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

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A new random terpolymer PTB7-Th-T2 has been designed and synthesized by incorporating a significantly lower cost monomer, 2,2′-bithiophen, for application as a donor material in polymer solar cells (PSCs). By 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 a comparable HOMO energy level and increased absorption intensity in the wide wavelength range of 400–700 nm. In addition, in a polymer/PC$_{71}$BM blended film, the hole mobility has improved from $1.67 \times 10^{-4}$ for PTB7-Th to $2.49 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for PTB7-Th-T2. A power conversion efficiency (PCE) of 7.05% has been achieved in a 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 a solvent additive. Furthermore, 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% have been obtained; these values are higher than those of the control polymer PTB7-Th of 63.26% and 7.93%, respectively at the same device conditions.

## 1. Introduction

Organic polymer solar cells (PSCs) with a bulk heterojunction (BHJ) structure have attracted intense attention as a potential technology to efficiently harvest electrical energy from sunlight due to their merits of simple fabrication by solution processing and capability of large-scale flexibility *etc.*[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), such as [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] BHJ PSCs have been successfully achieved.

The conjugated donor polymers are of intrinsic importance to realize 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 a 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 the fullerene derivatives, the donor polymers need to exhibit deep HOMO levels while still possessing a low bandgap; (iii) to facilitate the transport of carriers and charge separation, strong interchain π–π interactions between polymers and proper interface with the fullerene derivatives should be controlled.[23] However, the trade-off between requiring a deep HOMO and a low bandgap of these polymers leads to difficulties in 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 display satisfactory photovoltaic performance which can be attributed to their broad absorption spectra, suitable energy levels and high hole mobility *et al.*[24–29] For example, one of the represen-

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tative champion polymers PTB7 exhibited a small optical band gap ($E_g$) of ~1.6 eV and a 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] Additionally, chemical modifications through the 2-dimensional (2D) structure in conjugated polymers based on PTB7 have been made to further improve photovoltaic performance,[43–47] such as attaching a conjugated thiophene in PTB7-Th or introducing a phenoxy group in PBT-OP to take the 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 their photovoltaic properties.[50,51] For example, Zhan and Hou *et al.* reported PSCs with peak PCE values of 7.52% or 9.0% using the conventional structure of ITO/PEDOT:PSS/PTB7-Th: $PC_{71}BM$/PDIN or Ca/Al, respectively.[52,53] Moreover, Chen *et al.* reported a high PCE of 9.35% using the inverted structure of ITO/ZnO-C60/PTB7-Th:$PC_{71}BM$/$MoO_3$/Ag.[21]

In spite of the aforementioned success, the possibility of further improvements by chemical modification seems to face a bottleneck, not only because the chemical sites for modification are number-limited, but also the involvement of multi-step synthetic steps may lead to the higher costs for purification which are not beneficial for large-scale production. Recently, another strategy of synthesising random terpolymers has been found to be promising for the design of 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 *etc.*[65] To date, only a few random terpolymers have been reported and PCE values of 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 replace 25 mol% of the particularly expensive 3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (TTF) monomer, through random copolymerization. PSCs based on an active layer of PTB7-Th-T2:$PC_{71}BM$ with DIO (1,8-diiodooctane) additive displayed a 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, this 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 of the
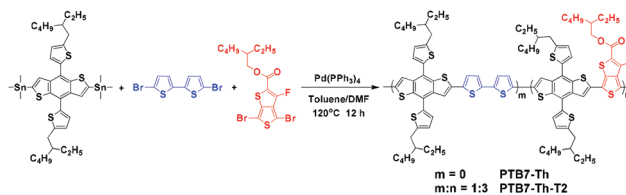


Scheme 1 Synthetic route for the polymers PTB7-Th and PTB7-Th-T2.
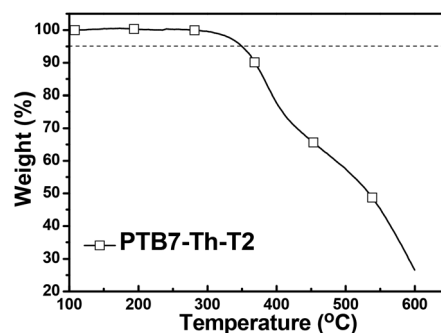


Fig. 1 TGA curve of the terpolymer PTB7-Th-T2 under nitrogen atmosphere.

three monomer compounds, and the control polymer PTB7-Th was prepared under the same polymerization conditions. The molecular weights of the two polymers were 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 $mol^{-1}$ with polydispersity indices (PDI) of 2.09 and 1.58, respectively. Thermogravimetric analysis (TGA) measurement was carried out to evaluate the thermal stability of PTB7-Th-T2 (Fig. 1), which exhibited a high decomposition temperature ($T_d$, 5% weight loss) of ~350 °C, which is slightly lower than that of reported PTB7-Th (383 °C).[45]

### 2.2 Optical properties

The UV-Vis absorption spectra of PTB7-Th-T2 in dilute $CHCl_3$ solution and neat film state are shown in Fig. 2. In solution, PTB7-Th-T2 displayed two distinct absorption bands, which
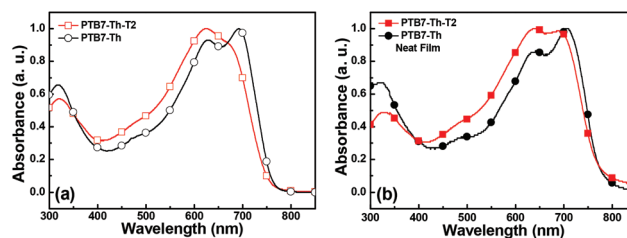


Fig. 2 Normalized UV-Vis absorption spectra of PTB7-Th and PTB7-Th-T2 in dilute $CHCl_3$ solution (a) and neat film (b).

can be attributed to the π–π* transitions from BDT to the 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. Consequently, the optical bandgap of PTB7-Th-T2 (1.61 eV) as calculated from the onset of the absorption spectra in the neat film was slightly larger than the 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 the film state for the terpolymer PTB7-Th-T2 was distinctly higher than that of the control PTB7-Th, indicating the stronger light harvesting ability of the photovoltaic device.

## 2.3 Electrochemical property and hole mobility

The electrochemical behavior of PTB7-Th-T2 was examined by cyclic voltammetry (CV) in acetonitrile solution. As shown in Fig. 3, PTB7-Th-T2 exhibited quasi-reversible oxidation behavior and a 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 the vacuum energy level). The introduction of the 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 the 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 are 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 Fig. 4, it is unexpected that PTB7-Th-T2 exhibited an even higher hole mobility ($2.49 \times 10^{-4}$ $cm^2$ $V^{-1}$ $s^{-1}$) than that of PTB7-Th (1.67 ×
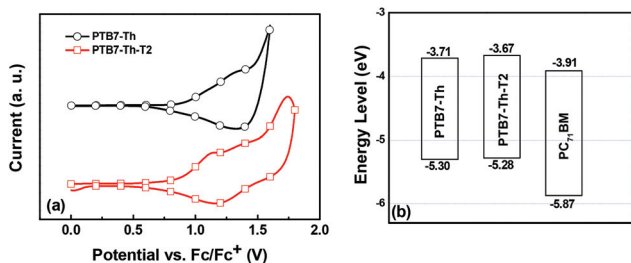


Fig. 3 Cyclic voltammograms of the oxidation curves (a) and HOMO and LUMO energy level diagrams of PTB7-Th-T2, PTB7-Th and $PC_{71}BM^{[45]}$ (b).

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

| Polymer | $M_n/M_w$ (kDa) | $\lambda_{abs,max}$[a] (nm) | $\lambda_{onset}$[b] (nm) | $E_g$[c] (eV) | HOMO[d] (eV) | LUMO[e] (eV) |
|---|---|---|---|---|---|---|
| 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 in film state. [c] $E_g$ was calculated from the onsets of UV-Vis spectra of neat film, $E_g = 1240/\lambda_{onset}$. [d] HOMO was measured by cyclic voltammetry. [e] Calculated from LUMO = HOMO + $E_g$.
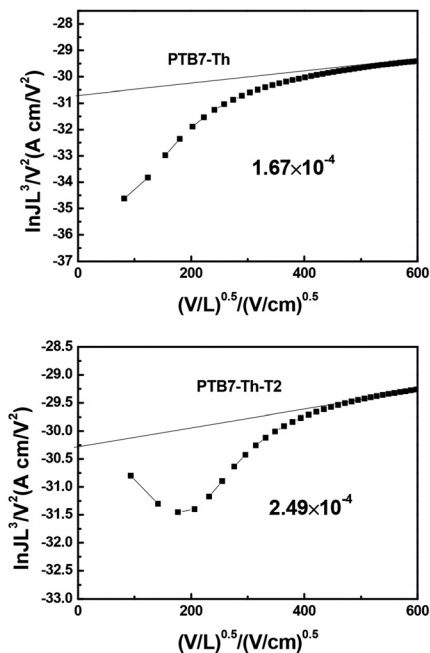


Fig. 4 Space-charge-limited current (SCLC) plots of the blended films of donor polymers PTB7-Th-T2 or PTB7-Th with $PC_{71}BM$.

$10^{-4}$ $cm^2$ $V^{-1}$ $s^{-1}$). Compared with the famous donor polymer PTB7-Th, the comparable HOMO energy levels, the introduction of lower cost monomers, the much stronger wide range absorption intensity as well as the higher charge transport ability suggest the potential application of the new terpolymer PTB7-Th-T2 in polymer solar cells.

## 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 are shown in Fig. 5. Device A based on PTB7-Th-T2 exhibited a satisfactory maximum PCE of 6.89%, which is comparable to 6.84% in device B. However, as shown in the AFM images in Fig. 6(a)
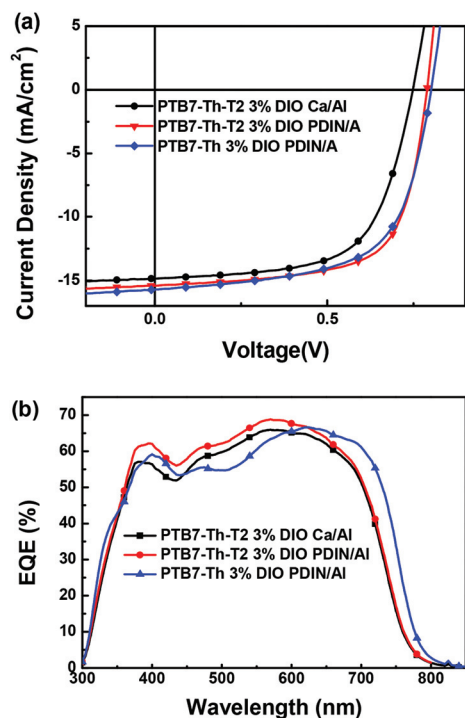
Fig. 5   $J-V$ curves (a) and external quantum efficiency (EQE) (b) of the representative polymer solar cell devices based on PTB7-Th-T2 and PTB7-Th under the illumination of AM 1.5G, 100 mW cm$^{-2}$.
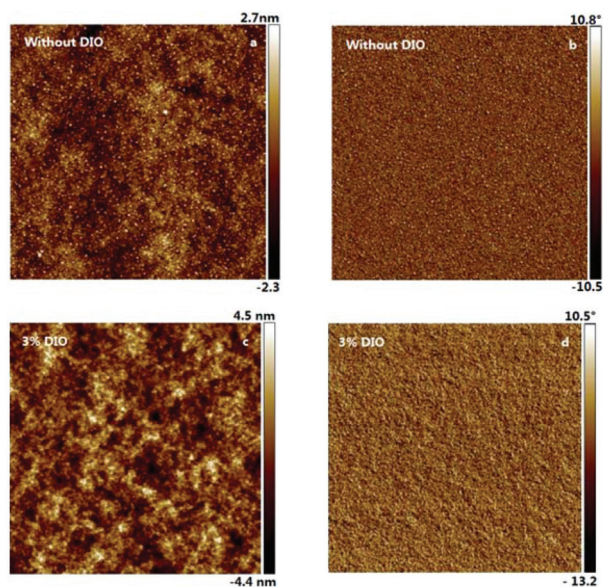


Fig. 6   AFM images: height image (a, c) and phase image (b, d) of PTB7-Th-T2:PC$_{71}$BM blended films: without (a, b) and with (c, d) 3% DIO, (scale bar: 5 × 5 μm$^2$).

and (b), it is noted that the blended film for the active layer of device A was too smooth, with a 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 nanoscale phase separation (Fig. 6c and d). Consequently, the PCE values 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 more attention should be paid to the new balance of hole and electron transportation as well as the charge separation in the modified device configuration.[71] One of the applicable strategies to solve these problems is to insert a functionalized interlayer between the active layer and metal cathode, which plays the roles of simultaneously lowering the work function of the metal cathode for more feasible electron-collecting efficiency and also 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 an inorganic interlayer is that it might result in poor interfacial contact with the organic active layers. Thus, organic interlayer materials (e.g., PDIN) have been found to be good alternatives.[42] Thus, an 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 (amino-substituted perylene diimide)[42] was employed as the organic interlayer material between the active layer and the Al cathode. PDIN exhibits high conductivity and good contact with the metal cathode, and in addition, the device performance shows little dependence on its film thickness.[42] Consequently the PCE value was significantly enhanced to 8.19%, along with 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 the 7.81% of the PTB7-Th containing devices at the same fabrication conditions. All the key device data are summarized in Table 2. The slightly superior FF and PCE, though lower $J_{sc}$ of the PTB7-Th-T2 device could be comprehensively influenced by its higher hole mobility,[66] stronger absorption intensity in the range of 450–600 nm though lower light-harvesting ability at longer wavelength over 700 nm (both from UV-Vis absorption and EQE curves) compared with the PTB7-Th based device.

**Table 2** Summary of the device performance with 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.

## 3. Conclusion

In summary, we have synthesized a new random terpolymer, PTB7-Th-T2, by incorporating a lower cost 2,2′-bithiophene monomer into the skeleton of PTB7-Th. PTB7-Th-T2 exhibited similar optoelectronic properties to those of PTB7-Th whereas both exhibited blue-shifted and stronger UV-Vis absorption capability ranging from 400–700 nm. In addition, a slightly higher HOMO level as well as higher hole mobility in the polymer/PC$_{71}$BM blended film have been achieved in PTB7-Th-T2 in comparison to the control PTB7-Th, due to the introduction of the electron-rich 2,2′-bithiophene segment. Through structural modification of the famous donor polymer PTB7-Th with a lower cost monomer, the new terpolymer PTB7-Th-T2 has been shown to exhibit a comparable or even better photovoltaic performance in different cathode interlayer device structures, with a PCE of 8.19% for PTB7-Th-T2 being achieved *versus* 7.89% for the 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 indicate that the strategy involved in this work affords a potentially cost-effective route to the molecular design of polymer photovoltaic materials for large-scale production of polymer solar cells.

## 4. Experimental section

### 4.1 Characterization

$^1$H NMR spectra were 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 °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 °C min$^{-1}$. 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 films were coated on the working electrode from chloroform solution. Tetrabutylammonium hexafluorophosphate (*n*-Bu$_4$NPF$_6$, 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 was 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 $E_{HOMO} = -(E_{(ox)}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$ eV. All the solutions were deaerated by bubbling nitrogen gas through them 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 per 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 per g.[75] The catalyst Pd(PPh$_3$)$_4$ was purchased from stream Inc. The other materials were common commercial grade and were 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-fluoro-thieno[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 °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 served as a cathode interlayer and could 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 °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.

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