controlled Keithley 2400 Source-Measure Unit. A xenon lamp coupled with an AM 1.5G solar spectrum filter was used as the light source, and the optical power was 100 mW cm^{-2}. The bulk resistance of samples (R) was calculated from Ohm's law: R = V/I, with at least six separate measurements made for each sample.

Acknowledgements

The authors thank the National Natural Science Foundation of China (21304047), Natural Science Foundation of Jiangsu Pr ovince (13KJB430017), Research Fund for the Doctoral Program of Higher Education (20133221120015) and Postgraduate Innovation Foundation of Jiangsu Province (2014, KYZZ_0226) for financial support.

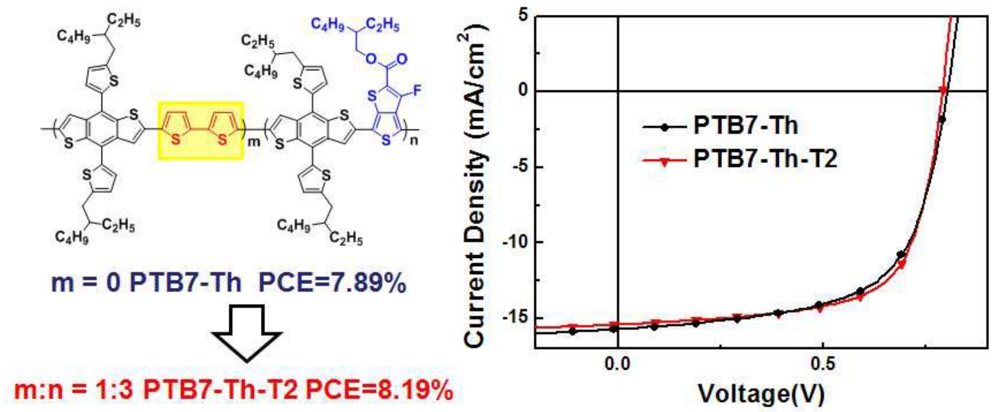
Notes and references

1 G. Li, R. Zhu and Y. Yang, *Nat. Photonics,* 2012, **6**, 153.
2 Y. F. Li, *Acc. Chem. Res.,* 2012, **45**, 723.
3 J. Chen and Y. Cao, *Acc. Chem. Res.,* 2009, **42**, 1709.
4 J. Peet, A. J. Heeger and G. C. Bazan, *Acc. Chem. Res.,* 2009, **42**, 1700.
5 Y. Lin, Y. Li and X. Zhan, *Chem. Soc. Rev.,* **2012**, 41, 4245.
6 F. C. Krebs, *Sol. Energy Mater. Sol. Cells,* 2009, **93**, 394.
7 W. Chen, X. Yang, G. Long, X. Wan, Y. Chen and Q. Zhang, *J. Mater. Chem. C*, 2015, **3**, 4698.
8 Y. Zhang, X.-D. Dang, C. Kim and T.-Q. Nguyen, *Adv. Energy Mater.*, 2011, **1**, 610.
9 M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, *Angew. Chem., Int. Ed.,* 2003, **42**, 3371.
10 W. Q. Chen, T. Salim, H. J. Fan, L. James, Y. M. Lam and Q. C. Zhang, *RSC Adv.*, 2014, **4**, 25291.
11 Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat. Commun.,* 2014, **5**, 5293.
12 S. H. Liao, H. J. Jhuo, P. N. Yeh, Y. S. Cheng, Y. L. Li, Y. H. Lee, S. Sharma and S. A. Chen, *Sci. Rep.*, 2014, **4**, 6813.
13 S. Zhang, L. Ye, W. Zhao, B. Yang, Q. Wang and J. Hou, *Sci. China: Chem.*, 2015, **58**, 248.
14 J. D. Chen, C. Cui, Y. Q. Li, L. Zhou, Q. D. Ou, C. Li, Y. Li, J. X. Tang, *Adv. Mater.,* 2015, **27**, 1035.
15 Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell, Y. Cao, *Nat. Photonics,* 2015, **9**, 174.
16 L. Huo, T. Liu, X. Sun, Y. Cai, A. J. Heeger and Y. Sun, *Adv. Mater.*, 2015, **27**, 2938.
17 C.-C. Chen, W.-H. Chang, K. Yoshimura, K. Ohya, J. You, J. Gao, Z. Hong, Y. Yang, *Adv. Mater.* 2014, **26**, 5670.
18 H. Q. Zhou, Y. Zhang, C. K. Mai, S. D. Collins, G. C. Bazan, T. Q. Nguyen and A. J. Heeger, *Adv. Mater.*, 2015, **27**, 1767.
19 L. J. Huo, S. Q. Zhang, X. Guo, F. Xu, Y. F. Li and J. H. Hou, *Angew. Chem., Int. Ed.*, 2011, **123**, 9871.
20 H.-Y. Chen, J. H. Hou, S. Q. Zhang, Y. Y. Liang, G. W. Yang, Y. Yang, L. P. Yu, Y. Wu and G. Li, *Nat. Photonics,* 2009, **3**, 649.
21 S.-H. Liao, H. J. J. huo, Y.-S. Cheng and S.-A. Chen, *Adv. Mater.*, 2013, **25**, 4776.
22 B. Hu, M. Li, W. Chen, X. Wan, Y. Chen and Q. Zhang, *RSC Adv.*, 2015, 5, 50137.
23 Y. Huang, X. Guo, F. Liu, L. J. Huo, Y. N. Chen, T. P. Russell, C. C. Han, Y. F. Li and J. H. Hou, *Adv. Mater.,* 2012, **24**, 3383.
24 Y. Y. Liang, Y. Wu, D. Q. Feng, S.-T. Tsai, G. Li, H. J. Son and L. P. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 56.
25 L. J. Huo, J. H. Hou, *Polym. Chem.,* 2011, **2**, 2453.
26 Y. Y. Liang, Z. Xu, J. B. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray and L. P. Yu, *Adv. Mater.,* 2010, **22**, E135.
27 Y. Y. Liang and L. P. Yu, *Acc. Chem. Res.,* 2010, **43**, 1227.
28 C. Bathula, C. E. Song, B. Sachin, S.-J. Hong, I.-N. Kang, S.-J. Moon, J. Lee, S. Cho, H.-K. Shim and S. K. Lee, *J. Mater. Chem.*, 2012, **22**, 22224.
29 J.-H. Kim, C. E. Song, H. U. Kim, A. C. Grimsdale, S.-J. Moon, W. S. Shin, S. K. Choi and D.-H. Hwang, *Chem. Mater.*, 2013, **25**, 2722.
30 Z. C. He, C. M. Zhong, S. J. Su, M. Xu, H. B. Wu and Y. Cao, *Nat. Photonics*, 2012, **6**, 591.
31 X. Gu, W. Cui, H. Li, Z. Wu, Z. Zeng, S.-T. Lee, H. Zhang, B. Sun, *Adv. Energy Mater.,* 2013, **3**, 1262.
32 S. Liu, K. Zhang, J. Lu, J. Zhang, H.-L. Yip, F. Huang, Y. Cao, *J. Am. Chem. Soc.* 2013, **135**, 15326.
33 C. H. Duan, K. Zhang, X. Guan, C. M. Zhong, H. M. Xie, F. Huang, J. W. Chen, J. B. Peng, Y. Cao, *Chem. Sci.,* 2013, **4** , 1298.
34 B. R. Lee, E. D. Jung, Y. S. Nam, M. Jung, J. S. Park, S. Lee, H. Choi, S.-J. Ko, N. R. Shin, Y.-K. Kim, S. O. Kim, J. Y. Kim, H.-J. Shin, S. Cho, M. H. Song, *Adv. Mater.,* 2014, **26**, 494.
35 S. M. Yoon, S. J. Lou, S. Loser, J. Smith, L. X. Chen, A. Facchetti, T. J. Marks, *Nano Lett.,* 2012, **12**, 6315.
36 L. Y. Lu, Z. Q. Luo, T. Xu, L. P. Yu, *Nano Lett.,* 2013, **13**, 59.
37 S. W. Baek, J. Noh, C. H. Lee, B. Kim, M. K. Seo, J. Y. Lee, *Sci. Rep.,* 2013, **3**, 1726.
38 H. Choi, J. P. Lee, S. J. Ko, J. W. Jung, H. Park, S. Yoo, O. Park, J. R. Jeong, S. Park, J. Y. Kim, *Nano Lett.*, 2013, **13**, 2204.
39 B. R. Lee, E. D. Jung, Y. S. Nam, M. Jung, J. S. Park, S. Lee, H. Choi, S.-J. Ko, N. R. Shin, Y.-K. Kim, S. O. Kim, J. Y. Kim, H.-J. Shin, S. Cho, M. H. Song, *Adv. Mater.,* 2014, **26**, 49.
40 S. M. Yoon, S. J. Lou, S. Loser, J. Smith, L. X. Chen, A. Facchetti, T. J. Marks, *Nano Lett.*, 2012, **12**, 6315.
41 D. Zhang, W. C. H. Choy, F. Xie, W. E. I. Sha, X. Li, B. Ding, K. Zhang, F. Huang, Y. Cao, *Adv. Func. Mater.,* 2013, **23**, 4255.
42 Z.-G. Zhang, B. Qi, Z. Jin, D. Chi, Z. Qi, Y. Li and J. Wang, *Energy Environ. Sci.*, 2014, **7**, 1966.
43 Y. Wu, Z. J. Li, W. Ma, Y. Huang, L. J. Huo, X. Guo, M. J. Zhang, H. Ade and J. H. Hou, *Adv. Mater.,* 2013, **25**, 3449.
44 J. H. Kim, C. E. Song, B. S. Kim, I. N. Kang and D. H. Hwang, *Chem. Mater.*, 2014, **26**, 1234.
45 C. Cui, W.-Y. Wong, Y. F. Li, *Energy Environ. Sci.,* 2014, **7**, 2276.
46 L. Ye, S. Q. Zhang, W. C. Zhao, H. F. Yao, J. H. Hou, *Chem. Mater.*, 2014, **26**, 3603.
47 W.-H. Chang, L. Meng, L. T. Dou, J. B. You, C.-C. Chen, Y. Yang, E. P. Young, G. Li, Y. Yang, *Macromolecules,* 2015, **48**, 562.
48 M. Zhang, X. Guo, S. Zhang, J. H. Hou, *Adv. Mater.*, 2014, **26**, 1118.
49 M. Zhang, X. Guo, W. Ma, S. Zhang, L. J. Huo, H. Ade, J. H. Hou, *Adv. Mater*., 2014, **26**, 2089.
50 J.-H. Kim, C. E. Song, I.-N. Kang, W. S. Shin and D.-H. Hwang, *Chem. Commun.,* 2013, **49**, 3248.
51 J.-H. Kim, C. E. Song, H. U. Kim, A. C. Grimsdale, S.-J. Moon, W. S. Shin, S. K. Choi and D.-H. Hwang, *Chem. Mater.,* 2013, **25**, 2722.
52 Y. Lin, J. Wang, Z. G. Zhang, H. Bai, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, 2015, **27**, 1170.
53 S Zhang, L. Ye, W. Zhao, D. Liu, H. Yao and J. H. Hou, *Macromolecules*, 2014, **47**, 4653.
54 Z. G. Zhu, D. Waller, R. Gaudiana, M. Morana, D. Mühlbacher, M. Scharber and C. Brabec, *Macromolecules*, 2007, **40**, 1981.
55 J. Li, K.-H. Ong, S.-L. Lim, G.-M. Ng, H.-S. Tan and Z.-K. Chen, *Chem. Commun.*, 2011, **47**, 9480.
56 P. P. Khlyabich, B. Burkhart, C. F. Ng and B. C. Thompson, *Macromolecules*, 2011, **44**, 5079.
57 K. Yao, L. Chen, Y. W. Chen, F. Li, X. Y. Ren, H. M. Wang and Y. F. Li*, Polym. Chem.,* 2012, **3**, 710.

58 C. B. Nielsen, R. S. Ashraf, B. C. Schroeder, P. D'Angelo, S. E. Watkins, K. Song, T. D. Anthopoulosb and I. McCulloch, *Chem. Commun.*, 2012, **48**, 5832.
59 J. W. Jung, F. Liu, T. P. Russell and W. H. Jo, *Energy Environ. Sci.*, 2013, **6**, 3301.
60 J. Jiang, H. Chen, H. Lin, C. Yu, S. Lan, C. Liu and K. Wei, *Polym. Chem.*, 2013, **4**, 5321.
61 J. Li, K.-H. Ong, P. Sonar, S.-L. Lim, G.-M. Ng, H.-K. Wong, H.-S. Tan and Z.-K. Chen, *Polym. Chem.*, 2013, **4**, 804.
62 L. W. Wang, S. W. Shi, D. Ma, S. Chen, C. Gao, M. Wang, K. L. Shi, Y. F. Li, X. Y. Li and H. Q. Wang, *Macromolecules*, 2015, **48**, 287-296.
63 M. Zhang, F. Wu, Z. Cao, T. Shen, H. Chen, X. Lia and S. Tan, *Polym. Chem.*, 2014, **5**, 4054.
64 L. Chen, F. Y. Wu, Z. Q. Deng, L. L. Feng, P.P. Gu, H. L. Dong, W. P. Hu and Y. W. Chen, *Polym. Chem.,* 2015, DOI: 10.1039/C5PY01208B.
65 T. E. Kang, K.-H. Kim and B. J. Kim, *J. Mater. Chem. A*, 2014, **2**, 15252.
66 W.-H. Chang, J. Gao, L. Dou, C.-C. Chen, Y. Liu and Y. Yang, *Adv. Energy Mater.,* 2014, **4**, 1300864.
67 P. Liu, K. Zhang, F. Liu, Y. Jin, S. Liu, T. P. Russell, H.-L. Yip, F. Huang and Y. Cao, *Chem. Mater.*, 2014, **26**, 3009.
68 Y. I. H. Chao, J.-F. Jheng, J.-S. Wu, K.-Y. Wu, H.-H. Peng, M.-C. Tsai, C.-L. Wang, Y.-N. Hsiao, C.-L. Wang, C.-Y. Lin and C.-S. Hsu, *Adv. Mater.*, 2014, **26**, 5205.
69 M. Qian, R. Zhang, J. Hao, W. Zhang, Q. Zhang, J. Wang, Y. Tao, S. Chen, J. Fang and W. Huang, *Adv. Mater.*, 2015, **27**, 3546.
70 M.-C. Yuan, M.-Y. Chiu, C.-M. Chiang and K.-H. Wei, *Macromolecules*, 2010, **43**, 6270.
71 J. A. Bartelt, D. Lam, T. M. Burke, S. M. Sweetnam, M. D. McGehee, *Adv. Energy Mater.* 2015, **5**, 1500577.
72 S. Chen, J. R. Manders, S.-W. Tsang and F. So, *J. Mater. Chem.,* **2012**, 22, 24202.
73 H.-L. Yip and A. K. Y. Jen, *Energy Environ. Sci.*, 2012, **5**, 5994.
74 R. Steim, F. R. Koglerand C. J. Brabec, *J. Mater. Chem.,* 2010, **20**, 2499.
75 D. Z. Mo, S. J. Zhen, J. K. Xu, W. Q. Zhou, B. Y. Lu, G. Zhang, Z. P. Wang, S. M. Zhang, Z. L. Feng, *Synthetic Metals*, 2014, **198**, 19.

Random Terpolymer with a Cost-Effective Monomer and Comparable Efficiency to PTB7-Th for Bulk-Heterojunction Polymer Solar Cells

Tao Jiang,[a+] Jie Yang,[ab+] Youtian Tao,*[a] Cong Fan,[a] Lingwei Xue,[b] Zhiguo Zhang,[b*] Hai Li,[a] Yongfang Li[b] and Wei Huang*[ac]



A new random terpolymer PTB7-Th-T2 by incorporating a significantly lower-cost 2,2'-bithiophene monomer to the famous PTB7-Th skeleton was designed and synthesized for high performance PSCs.