

Replacing Alkoxy Groups with Alkylthienyl Groups: A Feasible Approach To Improve the Properties of Photovoltaic Polymers**

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Polymer solar cells (PSCs) have attracted much attention because of their potential application in flexible, light-weight, and low-cost large-area devices through roll-to-roll printing.^[1] The bulk heterojunction PSCs showed advanced features in realizing high efficiencies and solution-processible devices. The active layer in this kind of device consists of an interpenetrating network formed by an electron-donor material blended with an electron-acceptor material.^[2,3] Typically, conjugated polymers^[4] are used as electron donors and fullerene derivatives are used as the electron acceptors^[5] in the PSCs. Recently, power conversion efficiencies (PCEs) of 6–7% have been realized by using new conjugated polymer donors^[6–8] or new fullerene-derived acceptors.^[9] Short circuit current density (J_{sc}), open circuit voltage (V_{oc}), and fill factors (FF) are key parameters for a PSC device, because the PCE of the device is proportional to the values of the three parameters. To broaden the response wavelength range of a PSC device by using conjugated side chains^[4c,10,11] or narrow-band-gap conjugated polymers^[12–19] is an effective way to realize high J_{sc} values. Conjugated polymers with lower HOMO levels are helpful in realizing high V_{oc} and PCE values, as the V_{oc} value of PSCs is directly proportional to the offset between the HOMO level of electron donor and the LUMO level of electron acceptor.^[20] PSiFDTBT,^[13] PFDTBT,^[21] and PCDTBT^[14] are three excellent examples for this concept. Consequently, by using conjugated polymers with lower HOMO levels and also narrow band gaps, high PCEs were realized in different families of conjugated polymers.^[6–8]

Conjugated polymers based on benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) units have attracted interest as electron donors

in the PSC field in recent years, since the report of Hou and Yang et al. on the synthesis and photovoltaic properties of a series of copolymers based on BDT.^[22] Many copolymers of BDT with different conjugated units, such as thieno[3,4-*b*]thiophene (TT),^[6,23,24] 4,7-dithiophene-2-yl-2,1,3-benzothiadiazole (DTBT),^[7a] N-alkylthieno[3,4-*c*]pyrrole-4,6-dione (TPD),^[15] and bithiazole,^[25] etc. were synthesized, and the copolymers showed promising photovoltaic properties. In these BDT-based polymers, the alternative copolymers of BDT and TT, namely PBDTTTs, are an important family of photovoltaic materials. For additional improvements in the photovoltaic performance of the PBDTTTs, structural modifications brought about by using different substituents on BDT, or the copolymerized moieties is of great importance. For example, Liang et al. introduced a fluorine atom into the TT unit of the PBDTTTs, and the HOMO level of the resulting polymer was successfully lowered by approximately 0.12 eV, and thus a higher V_{oc} value was achieved, resulting in a great improvement of PCE.^[26] Hou et al. optimized PBDTTTs further by replacing the alkoxy-carbonyl group on the TT unit with the alkylcarbonyl groups.^[24]

The structural modification can also be carried out on the BDT units.^[27,28] In this work, we designed a 5-alkylthiophene-2-yl-substituted BDT monomer and synthesized two new PBDTTT-based polymers having either the thienyl-substituted BDT with alkoxy-carbonyl-substituted thieno[3,4-*b*]thiophene (TT-E) or the alkylcarbonyl-substituted thieno[3,4-*b*]thiophene (TT-C); that is PBDTTT-E-T and PBDTTT-C-T, respectively (Scheme 1). To fully investigate the effect of the thienyl-substituted BDT on the photovoltaic properties of the polymers, two corresponding PBDTTT polymers based on the alkoxy-substituted BDT (BDT-O), PBDTTT-E and PBDTTT-C (Scheme 1), were also prepared.

The synthetic route of the thienyl-substituted BDT monomer (BDT-T) is shown in Scheme 1. The branched alkyl group 2-ethylhexyl was employed as the side chain on the thiophene to guarantee high solubility of the target polymers. The TT-E and TT-C monomers are commercially available. The polymers were prepared through a Stille coupling reaction between the bis(trimethyltin) BDT monomers (BDT-T and BDT-O) and the bromides (TT-E and TT-C) as shown in Scheme 1. All the polymers are soluble in chloroform (CHCl_3), chlorobenzene, and dichlorobenzene.

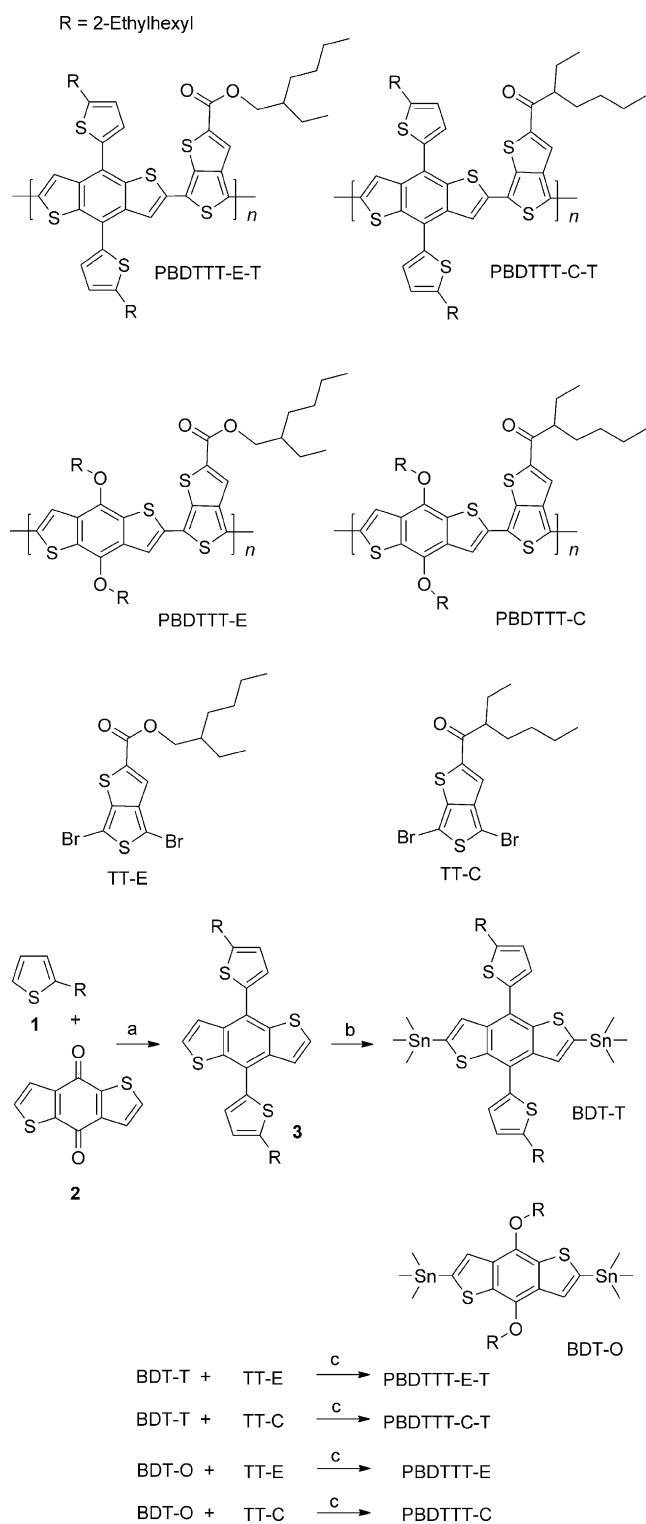
Thermogravimetric analysis (TGA) measurements were employed to evaluate the thermal stability of the polymers. We found that the two-dimensional (2D) conjugated^[10,11] polymers based on alkylthienyl-substituted BDTs are much more stable than their analogues, the alkoxy-substituted BDTs. The TGA plots of these four polymers are shown in Figure 1. It can be seen that the decomposition temperatures

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Scheme 1. Molecular structures and the synthetic routes to the polymers based on 5-alkylthiophene-2-yl- and alkoxy-substituted BDT.

a) Butyllithium, THF, 1 h; then compound **2**, 50°C, 1 h; then SnCl₂/HCl/H₂O, 50°C, 1.5 h; b) Butyllithium, THF, ambient temperature, 2 h; then (CH₃)₃SnCl, ambient temperature, 1 hour; c) [Pd(PPh₃)₄], toluene/DMF (5:1), reflux, 16 h. DMF = *N,N'*-dimethylformamide.

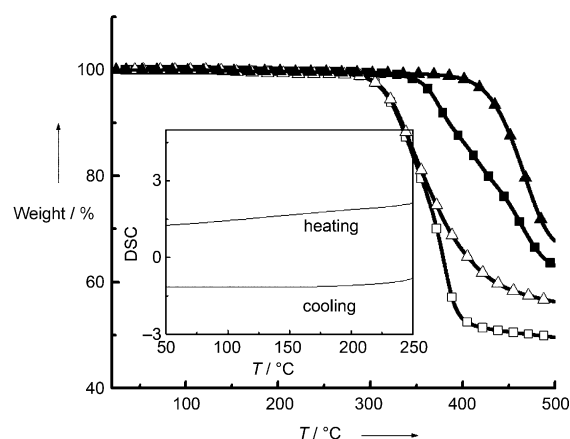


Figure 1. TGA plots of PBDTTT-E (□), PBDTTT-E-T (■), PBDTTT-C (△), and PBDTTT-C-T (▲) with a heating rate of 10°C min⁻¹ under an inert atmosphere; the inset shows the DSC plot of PBDTTT-C-T.

(T_d) at 5% weight loss of PBDTTT-E and PBDTTT-C are approximately 320°C because of the elimination of the alkoxy groups from their BDT units; therefore, when the alkoxy groups were replaced with alkylthienyl groups, the stability of the polymers improved greatly. The T_d values of the polymers are provided in the experimental section. Through differential scanning calorimetry (DSC) measurements, we found that neither endo- nor exothermic processes were observed in the range of 0–280°C. As a representation, the DSC plot of PBDTTT-C-T is shown in the inset of Figure 1.

The absorption spectra of the four polymers in a chloroform solution and of solid films are shown in Figure 2. The absorption data were collected and are listed in Table 1.

Table 1: Absorption spectral properties and molecular energy level data of the polymers.

Polymer	λ_{max} [nm]		E_g^{opt} [eV]	HOMO [eV]	LUMO [eV]
	Solution ^[a]	Film			
PBDTTT-E	625	675	1.63	-5.04	-3.19
PBDTTT-E-T	637	692	1.58	-5.09	-3.22
PBDTTT-C	632	682	1.60	-5.07	-3.21
PBDTTT-C-T	629	692	1.58	-5.11	-3.25

[a] Dilute solution in chloroform.

Clearly, the main absorption bands of PBDTTT-E-T and PBDTTT-C-T are red-shifted and broadened to some extent when compared to that of their alkoxy-substituted analogues. This difference can be ascribed to the enhanced intermolecular π - π interaction^[29] that results from the extended conjugation of the alkylthienyl side chains of the 2D conjugated polymers. The absorption edge of the PBDTTT-E and PBDTTT-C films is at 762 nm and 776 nm, respectively, which are red-shifted to 787 nm and 788 nm, respectively for the PBDTTT-E-T and PBDTTT-C-T films. The band gap of PBDTTT-E-T is 1.58 eV, which is reduced by 0.05 eV in comparison with that of PBDTTT-E (1.63 eV), and the band

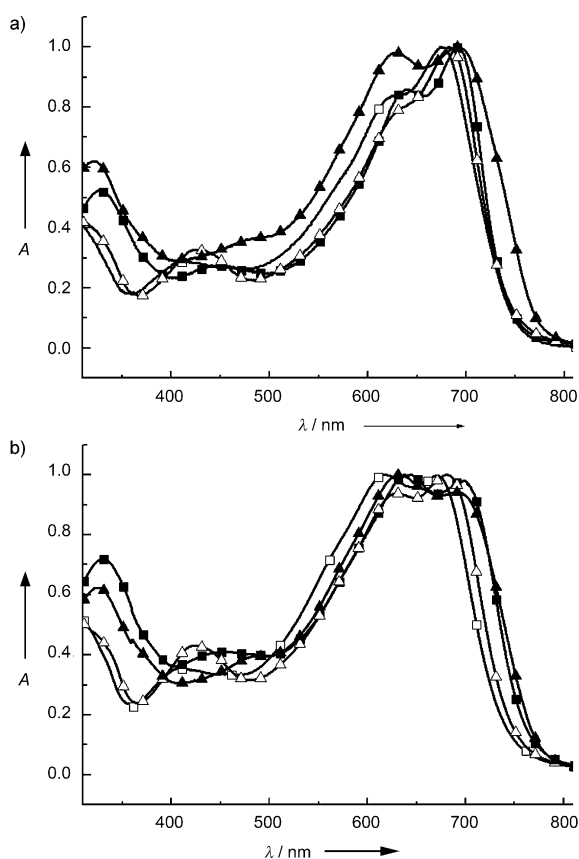


Figure 2. Normalized UV/Vis absorption spectra of PBDTTT-E (\square), PBDTTT-E-T (\blacksquare), PBDTTT-C (\triangle), and PBDTTT-C-T (\blacktriangle) in a chloroform solution (a) and as a solid film on quartz (b).

gap of PBDTTT-C-T is 1.58 eV, which is reduced by 0.02 eV in comparison with that of PBDTTT-C (1.60 eV).

Electrochemical cyclic voltammetry (CV) was employed to measure the molecular energy levels of the materials.^[30] The molecular energy level values of the polymers are listed in Table 1. When the alkoxy side chain was replaced by the alkylthiophene conjugated side chain, the HOMO and LUMO levels of the polymers are shifted to slightly lower energy levels. For example, both the HOMO and the LUMO of PBDTTT-C-T are 0.04 eV lower than those of PBDTTT-C. The lower HOMO of the 2D conjugated BDT polymers should be beneficial for a higher V_{oc} value for the PSCs having the polymers as donors, because the V_{oc} value of the PSC is related to the difference between the energy levels of the LUMO of the electron acceptor and the HOMO of the electron donor.^[20]

The optimized fabrication process of a PSC device using PBDTTT-E and PBDTTT-C was reported in previous work, and were therefore used to make the PSC devices herein.^[6a] For the PSCs based on PBDTTT-E and PBDTTT-E-T, a donor/acceptor (D/A) ratio of 1:2 was used in the active layers; for the PSCs based on PBDTTT-C and PBDTTT-C-T, a D/A ratio of 1:1.5 was used. About 3% (1,8-diiodooctane (DIO)/1,2-dichloro-

benzene (DCB), v/v) of DIO as an additive is helpful to get better photovoltaic results.^[31]

The photovoltaic results of the PSC devices fabricated under the optimal conditions are listed in Table 2, and the corresponding J - V curves of these devices are shown in Figure 3a. The PSCs based on the 2D conjugated polymers clearly exhibit better photovoltaic performances than the PSCs based on the alkoxy-substituted analogues. The V_{oc} values of the PSCs based on PBDTTT-E-T and PBDTTT-C-T are a little higher than those of the corresponding polymers PBDTTT-E and PBDTTT-C, which should benefit from the lower HOMO energy levels of the

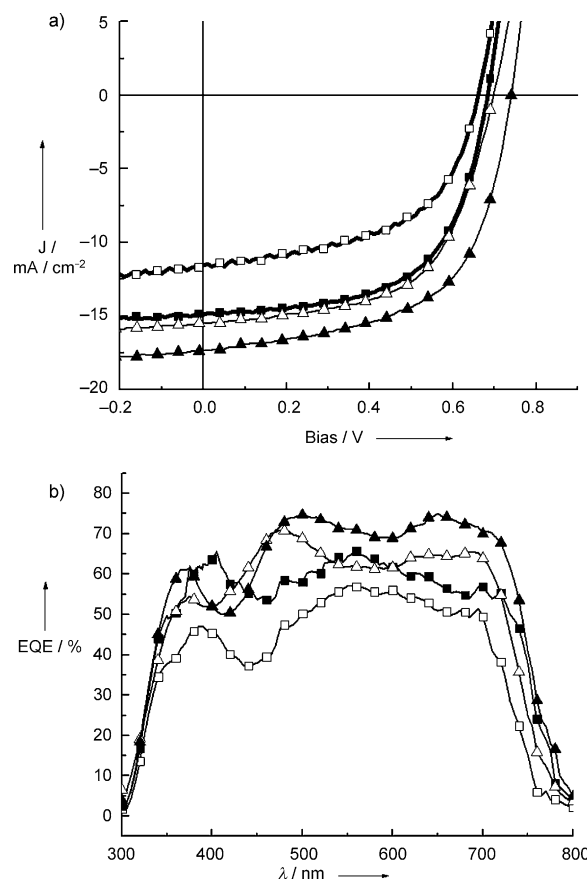


Figure 3. a) J - V curves of the polymer solar cells based on PBDTTT-E (\square), PBDTTT-E-T (\blacksquare), PBDTTT-C (\triangle), and PBDTTT-C-T (\blacktriangle) under illumination of AM 1.5G, 100 mWcm^{-2} . b) EQE curves of the corresponding polymer solar cells.

Table 2: Photovoltaic properties of the PSCs based on the polymers, the hole mobilities of the blends of the polymers, and the PC₇₀BM and FET hole mobilities of the polymers.

Polymer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	μ_{hole}^a [$\text{cm}^2 \text{Vs}^{-1}$]	μ_{hole}^b [$\text{cm}^2 \text{Vs}^{-1}$]
PBDTTT-E	0.66	11.53	54.7	4.16	1.50×10^{-3}	8.2×10^{-4}
PBDTTT-E-T	0.68	14.59	62.6	6.21	6.74×10^{-3}	1.2×10^{-3}
PBDTTT-C	0.70	15.51	59.2	6.43	5.53×10^{-4}	8.6×10^{-4}
PBDTTT-C-T	0.74	17.48	58.7	7.59	0.27	1.1×10^{-2}

[a] Measured by using the space-charge-limited current (SCLC) method. [b] Measured by using the organic field-effect transistor (OFET) method.

polymers having the thiophene side group. The J_{sc} values of the PSCs based on PBDTTT-E-T and PBDTTT-C-T are significantly increased in comparison with those of PBDTTT-E and PBDTTT-C, respectively, which is probably due to the improved hole mobility and the broadened absorption of the 2D conjugated structure. The increase in both the V_{oc} and J_{sc} values results in great improvement of the PCEs of the devices. The PCE is increased by approximately 50% for PBDTTT-E-T relative to PBDTTT-E, and approximately 20% for PBDTTT-C-T relative to PBDTTT-C. Notably, the PCE of the PSC based on PBDTTT-C-T reached 7.59% in comparison to 6.43% for the device based on PBDTTT-C.

To find the reason for the higher J_{sc} value, the hole mobilities, μ_{hole} , of the blends of the polymers and PC₇₀BM were measured by using the space-charge-limited current (SCLC) method,^[32] and the results are listed in Table 2. Surprisingly, the μ_{hole} value for PBDTTT-C-T reached an order of $2 \times 10^{-1} \text{ cm}^2 \text{ Vs}^{-1}$, which is an increase of three orders compared with that ($5 \times 10^{-4} \text{ cm}^2 \text{ Vs}^{-1}$) of PBDTTT-C. The hole mobilities of the four polymers were also measured by field-effect transistors (FETs) and listed in Table 2. It can be seen that the same trend was observed as that for the SCLC method; the two BDT-T-based polymers exhibited higher hole mobilities than the two BDT-O-based polymers. It seems that the higher J_{sc} values of the PSC devices based on the 2D conjugated polymers might be ascribed to their higher hole mobilities.

The accuracy of the photovoltaic measurements can be confirmed by the external quantum efficiency (EQE) of the devices. Figure 3b shows the EQE curves of the PSCs fabricated under the same optimized conditions as those used for the J - V measurements. Obviously, the EQE values for PBDTTT-E-T and PBDTTT-C-T are all higher than those of PBDTTT-E and PBDTTT-C, which agree with the higher J_{sc} values of the devices derived from PBDTTT-E-T and PBDTTT-C-T. To evaluate the accuracy of the photovoltaic results, the J_{sc} values were calculated by integrating the EQE data with the AM 1.5G reference spectrum. The J_{sc} values obtained using integration and J - V measurements are rather close (within 6% error). For example, the calculated J_{sc} value of the device based on PBDTTT-C-T was 16.5 mA cm^{-2} , which is 5.6% lower than the value obtained from the J - V curve. The EQE results indicate that the photovoltaic results are reliable.

In conclusion, two new 2D conjugated copolymers based on 4,8-bis(5-(2-ethyl-hexyl)-thiophene-2-yl) BDT, PBDTTT-E-T and PBDTTT-C-T, were synthesized by copolymerizing the BDT-T unit with TT-E or TT-C units, and used as donor materials in PSCs. To make a clear comparison, the corresponding polymers based on 4,8-bis(2-ethyl-hexyloxy) BDT, PBDTTT-E and PBDTTT-C, were also synthesized and characterized in parallel. The 2D conjugated polymers exhibit better thermal stabilities, red-shifted absorption spectra, lower HOMO and LUMO energy levels, significantly higher hole mobility, and greatly improved photovoltaic properties, in comparison with their corresponding alkoxy-substituted analogues. The results indicate that 2D conjugated BDT will potentially be a highly useful unit for the design of high performance photovoltaic polymers.

Experimental Section

Materials: 2-(2-ethyl-hexyl)thiophene (**1**), 4,8-dehydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (**2**), 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT-O), 2-ethylhexyl 4,6-dibromothiopheno[3,4-*b*]thiophene-2-carboxylate (TT-E), and 1-(4,6-dibromothiopheno[3,4-*b*]thiophen-2-yl)-2-ethylhexan-1-one (TT-C) were purchased from Solarmer Materials Inc.; [Pd(PPh₃)₄] was purchased from Frontiers Scientific Inc. All of these chemicals were used as received. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. The other materials were commercially available and used as received.

Instruments: ¹H and ¹³C NMR spectra were measured on a Bruker arx-400 spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV-Vis spectrophotometer. The molecular weight of polymers was measured by the GPC method, and polystyrene was used as a standard by using chloroform as eluent. TGA measurements were performed on a TA Instruments, Inc., TGA-2050. DSC measurements were performed on a TA Instruments, Inc., MDSC-2910. The electrochemical cyclic voltammetry experiments were conducted on a Zahner IM6e Electrochemical Workstation with glassy carbon disk, Pt wire, and a 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.

Fabrication of polymer solar cells. Polymer solar cell devices were fabricated under conditions as follows: After spin-coating a 35 nm layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) onto a precleaned indium/tin oxide (ITO) coated glass substrates, the polymer/PCBM blend solution was spin-coated. The concentration of the polymer/PCBM blend solution used in this study for spin-coating was 10 mg mL⁻¹ (polymer/*o*-dichlorobenzene), and *o*-dichlorobenzene was used as the solvent. The additive, DIO, was added prior to spin-coating process. The thickness of the active layer was controlled by changing the spin speed during the spin-coating process and measured on an Ambios Tech. XP-2 profilometer. The devices were completed by evaporating Ca/Al metal electrodes with an area of 4 mm² as defined by masks.

Synthesis: 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**3**). Using a 250 mL argon purged flask, *n*-butyl lithium (2.88 M, 4.39 mL) was added dropwise to a solution of 2-(2-ethylhexyl)thiophene, compound 1-EH, (2.53 g, 12.9 mmol) in THF (60 mL) at 0 °C. The mixture was then warmed to 50 °C and stirred for 1 hour. Subsequently, 4,8-dehydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (0.7 g, 3.18 mmol) was added to the reaction mixture, which was then stirred for 1 h at 50 °C. After cooling the reaction mixture to ambient temperature, a mixture of SnCl₂·2H₂O (5.6 g, 25 mmol) in 10% HCl (12 mL) was added and the mixture was stirred for additional 1.5 h, after which it was poured into ice water. The mixture was extracted with diethyl ether twice and the combined organic phases were concentrated to obtain the crude compound 3-EH. Further purification was carried out by column chromatography on silica gel using petroleum ether as the eluent to obtain pure compound 3-EH as pale yellow viscous liquid (0.95 g, yield 52%). ¹H NMR (CDCl₃, 400 MHz), δ = 7.67(d, 2H), 7.46 (d, 2H), 7.32 (d, 2H), 6.92 (d, 2H), 2.87 (d, 4H), 1.75 (m, 2H), 1.53–1.18 (br, 16H), 0.92–0.83 ppm (m, 12H). ¹³C NMR (CDCl₃, 100 MHz), δ = 145.19, 139.06, 137.51, 136.44, 127.61, 127.30, 125.30, 124.03, 123.29, 41.55, 34.33, 32.53, 29.42, 25.83, 23.06, 15.67, 11.00 ppm.

2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT-T). A solution of compound (**2**) (0.58 g, 1.0 mmol) in THF (20 mL) at 0 °C was placed in a 50 mL argon purged flask, and then *n*-butyl lithium (2.88 M, 0.73 mL) was added. The reaction mixture was then stirred for 2 h at ambient temperature. Subsequently, chlorotrimethylstannane (1.0 M in hexane, 2.4 mL) was added and the mixture was stirred for an additional 1 h at ambient temperature. Then the mixture was extracted by diethyl ether and the combined organic phase was concentrated to obtain

compound BDT-T-EH. Further purification was carried out by recrystallization using ethanol to obtain the pure compound BDT-T-EH as a light-yellow solid (0.77 g, yield 84%). ¹H NMR (CDCl₃, 400 MHz), δ = 7.69(s, 2H), 7.33 (d, 2H), 6.91 (d, 2H), 2.88 (d, 4H), 1.73 (m, 2H), 1.57–1.35 (br, 16H), 0.94 (m, 12H), 0.40 ppm (s, 18H) ¹³C NMR (CDCl₃, 100 MHz), δ = 145.39, 143.28, 142.24, 138.00, 137.31, 131.18, 127.54, 125.30, 122.41, 41.57, 34.25, 32.52, 28.97, 25.81, 23.04, 15.42, 10.99, –8.34 ppm.

General method of polymerization by Stille coupling. The bis(trimethyltin) BDT monomer (0.5 mmol) and the dibromo TT monomer (0.5 mmol) were mixed in 10 mL of toluene and 2 mL of DMF. After being purged with argon for 5 min, [Pd(PPh₃)₄] (30 mg) was added as the catalyst, and the mixture was then purged with argon for 25 min. The reaction mixture was stirred and heated to reflux for 16 h. Then the reaction mixture was cooled to room temperature, and the polymer was precipitated by addition of 50 mL methanol, filtered through a Soxhlet thimble. The precipitate was then subjected to Soxhlet extraction with methanol, hexanes, and chloroform. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum. The yield and elemental analytical results of the polymers are as follows.

PBDTTT-E. Yield: 37%. Elemental analysis calcd (%) for C₄₁H₅₄O₄S₄: C 66.62, H 7.36; found: C 66.93, H 7.36. M_n = 33k, PDI = 2.8. T_d = 318 °C.

PBDTTT-E-T. Yield: 29%. Elemental analysis calcd (%) for C₄₉H₅₈O₂S₆: C 67.54, H 6.71; found: C 66.20, H 6.76. M_n = 21k, PDI = 3.4. T_d = 368 °C.

PBDTTT-C. Yield: 51%. Elemental analysis calcd (%) for C₄₀H₅₂O₃S₄: C 67.75, H 7.39; found: C 67.94, H 7.36. M_n = 21k, PDI = 3.7. T_d = 320 °C.

PBDTTT-C-T. Yield: 58%. Elemental analysis calcd (%) for C₄₈H₅₆O₅S₆: C 68.52, H 6.71; found: C 68.33, H 6.83. M_n = 20k, PDI = 3.2. T_d = 428 °C.

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