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## Molecular Design and Synthesis of Low-Bandgap Polymers Containing Furan in the Main Chain

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**Abstract:** To improve the solubility and optimize energy levels of low-bandgap polymers, two conjugated polymers based 4,7-bis(5'-bromo-2'-thiophene)-2,1,3-benzodithiazole (DTBT) and 4,7-bis(5'-bromo-2'-furan)-2,1,3-benzodithiazole (DFBT) as acceptor were prepared by donor-acceptor alternating strategy. Through replacing thiophene unit with furan unit in the polymer main chain, the polymer (PCDFBT) with furan unit in the backbone exhibited a deeper highest occupied molecular orbital (HOMO) energy levels compared with the polymer (PCDTBT) containing thiophene unit in the backbone. Furthermore, the maximum absorption peak of the furan substituent polymer PCDFBT was red shift 20 nm compared with PCDTBT, which indicated PCDFBT showed better exciton harvesting ability.

**Key words:** low-bandgap; thiophene; furan; solubility; energy level

## 基于主链中含有呋喃基窄能带隙聚合物的设计与合成

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**摘要:** 为了提高窄能带隙聚合物的溶解性和优化窄能带隙聚合物的能级分布,分别以 4,7-双(5'-溴-2'-噻吩)-2,1,3-苯并噻唑(DTBT)和 4,7-双(5'-溴-2'-呋喃)-2,1,3-苯并噻唑(DFBT)为受体,采用给体-受体交替排列的策略,分别合成了 2 个窄能带隙共轭聚合物(PCDTBT, PCDFBT)。通过取代主链中的噻吩基团,基于呋喃的窄能带隙聚合物 PCDFBT 具有更好的溶解性和更低的最高未占轨道。而且,相比聚合物 PCDTBT,呋喃取代的聚合物 PCDFBT 的最大吸收峰红移了 20nm,这表明聚合物 PCDFBT 具有更好的光学吸收能力。

**关键词:** 窄能带隙;噻吩;呋喃;溶解性;能级分布

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Polymer solar cells (PSCs) are a promising alternative for producing clean and renewable energy because of their unique advantages, such as low in cost, light weight, as well as their potential application in flexible large-area device<sup>[1-3]</sup>. Usually,

PSCs adopt a bulk-heterojunction (BHJ) structure, which blends donor and acceptor materials as active layer, and in most cases, fullerene derivatives such as [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) or [6,6]-phenyl-C<sub>71</sub>-

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butyric acid methyl ester (PC<sub>71</sub>BM), are used as acceptors. As for a polymer to serve as an effective donor material, it should possess good film-forming properties, strong absorption ability, high hole mobility, and suitable energy levels, simultaneously.

To harvest much more photons and hence to increase the short circuit current ( $J_{sc}$ ), large quantities of low-bandgap polymers have been designed and used for PSCs through donor-acceptor alternating strategy<sup>[4-6]</sup>. Unfortunately, it is still a challenge to prepare a low-bandgap polymer with a deep highest occupied molecular orbital (HOMO) energy levels and good solubility. In this regard, it is well worth exploring a way to synthesize polymers with a lower HOMO energy level and good solubility. Lately, Fluorination of the polymer backbone is considered as an impactful way to lower HOMO level<sup>[7-11]</sup>, but with increasing number of fluorine atom in the polymer backbone, the compatibility with acceptor became poor, and it is a tough task to synthesize a fluorinated monomer<sup>[12]</sup>. Therefore, it is necessary to develop a new way to optimize the energy level.

Until now, polymers based thiophene have received considerable attention, just a limited research has focused on furan-containing conjugated polymers for organic photovoltaic devices, although furan shows similar optical and electronic properties with thiophene. Compared with thiophene, furan possess these features: a) Due to smaller size of oxygen atom, there is lesser steric hindrance between the furan and neighboring unit. Consequently, incorporation of furan into the polymer backbone could improve the solubility greatly. b) Oxygen atom is an electron-withdrawing group relative to sulfur atom, thence, introduction of furan into the conjugated polymer could lower the lowest unoccupied molecular orbital (LUMO) and HOMO energy levels relative to thiophene counterpart<sup>[13-15]</sup>. Overall, these properties enable furan to be used as an alternative to thiophene and thiophene-based building units in the design and synthesis of low-bandgap conjugated poly-

mers with efficient solar cell performance.

On the basis of these theoretical analysis mentioned above, we intended to introduce furan into the conjugated polymer main chain. It has been reported that 4,7-dithien-5-yl-2,1,3-benzodithiazole (DTBT) is one of the excellent acceptor units to synthesize donor-acceptor conjugated polymers by copolymerizing with various donor units<sup>[16-18]</sup>. Therefore, we replaced thiophene unit with furan unit in DTBT. As for donor, 2,7-carbazole is chosen because polymers based this donor exhibited a suitable HOMO level and good charge transfer ability<sup>[19-23]</sup>. Furthermore, compared to the corresponding benzene ring based materials, thiophene based material has an even lower aromaticity and can more easily pack in planar structures, consequently, end-capping with thiophene could improve performance by making the devices less sensitive to active layer thickness and to thermal degradation. Herein, we report application of DTBT and 4,7-bis(5'-bromo-2'-furan)-2,1,3-benzodithiazole (DFBT) as acceptor to synthesize two donor-acceptor alternating polymers (PCDTBT and PCDFBT), and their optical and electrochemical properties are discussed.

## 1 Experimental

### 1.1 Materials

2-furanboronic acid, 2-thienylboronic acid, 2-bromothiophene, potassium carbonate ( $K_2CO_3$ ), tri(o-tolyl)phosphine ( $P(o-Tol)_3$ ), tetrakis(triphenylphosphine) palladium (0) ( $Pd(PPh_3)_4$ ), tris(dibenzylideneacetone) dipalladium (0) ( $Pd_2dba_3$ ) were purchased from Sigma-Aldrich. Bromosuccinimide (NBS) and tetraethylammonium hydroxide ( $Et_4NOH$ ) were purchased from Tokyo Chemical Industry (TCI). 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole was purchased from Luminescence Technology Corp. (Lumtec).

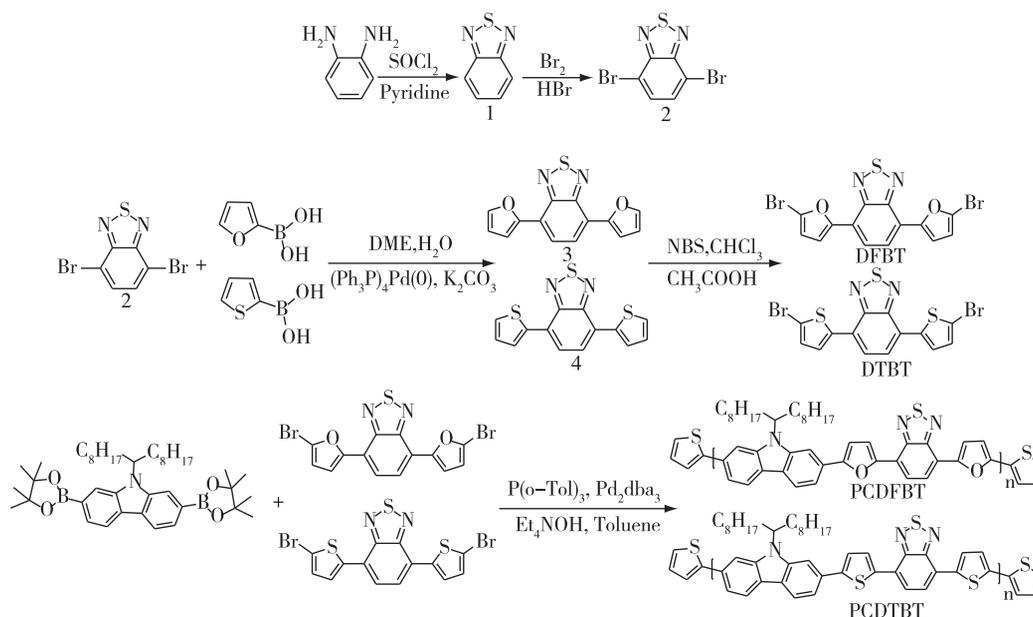
### 1.2 Measurements

<sup>1</sup>H NMR spectra were recorded on a JEOL

JNM-AL400 (400 MHz) in deuterated chloroform. The relative molecular weights were determined by gel permeation chromatography (GPC) at room temperature on a waters instrument calibrated with polystyrene standards with dichlorobenzene as an eluent. Absorption spectra were measured with a Hitachi U-3500. The HOMO energy levels of low-bandgap polymers (PCDTBT and PCDFBT) neat films were estimated by photoelectron yield spectroscopy (Riken Keiki, AC-3) spectrophotometer.

### 1.3 Synthesis of Monomers and Polymers

Scheme 1 shows the synthetic routes of com-



Scheme 1 Synthetic routes of the monomers and polymers

**Compound 1:** Thionyl chloride (53mL) and o-phenylenediamine (10.8g, 100mmol) were added into a three-necked round-bottom flask. Then pyridine (1mL) was added at 0°C, and the mixture was heated slowly to reflux for 24h. The mixture was cooled down to room temperature, and the excessive thionyl chloride was removed under reduced pressure. The remnant mixture was poured into water (250mL). The crude product was purified by distillation, extracted with dichloromethane (100mL), dried over anhydrous magnesium sulfate ( $\text{MgSO}_4$ ), and finally filtered. The extracted liquid was concentrated to obtain yellow compound 1 in 82% yield.

pounds 1-4, the target monomers (DFBT and DTBT), and the polymers. The synthesis of compound 1 and 2 has been described in our previous report [24]. And compounds 3-4, monomers DFBT and DTBT were prepared in a similar method according to the reference [25-26]. Finally, polymers PCDTBT and PCDFBT were synthesized according to reference [19].

**Compound 2:** Compound 1 (13.6g, 100mmol) and hydrobromic acid (40%, 30mL) were added in a three-necked round-bottom flask, and heated to reflux slowly. Then, bromine (48.0g, 300mmol) was added. When the bromine was completely added, the mixture became a suspension solution. The hydrobromic acid (40%, 15mL) was added again and the reaction mixture was kept reflux for another 2.5h. And then, the reaction mixture was filtrated, washed with water, and recrystallized from chloroform. Finally, compound 2 was obtained as yellow needle crystal in 75% yield.

**Compound 3:** Compound 2 (1.46g, 4.97mmol) and 2-furanboronic acid (1.54g,

13.76mmol), and tetrakis (triphenylphosphine) palladium (0) ( $\text{Pd}(\text{PPh}_3)_4$ ) (111.40mg, 0.096mmol) were dissolved in 1, 2-dimethoxyethane (DME) (80mL), followed by the addition of aqueous potassium carbonate ( $\text{K}_2\text{CO}_3$ ) ( $2\text{mol}\cdot\text{L}^{-1}$ , 20mL), and the reaction mixture was vigorously stirred at  $90^\circ\text{C}$  for 24h under a nitrogen atmosphere. After cooling to room temperature, the reaction solution was extracted with methylene chloride, the combined organic layers were washed with  $1\text{mol}\cdot\text{L}^{-1}$  aqueous solution of sodium hydroxide and water alternatively, dried over anhydrous  $\text{MgSO}_4$ , concentrated under reduced pressure. Further purification was performed using silica gel column chromatography (methylenechloride/hexane=2:3 as eluent), and then recrystallized from ethanol, red needle crystals were obtained (yield: 57%). The compound 4 was synthesized in a similar method (yield: 63%).

**Monomer DFBT:** Under nitrogen, compound 3 (142.18mg, 0.57mmol) and bromosuccinimide (NBS) (267mg, 1.50mmol) were dissolved in chloroform (5mL) and acetic acid (5mL), and the resulting solution was vigorously stirred at room temperature for 6h. The reaction solution was extracted with chloroform and the organic phase was washed with 10% sodium bisulfite, hydrochloric acid aqueous solution ( $2\text{mol}\cdot\text{L}^{-1}$ ) and water successively, dried over  $\text{MgSO}_4$ , and then concentrated under reduced pressure. Further purification was performed using silica gel column chromatography (chloroform/hexane=2:3 as eluent), red needle crystals were obtained (yield: 64.9%). The monomer DTBT was synthesized in a similar method (yield: 72%).

**Polymer PCDTBT:** In a 25mL flame dried flask, 108.58mg (0.165mmol) of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9Hcarbazole, 75.66mg (0.165mmol) of DTBT, 0.76mg (0.826 $\mu\text{mol}$ ) of tris(dibenzylideneacetone)dipalladium(0) ( $\text{Pd}_2\text{dba}_3$ ) and 1mg (3.30 $\mu\text{mol}$ ) of tri(o-tolyl)phosphine ( $\text{P}(\text{o-Tol})_3$ ) were dissolved in 5mL of degassed toluene and

1.25mL of 20% aqueous tetraethylammonium-hydroxide ( $\text{Et}_4\text{NOH}$ ). The reaction mixture was vigorously stirred at  $92^\circ\text{C}$  for 72h. 2-bromothiophene (1.60 $\mu\text{L}$ , 16.51mmol) was added to the reaction, one hour later, 2-thienylboronic acid (2.11mg, 16.51mmol) was added and the reaction refluxed overnight to complete the end-capping reaction. The polymer was purified by precipitation in methanol/water (10:1), filtered and washed on Soxhlet apparatus with acetone, hexane and chloroform successively. The chloroform solution was reduced under reduced pressure, get polymer (43.6mg, 37.5%). Polymer PCDFBT was synthesized in a similar method (yield: 42%).

## 2 Results and Discussion

### 2.1 Synthesis and Characterization of Monomers and Polymers

As shown in the Scheme 1, commercially available o-phenylenediamine was treated with freshly distilled thionyl chloride in the presence of pyridine as solvent, affording 2,1,3-benzothiadiazole (compound 1) after steam distillation. Upon reaction with molecular bromine (added drop-wise slowly) in hydrobromic acid, compound 1 gave the 4,7-disubstituted regioisomer (compound 2). The compounds 3 and 4 were prepared by Suzuki coupling reaction of compounds 2 with 2-furanboronic acid and 2-thienylboronic acid, respectively. The target monomers DFBT and DTBT were synthesized by further bromination of compounds 3 and 4 with N-bromosuccinimide (NBS). Finally, the polymers PCDFBT and PCDTBT were prepared by Suzuki coupling reaction of monomers DFBT and DTBT with 2,7-carbazole derivative. The chemical structure of the monomers and polymers was verified by  $^1\text{H}$  NMR spectroscopy, as an example, the data of compounds 1-3, monomer DTBT, and polymer PCDTBT was collected as shown in the table 1.

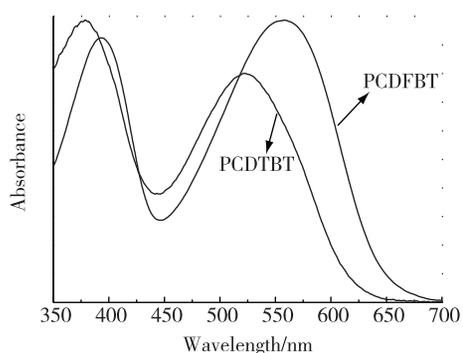
### 2.2 Solubility and Molecular Weight of Polymers

Both of the two polymers (PCDTBT and PC-

DFBT) can be easily dissolved in some common organic solvents such as chloroform, and chlorobenzene at room temperature, and were also soluble at hot tetrahydrofuran (THF), toluene. The good solubility can be attributed to the bulky side chain. Furthermore, PCDFBT could be dissolved in hexane partly, and the improved solubility of PCDFBT compared to PCDTBT might be ascribed to the smaller size of oxygen atom, which led to lesser steric hindrance between furan and its neighboring units. The molecular weights and polydispersities of the resulting polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. The average molecular weights and polydispersity indexes of PCDTBT and PCDFBT were 7 000 and 21 000, 1.36 and 2.44, respectively. The higher molecular weight of PCDFBT could increase the conjugated length, which is useful for improving optical absorption ability.

**Table 1**  $^1\text{H}$  NMR data of compounds 1–3, monomer DTBT, and polymer PCDTBT

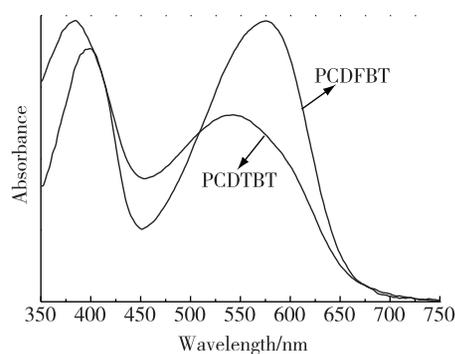
$^1\text{H}$ NMR data (CDCl <sub>3</sub> , TMS)	
compound 1	7.52 (2H, s), 7.94 (2H, s)
compound 2	7.73 (2H, s)
compound 3	8.05(2H, s), 7.69 (2H, d), 7.59 (2H, dd), 6.63 (2H, dd)
DTBT	8.00 (2H, s), 7.65 (2H, d), 6.55(2H, d)
PCDTBT	8.11 (2H, d), 8.02 (2H, d), 7.94 (2H, br), 7.74 (2H, br), 7.56 (2H, d), 7.45 (2H, d), 4.73 (1H, br), 2.42 (2H, br), 2.05 (2H, m), 1.23 (24H, br), 0.70 (6H, t).



**Fig. 1** UV-Vis absorption spectra of polymers PCDTBT (gray line) and PCDFBT (black line) in CHCl<sub>3</sub> solution

## 2.3 Optical Properties

The UV-vis absorption spectra of the two copolymers in CHCl<sub>3</sub> solutions are shown in Figure 1. These two polymers exhibited two major absorption bands in the ranges of 300–450 nm and 450–700 nm. The peak at longer wavelength could be attributed to the intramolecular charge transfer (ICT) effect, and the other at shorter wavelength was the result of a higher energy transition. The absorption spectra of the two polymers in thin films are shown in Figure 2, and the optical properties are summarized in Table 2. The shape of the peaks and the trend of the absorption wavelength are generally similar to those in solution. The absorption maxima in the films were red shifted to 578 and 547 nm for PCDFBT and PCDTBT, respectively, the relative large red shifted of absorption spectra from solution to thin film might be resulted from a higher structural organization in solid state. It is found that optical band gap of copolymer PCDFBT (2.14 eV) is smaller than that of the analogous copolymer PCDTBT (2.26 eV), which indicated that polymer PCDFBT could harvest exciton more effectively.



**Fig. 2** UV-Vis absorption spectra of polymers PCDTBT (gray line) and PCDFBT (black line) in film state

**Table 2** Optical properties of the polymers

Polymers	Solution		Film	
	$\lambda_{\max}/\text{nm}$	$\lambda_{\min}/\text{nm}$	$\lambda_{\max}/\text{nm}$	$E_g/\text{eV}$
PCDTBT	379/523	655	385/547	2.26
PCDFBT	394/559	690	402/578	2.14

Note:  $\lambda_{\max}$  is the maximum absorption,  $\lambda_{\min}$  is edge absorption,  $E_g$  is optical energy gap which is estimated from the maxima absorption of thin film.

## 2.4 Electrochemical Properties

It is well known that the magnitude of the band gap and energy positions of HOMO and LUMO energy levels are the most important characteristics for determining the optical and electrical properties of a given conjugated polymer. These in turn greatly affect the photovoltaic performance. Herein, HOMO energy levels of the two polymers PCDTBT and PCDFBT were investigated by photoemission yield spectroscopy (PYS) as shown in Figure 3. As predicted, the HOMO level of copolymer PCDFBT ( $-5.48\text{eV}$ ) is lower than that of copolymer PCDTBT ( $-5.34\text{eV}$ ) as Summarized in Table 3. It is suggested that the open-circuit voltage ( $V_{oc}$ ) in BHJ solar cells with ohmic contacts is linearly dependent on the magnitude of the built-in potential, defined as the difference between the HOMO level of a p-type polymer and the LUMO level of an n-type fullerene derivatives. In other words, the donor with the lower HOMO level will better reach the theoretically attainable  $V_{oc}$ . And due to the lower-lying HOMO level, polymer solar cell based low-bandgap polymer PCDFBT could get a higher  $V_{oc}$ . The LUMO level was evaluated to be  $-3.08\text{eV}$  for PCDTBT, and  $-3.34\text{eV}$  for PCDFBT from the HOMO level and the optical band gap estimated from the maximum absorption. These energy levels result in efficient charge separation between the two low-bandgap polymers and fullerene derivatives.

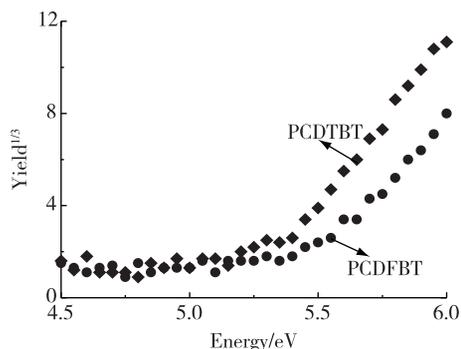


Fig.3 The PYS spectra of two polymers PCDTBT (diamond) and PCDFBT (circle)

Table 3 The energy levels of two polymers eV

polymers	HOMO	LUMO
PCDTBT	$-5.34$	$-3.08$
PCDFBT	$-5.48$	$-3.34$

## 3 Conclusions

We have successfully demonstrated that the energy levels of conjugated polymers could be optimized through furan substituent. By replacing the thiophene unit with furan unit in the main chain, the HOMO energy level was lowered from  $-5.34$  to  $-5.48\text{eV}$ , the improved energy levels is useful for getting a higher open-circuit voltage for polymer solar cells. Furthermore, due to the higher molecular weight of low-bandgap polymer PCDFBT, the exciton harvesting ability was also enhanced.

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