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Synthesis of a polythieno[3,4-b]thiophene derivative with a low-lying HOMO level and its application in polymer solar cells[†]

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A planar benzodithiophene with lower HOMO was copolymerized with the thieno[3,4-b]thiophene unit to obtain a new low band gap polymer of PBDPTT-C, which exhibited a higher opencircuit voltage ($V_{\rm oc}$) of 0.8 V and a promising efficiency of 5.2%.

In recent years, tremendous developments in polymer solar cells (PSCs) intrigue more researchers to focus on studying new conjugated polymer materials. The design and preparation of low band gap (LBG) conjugated polymer donor materials has been proved to be an effective approach to realize high power conversion efficiencies (PCEs) for the PSCs.¹⁻¹⁰ LBG polymers exhibit broad absorption range, which extend to the near-infrared region, correspondingly enhancing the short-circuit current (J_{sc}) and PCE value. Besides the broad absorption range, appropriately lowering the HOMO energy level of the LBG polymers is also very important for achieving higher open-circuit voltage (V_{oc}) and higher PCEs, because the V_{oc} of PSC is closely related to the gap between the HOMO level of the donor and LUMO level of the acceptor.^{11,12} Therefore, to lower the HOMO level of the LBG polymers is one of the effective ways to get highly efficient donor material of PSCs.

Thieno[3,4-b]thiophene (TT)-benzo[1,2-b:4,5-b']dithiophene (BDT)-based LBG polymers (PBDTTTs) are one kind of star photovoltaic polymer donor materials in PSCs, and several promising results have been reported in the past three years.^{4,6,7} In this series of materials, the HOMOs of PBDTTTs have been tuned effectively by introducing electron-withdrawing functional groups on the TT unit and hence the V_{oc} of the PSC based on PBDTTTs has been successfully improved from 0.6 V to 0.78 V.⁴ For example, the HOMO level of PBDTTTs, as shown in Scheme 1, can be lowered from -5.01 eV (for PBDTTT-E in Scheme 1) to -5.12 eV (for PBDTTT-C in Scheme 1) by replacing the carboxylate group with the carbonyl group,¹³ and when a fluorine was introduced, the HOMO of PBDTTT-CF is further lowered to -5.22 eV.⁴ Although the





Scheme 1 Molecular structures of PBDTTTs and PBDPTT-C.

introduction of fluorine reduced the HOMO level of PBDTTTs effectively, the synthesis routes of the fluorine substituted derivatives are quite tedious and also their HOMO levels are still not deep enough to get high V_{oc} materials. Thus it would be useful and also necessary to find another effective way to lower the HOMO level of TT-based LBG polymers.

Two isomers of benzodithiophene, benzo[1,2-b:4,5-b']dithiophene¹⁴(BDT) and benzo[2,1-b:3,4-b']dithiophene^{8,15} (named as BDP for easier discrimination), have been proved to be useful conjugated building blocks in photovoltaic polymer materials. However, although the relationship between molecular structures and photovoltaic properties of PBDTTTs has been well investigated, the alternate copolymer of BDP and TT is still not studied.^{15,16} From molecular simulation and experimental results in some papers, the HOMO levels of the homopolymers of BDT and BDP are -5.16 eV and -5.70 eV, respectively.^{8b,14} Obviously, the latter exhibits a lower HOMO level than that of the former, which indicates that the new polymer containing the BDP unit can show a lower-lying HOMO than those similar structure based PBDTTT-C polymers. Therefore, a new conjugated polymer, poly [(4,5-bis-(3,7-dimethyloctyl)-benzo[2,1-b:3,4-b']dithiophene-2,7-diyl)-alt-(2-(2-ethyl-hexanoyl)-thieno[3,4-b]thiophene-4,5diyl)] (PBDPTT-C), as shown in Scheme 1, was designed and synthesized in this work.

PBDPTT-C was prepared through the synthetic route shown in Scheme 2. In order to keep good solubility, branched alkyl groups, 3,7-dimethyloctyl (DMO), were used as the substituents on 4 and 5 positions of the BDP unit. And on the TT unit, the 2-ethylhexynoyl group was used to keep a good electron-withdrawing effect of the side group. The dialkyl-yne, compound **2**, was prepared through two steps by lithium-halogen exchange reaction with $\sim 70\%$ yield for each step. Compound **4** was synthesized from compound **3** with 3 equiv. of dialkyl-yne in the presence of 5% equiv. of palladium(II) acetate as a catalyst by an annulative coupling

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Scheme 2 Synthetic route of the copolymer PBDPTT-C. (i) 1-bromo-3,7-dimethyloctane, DMSO, 0 °C, then 12 h at ambient temp.; (ii) *n*-butyllithium, THF, -25 °C, 20 min; hexamethylphosphoramide and 1-bromo-3,7-dimethyloctane; (iii) Zn, HOAc, CH₃OH, 0 °C; (iv) compound **2**, Pd(OAc)₂, Et₃N, DMF, 130 °C, 12 h; (v) NBS, DMF, 15 h; (vi) *n*-butyllithium, THF, -78 °C, 30 min, then trimethyltin chloride, 1 h at ambient temp.; (vii) Pd(PPh₃)₄, toluene, DMF, 110 °C, 18 h.

reaction in 50% isolated yields. The BDP monomer, **M1**, can be prepared directly from compound **4**; however, since compound **4** can be easily oxidized by the air, it would be better to make the bromide, compound **5**, for long term storage. The TT monomer, **M2**, was synthesized by the reported method.¹³ The final product, PBDPTT-C, was prepared through the Stille coupling reaction, which shows a low molecular weight ($M_w = 16.5$ K) and a rather big polydispersity index (PDI = 2.8). The polymer can be readily dissolved in common organic solvents like toluene, chlorobenzene, tetrahydrofuran or others, and also possesses good film-forming ability. It has to be mentioned that since **M1** cannot be purified by flash column or recrystallization, we tried different polymerization conditions but failed to make a higher molecular weight polymer.

Fig. 1 shows the absorption spectra of PBDPTT-C solution and film. The main absorption peak and the absorption onset of the solution are at 619 nm and 752 nm, respectively, and the thin film exhibits a peak at 662 nm and a onset of 800 nm. The obvious red-shifted absorption can be attributed to the strong aggregation of the polymer in the solid state. Based on the absorption edge, optical band-gap (E_g^{opt}) of PBDPTT-C is 1.55 eV, which is similar with the optical band gap of PBDTTTS.⁴

Electrochemical cyclic voltammetry is employed to investigate the redox behavior.¹⁷ The cyclic voltammogram (see Fig. 2) shows that there is a reversible p-doping/dedoping (oxidation/ re-reduction) process at a positive potential range and an irreversible n-doping/dedoping (reduction/reoxidation) process



Fig. 1 Normalized UV-Vis absorption spectra of PBDPTT-C in diluted chloroform solution and as a solid thin film.



Fig. 2 Cyclic voltammogram of a PBDPTT-C film on a platinum electrode in acetonitrile solution containing 0.1 mol L^{-1} Bu₄NPF₆ at a scan rate of 20 mV s⁻¹.

at a negative potential range. Based on the onset oxidation potentials (E_{ox}) and the onset reduction potentials (E_{red}) of the polymer, HOMO and LUMO energy levels and the energy gap of the polymer were calculated: E_{HOMO} is -5.35 eV, E_{LUMO} is -3.80 eV, and the electrochemical bandgap (E_g^{cc}) of PBDPTT-C is 1.58 eV which well matches its optical bandgap of 1.55 eV. As listed in Table 1, for PBDTTT-CF which exhibits a lowest HOMO level in PBDTTTs, the HOMO level value is -5.22 eV.⁴ In comparison with PBDTTTs, PBDPTT-C exhibits a deeper HOMO level, which is helpful to get higher V_{oc} in PSCs.

The mobility of a blend of PBDPTT-C and PC₇₀BM was measured by the space-charge-limited-current (SCLC) method. A hole mobility of 2.7×10^{-4} cm² V⁻¹ s⁻¹ was observed. PSC devices were fabricated with a structure of ITO/PEDOT:PSS/ PBDPTT-C: PC₇₀BM/Ca/Al. Different donor/acceptor weight ratio values were tested to optimize the photovoltaic process, the devices results are listed in Table 2. It was found that the best photovoltaic performance was obtained under a 1:2 ratio (w/w, polymer/PC₇₀BM) by using dichlorobenzene with 3% (v/v) DIO (diiodooctane)¹⁸ as the solvent to make solution for a spin-coating process of the active layers. As shown in the AFM images (see ESI†), we found that when DIO was used as an additive, smaller domain size can be observed in the active layer. Fig. 3 shows the *I*–*V* curve of the PBDPTT-C-based PSC device with champion performance. It shows that under

Table 1 Properties of several TT-based polymers

	HOMO/eV	$E_{\rm g}^{ m opt}/{ m eV}$	$V_{\rm oc}/{ m V}$	Ref.
PBDTT-E	-5.01	1.60	0.62	4
PBDTTT-C	-5.12	1.59	0.70	4
PBDTTT-EF	-5.12	1.63	0.74	6
PBDTTT-CF	-5.22	1.58	0.76	4
PBDPTT-C	-5.35	1.55	0.82	_

Table 2 Photovoltaic results based on PBDPTT-C:PC $_{70}$ BM with different weight ratios

D:A (weight ratio)	$V_{\rm oc}/{ m V}$	$J_{\rm sc}/{\rm mA~cm^{-2}}$	FF (%)	PCE (%)
1:1	0.79	-9.52	53.7	4.04
1:2	0.78	-10.98	51.1	4.38
$1:2^{a}$	0.82	-11.76	54.1	5.21
1:3	0.80	-7.17	42.2	2.42
4 20/ DIO 11:				

^{*a*} 3% DIO additive (v/v).



Fig. 3 I-V curve of the PSC device based on PBDPTT-C under illumination of AM 1.5G, 100 mW cm⁻².

the illumination of AM 1.5G, 100 mW cm⁻², the device exhibited an open circuit voltage (V_{oc}) of 0.82 V, a short circuit current (J_{sc}) of 11.76 mA cm⁻², a fill factor (FF) of 0.54, and a power conversion efficiency (PCE) of 5.21%. As listed in Table 1, benefitting from the deeper HOMO level value, the V_{oc} of the device based on PBDPTT-C is higher than that of the PSCs based on PBDTTTs.⁴ Since the length of alkyl side chains and the molecular weight influence the photovoltaic properties of a conjugated polymer greatly, the alkyl side chains and the molecular weight of PBDPTT-C should be optimized further to explore its photovoltaic properties fully. For example, different side chains, like octyl, dodecyl, or 2-ethyl-hexyl, can be used to get an optimized molecular structure.

From the external quantum efficiency (EQE) plot of the PSC based on PBDPTT-C/PC₇₀BM (3% additive), as shown in Fig. 4, it can be seen that the device has a broad response range in the whole visible range, from 380 nm to 780 nm, which is much similar to the PSC devices based on the PBDTTTs. However, the maximum EQE value of PBDPTT-C-based PSC device, which is near to 50%, is lower than the best value of *ca*. 70% for the PBDTTT-based PSCs, which agrees with the lower J_{sc} of the device based on PBDPTT-C in comparison with that of the PBDTTTs-based devices.

In conclusion, a new thieno[3,4-b]thiophene-based LBG polymer, PBDPTT-C, was synthesized for the application as donor material in PSCs. PBDPTT-C exhibited a deeper



Fig. 4 EQE curves of the PSCs based on PBDPTT-C.

HOMO level at -5.35 eV, a similar narrow bandgap of 1.55 eV and a similar broad visible absorption in comparison with PBDTTTs. The PSC based on PBDPTT-C as a donor and PC₇₀BM as an acceptor with a weight ratio of 1:2, w/w showed a high PCE of 5.21% with a higher $V_{\rm oc}$ of 0.82 V. Moreover, even higher $V_{\rm oc}$ can be expected if the fluorine-substituted thieno[3,4-b]thiophene, like that used in PBDTTT-CF,⁴ was used in the copolymer. Furthermore, since the photovoltaic properties of conjugated polymers are susceptible to molecular structural changes, even a very little change in their side chain can make big difference in photovoltaic properties. Further optimization of the molecular structure would be necessary to fully explore the potential of the copolymers (PBDPTTs) of BDP and TT. Therefore, PBDPTTs should be another type of promising high performance photovoltaic polymer donor materials for PSCs.

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