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Synthesis of Conjugated Polymers *via* Exclusive Direct-Arylation Coupling Reaction: A Facile and Straightforward Way to Synthesize Thiophene-Flanked Benzothiadiazole Derivatives and Their Copolymers

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ABSTRACT

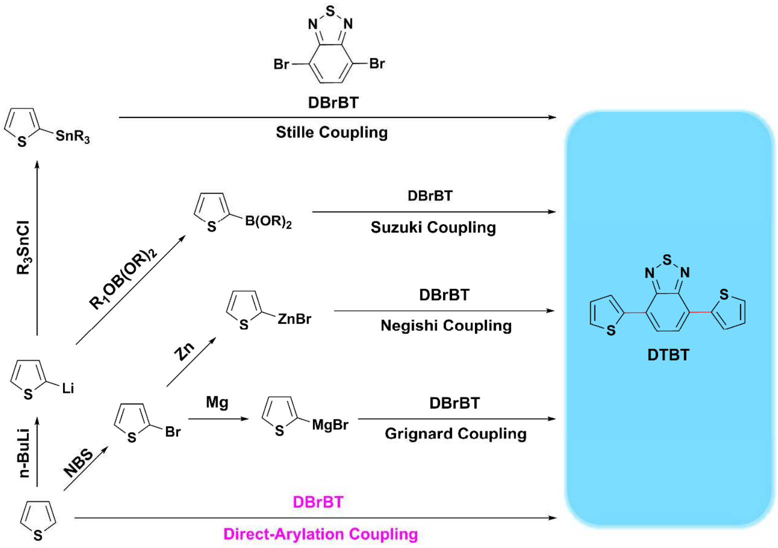
Thiophene-flanked benzothiadiazole derivatives (**DTBTs**) have been among the most widely used building blocks for synthesis of a myriad of high-performance conjugated polymers for applications such as optoelectronic devices, sensing and bioimaging. We first report that these building blocks were able to be synthesized *via* a facile and straightforward method called direct arylation coupling. Our optimization of Pd_2dba_3-catalyzed direct arylation coupling gave **DTBTs** with comparable yield to that of Suzuki or Stille coupling reaction. **DTBTs** were further polymerized with fluorene dibromide *via* direct arylation polycondensation to give well-defined alternating polymers. One-pot direct arylation polymerizations were also carried out between benzothiadiazole dibromide, fluorene dibromide and thiophene derivatives, to form **DTBTs**-containing random copolymers. These random copolymers showed typical multichromophores characteristics. The property difference between the alternating polymers and random polymers were evaluated.

Keywords: direct arylation; polymerization; thiophene; benzothiadiazole; conjugated polymers; organic semiconductors

INTRODUCTION

During the past decades, conjugated polymers (CPs), with excellent optical and electronic properties, have been the focus of both scientific research and industrial application, due to their potential applications in optoelectronic devices and biological science. Thiophene-flanked benzothiadiazoles (4,7-di-2-thienyl-2,1,3-benzothiadiazole, denoted as **DTBT**, and its derivatives), due to their unique electrical and optical characteristics as well as chemical and thermal stability, are one type of the most important building blocks in conjugated polymers for high-performance optoelectronic devices including solar cells, field-effect transistors and light-emitting diodes.[1-16] **DTBT** was synthesized by coupling reaction, largely Stille or Suzuki coupling reaction[17-19], between thiophene-2-metallic (boronate) compound nucleophiles and 4,7-dibromo-2,1,3-benzothidiazole (**DBrBT**) electrophiles (**Scheme 1**). To prepare the corresponding nucleophiles, however, these traditional coupling reactions require tedious preactivation of C-H bonds using organometallic reagents under critically dry and oxygen-free conditions. Direct arylation reaction as a carbon–hydrogen (C-H) bond activation method enables coupling reaction between arenes (i.e. nucleophiles without preactivation of C-H bonds) and aryl(pseudo)halides (i.e. electrophiles).[20-27] As a result, direct arylation coupling offers advantages over traditional couplings (e.g. Suzuki and Stille couplings) such as fewer synthetic steps, safer and more convenient operation, better atom economy and cost-effectiveness as well as no formation of highly toxic wastes such as those generated from Stille coupling reactions. We have recently investigated the effect of reaction factors in direct arylation polycondensation between benzo[1,2-*b*:4,5-*b′*]dithiophene and 2,1,3-benzothiadiazole derivatives, using tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3) as the catalyst and 1,2-dimethylbenzene (ODMB) as the reaction media. The systematical optimization of the reaction conditions led to high reaction activity and excellent C–H selectivity.[28]

Although a few direct arylation reactions involving thiophene derivatives as nucleophiles have been reported,[29-31] using 2,5-unsubstituted thiophene derivatives as capping agents to synthesize functional π-conjugated building blocks such as **DTBTs**, however, still remains a challenge, because the indistinguishable (axisymmetric thiophene derivatives, e.g. **T** and **EDOT**) or similar reactivity (unsymmetric thiophene derivatives, e.g. **HT**) of C–H bonds at 2-, 5- position of thiophene ring may lead to the further reaction of the target compounds (**DTBTs**) to form higher molecular weight oligomers or even polymers.



Scheme 1. Different synthetic routes to **DTBT**.

In this study, **DTBTs** and corresponding polymers were synthesized under the optimized reaction condition of direct arylation. Representative bare thiophene (**T**), alkyl-substituted thiophene (i.e. 3-hexylthiophene, **HT**) and alkoxy-substituted thiophene (i.e. 3,4-ethylenedioxythiophene, **EDOT**) were selected to study the direct arylation reaction and form the target thiophene-flanked benzothiadiazole derivatives, **DTBT**, 4,7-bis(4-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (**DHTBT**) and 4,7-bis(3,4-ethylenedioxythiophene-2-yl)-2,1,3-benzothiadiazole (**DEDOTBT**), as shown in **Scheme 2**. Moreover, we employed **DTBTs** as nucleophiles to synthesize conjugated copolymers, **PFTBTs**, *via* exclusively two-step direct arylation couplings, as illustrated in **Scheme 3**. 9,9-Dioctyl-2,7-dibromofluorene (**DBrF**) was selected as the electrophile co-monomer. The octyl groups on **DBrF** endow the resulting polymers with appropriate solubility in normal organic solvents. In addition, random copolymers (**PFTBTs-R**) containing the fluorene, benzothidiazole and thiophene derivatives were synthesized by an even simpler one-pot direct arylation polycondensation (**Scheme 4**).

EXPERIMENTAL SECTION

Materials. DBrBT (Assay 95%), **DBrF** (Assay 96%) and other reagents, solvents were commercial grade and used as received without further purification. All reactions were performed under nitrogen atmosphere.

Measurements and Characterization. The nuclear magnetic resonance spectra (NMRs) were recorded on a Bruker AV 300 spectrometer in $CDCl_3$ at room temperature for monomers and in $C_2D_2Cl_4$ at 100 °C for polymers. Chemical shifts of ^1H NMR were reported in ppm. Splitting patterns were designated as s (singlet), d (doublet), dd (doublet of doublets), t (triplet) and m (multiplet). UV-Vis absorption spectra were recorded on a Shimadzu spectrometer model UV-2450. Emission spectra were measured with a PerkinElmer LS55 fluorescence spectrometer. The optical spectra measurements of the monomers and polymers were carried out in *p*-xylene solutions at room temperature. The number-average molecular weights (M_n), weight-average molecular weights (M_w) and polydispersity index (PDI, M_w/M_n) of the polymers were measured with gel permeation chromatography (GPC) from Agilent 1260 Infinity system at 30 °C, with polystyrenes as reference standard and THF as an eluent.

General Synthesis Procedures for the DTBTs. Under nitrogen atmosphere, **DBrBT** (0.4 mmol, 118 mg), $Pd_2(dba)_3$ (20 μmol, 18 mg), tris(2-methoxyphenyl)phosphine ((*o*-MeOPh)$_3$P, 40 μmol, 14 mg), potassium carbonate (K_2CO_3, 1.4 mmol, 193 mg), pivalic acid (PivOH, 0.12 mmol, 12 mg), thiophene derivatives (**Ts**, 8 mmol) and 1,2-dimethylbenzene (ODMB, 2 ml) were added in a reaction vial with a magnetic stirring bar. The vial was sealed with a rubber cap and then heated in a 100 °C oil bath for 24 hours (for **DTBT**, the reaction mixture was heated for 48 hours at 120 °C). After being cooled to room temperature, the reaction mixture was diluted with chloroform and then filtered to remove the insoluble species. The filtrate was concentrated and purified by column chromatography.

DTBT. Orange crystals. Yield: 67%. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.06 (dd, 2H), 7.78 (s, 2H), 7.42 (dd, 2H), 7.18 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.6, 139.4, 128.0, 127.5, 126.8, 125.9, 125.7.

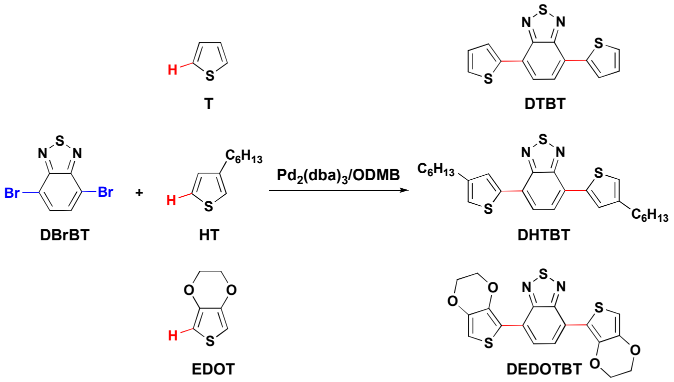
DHTBT. Orange crystals. Yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.97 (d, 2H), 7.82 (s, 2H), 7.04 (m, 2H), 2.69 (t, 4H), 1.70 (m, 4H), 1.34 (m, 12H), 0.92 (t, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.6, 144.3, 139.0, 129.0, 126.0, 125.4, 121.5, 31.8, 30.7, 30.5, 29.1, 22.7, 14.2.

DEDOTBT. Dark red needle-like crystals. Yield: 43%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.39 (s, 2H), 6.56 (s, 2H), 4.40 (m, 4H), 4.32 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): Solubility is too low to obtain a satisfactory ^{13}C NMR.

General Synthesis Procedures for the Alternating Polymers. Under nitrogen atmosphere, **DTBTs** (0.2 mmol), **DBrF** (0.2 mmol, 109.6 mg), $Pd_2(dba)_3$ (10 μmol, 9.2 mg), (*o*-MeOPh)$_3$P (20 μmol, 7 mg), K_2CO_3 (0.8 mmol, 110 mg), PivOH (0.1 mmol, 10 mg) and ODMB (1 ml) were added in a reaction vial with a magnetic stirring bar. The vial was sealed with a rubber cap and then heated in a 100 ^{o}C oil bath for 24 hours. After being cooled to room temperature, the reaction mixture was diluted with chloroform and then filtered to remove the insoluble species. The filtrate was concentrated and added dropwise to 100 mL of ethanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with methanol, hexane (for **PFHTBT**, isopropanol was used instead of hexane) and chloroform sequentially. The chloroform fraction was concentrated and precipitated into 100 mL of ethanol. The precipitates were collected by filtration and dried under vacuum for one day to yield the target polymers.

General Synthesis Procedures for the Random Polymers. Under nitrogen atmosphere, **DBrBT** (0.25 mmol, 73.5 mg), **DBrF** (0.25 mmol, 137 mg), $Pd_2(dba)_3$ (25 μmol, 23 mg), (*o*-MeOPh)$_3$P (50 μmol, 17.6 mg), K_2CO_3 (2 mmol, 270 mg), PivOH (0.15 mmol, 15 mg), thiophene derivatives (0.5 mmol) and ODMB (2.5 ml) were added in a reaction vial with a magnetic stirring bar. The vial was sealed with a rubber cap and then heated in a 100 ^{o}C oil bath for 24 hours (for **PFTBT-R**, the reaction vial was shaken from time to time). After being cooled to room temperature, the reaction mixture was diluted with chloroform and then filtered to remove the insoluble species. The filtrate was concentrated and added dropwise to 100 mL of ethanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with methanol, hexane and chloroform sequentially. The chloroform fraction was concentrated and precipitated into 100 mL of ethanol. The precipitates were collected by filtration and dried under vacuum for one day to yield the target polymers.

RESULTS AND DISCUSSION



Scheme 2. Synthesis of **DTBTs** *via* direct arylation couplings.

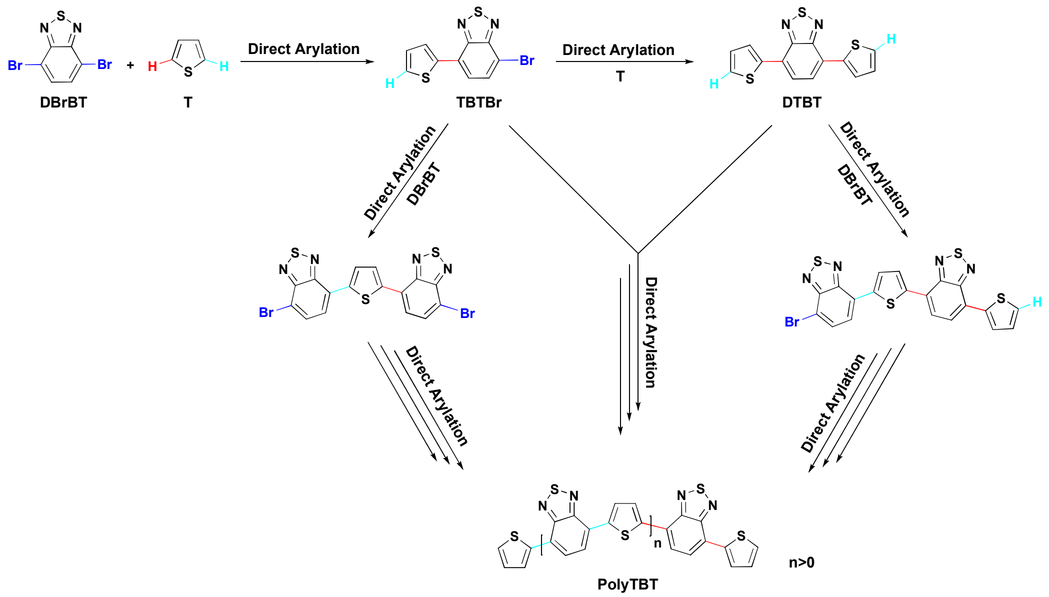
Table 1. Direct-aryltion coupling reaction of **DBrBT** with thiophene derivatives (**Ts**) under various conditions and optical properties of **DTBTs**.

Entry	Target	**Ts/DBrBT**	Concentration[a]	Temperature	Yield[c]	λ_{abs} (nm)	λ_{em}
No.	Product	(mol/mol)	(mol/L)	(^{o}C) [time (h)]	(%)		(nm)
1	**DTBT**	5	0.33	100[24]	27	309, 449	535
2		10	0.2	120[48]	43		
3		10	0.1	120[72]	37		
4		20	0.2	120[48]	67		
5		62.5	0.2[b]	120[72]	16		
6	**DHTBT**	20	0.2	100[24]	76	311, 460	546
7	**DEDOTBT**	20	0.2	100[24]	43	322, 483	574

[a] Concentration of **DBrBT** in ODMB.

[b] Concentration of **DBrBT** in thiophene, without ODMB.

[c] Isolated yield.



Scheme 3. Possible side reactions in the synthesis of **DTBT** *via* direct arylation coupling.

Synthesis of the DTBTs. Thiophene derivatives, including bare thiophene, 3-hexylthiophene and 3,4-ethylenedioxythiophene, were reacted with **DBrBT** *via* $Pd_2(dba)_3$-catalyzed direct arylation coupling reaction in ODMB, as shown in **Scheme 2**. The feed ratio of thiophene to **DBrBT** and concentration of reactants were found to influence the reaction significantly. With a feed ratio of thiophene/**DBrBT** of 5, at 0.33 M of **DBrBT** in ODMB**,** the target product **DTBT** was obtained with an isolated yield of 27% (Entry 1, **Table 1**). Under this condition, a lot of insoluble or partially soluble purple byproducts formed, which were expected to be mainly the thiophene-**BT** oligomers or even polymers.

Scheme 3 shows the synthetic route to **DTBT** and possible side reactions. After being substituted on electron-deficient **BT**, the Brönsted acidity of the remaining α-H on thiophene ring was enhanced. Consequently, the activity of C-H bonds on 5-position of the thiophenes in **TBTBr** and **DTBT** were higher than that of bare thiophene.[32] As a result, these thiophene-flanked **BT** derivatives further reacted with remaining aryl bromide to form higher molecular weight byproducts. Finally, all of the aryl bromides were substituted by excess thiophene ring. To suppress the formation of oligomeric byproducts, more thiophene was added to the reaction mixture and, at the same time, the concentration of the reactants was reduced. However, the excess thiophene and dilution led to decrease of the reaction rate. To improve the reaction rate, the reaction temperature was increased to 120 ^{o}C. The reaction results were listed in **Table 1**. With a feed ratio of thiophene/**DBrBT** of 10, at 0.2 M of **DBrBT** in ODMB**, DTBT** was obtained with an isolated yield increased to 43% (Entry 2, **Table 1**). Further decrease of the concentration of **DBrBT** to 0.1 M in ODMB resulted in a lower yield of target product (Entry 3, **Table 1**). Even with the reaction time prolonged to 72 h, there was still a large amount of monothiophene-substituted **TBTBr** remaining in the reaction system. At the concentration of 0.2 M **DBrBT** in ODMB**,** with the feed ratio of thiophene/**DBrBT** raised to 20, the reaction yield was further increased to 67% (Entry 4, **Table 1**).

It appears that maintaining a relatively high feed ratio of thiophene/**DBrBT** promoted this direct arylation reaction. Therefore we tried to use excess thiophene instead of ODMB as the reaction media (i.e. under neat reaction conditions, Entry 5, **Table 1**). The reaction was performed at a concentration of 0.2 M **DBrBT** in thiophene without adding ODMB. Under this condition, the feed ratio of thiophene/**DBrBT** was about 62.5. Unfortunately, the reaction was slowed down dramatically. Even being heated at 120 ^{o}C for 72 h, only 16% of **DTBT** was obtained together with nearly 80% monothiophene substituted product **TBTBr**. These results suggested that thiophene was not a suitable solvent for this coupling reaction.

We further applied the optimized reaction condition to couple alkyl substituted (**HT**) and alkoxy substituted thiophene (**EDOT**) to **DBrBT**, respectively. Surprisingly, the excess **HT** or **EDOT** did not slow down the direct arylation obviously. The coupling reactions were completed at 100 ^{o}C within 24 h (no **DBrBT** and **TBTBr** left in the reaction system). From this point of view, the influence of thiophene on the reaction rate of the direct arylation could not be attributed to its heterocyclic structure, but to its low boiling point (84 ^{o}C for thiophene *vs.* 225.6 ^{o}C for **HT** and 193 ^{o}C for **EDOT**) or possible impurities in it. The improvement in the yield of **DHTBT**, compared to that of **DTBT**, should be mainly attributed to the different reactivity of the 2- and

5-position C-H bonds on **HT**. As a consequence, the formation of higher molecular weight oligomers was suppressed. In addition, little formation of isomers could be observed in the reaction mixture, implying that the cooperation of Pd_2dba_3 and ODMB assured excellent C-H selectivity despite the slight activity difference between 2- and 5-position C-H bonds on **HT**. Compared to **HT**, **EDOT** with higher reactivity of C-H bonds and axi-symmetric structure tended to form polymeric products in direct arylation coupling with dibromo aryl reactants, resulting an obviously lower yield of **DEDOTBT** compared to that of **DTBT** or **DHTBT**.

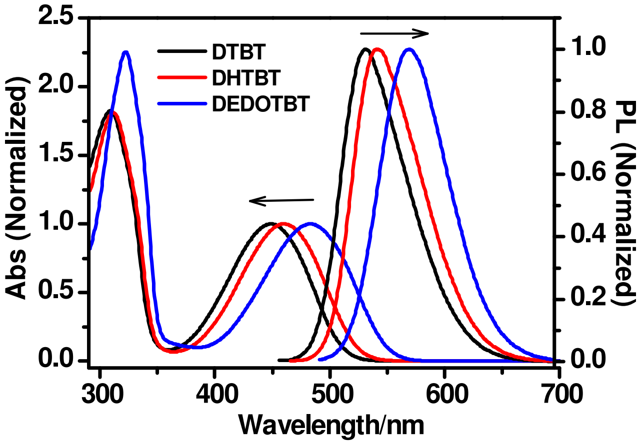


Figure 1. Normalized UV-vis absorption and PL emission spectra (excited at the maximum absorption wavelength in the visible region) of **DTBTs**.

Figure 1 shows UV-vis absorption and photoluminescence (PL) spectra of the **DTBTs** in diluted *p*-xylene solution. The maximum absorption (λ_{abs}) and emission wavelengths (λ_{em}) are summarized in **Table 1**. The absorption spectra feature two absorption bands: the first one at 290–360 nm, which can be assigned to localized π–π* transitions, and the second broader band from 360 to 570 nm in the long wavelength region, corresponding to intramolecular charge transfer (ICT) between thiophene derivatives and **BT** units. The increase of electron-donating ability of thiophene derivatives by attaching alkyl and alkoxyl groups led to the enhancement of ICT in corresponding **DTBTs**. As a result, both the absorption and PL spectra bathochromic shifted from **DTBT** to **DHTBT** and **DEDOTBT**. The magnitude of the shift was determined by the electron-donating ability of thiophene derivatives. Electron-richer **EDOT** gave larger red shift. All of the three thiophene-flanked benzothiadiazole derivatives show strong fluorescence under UV light (365 nm) irradiation (**Figure 2**).

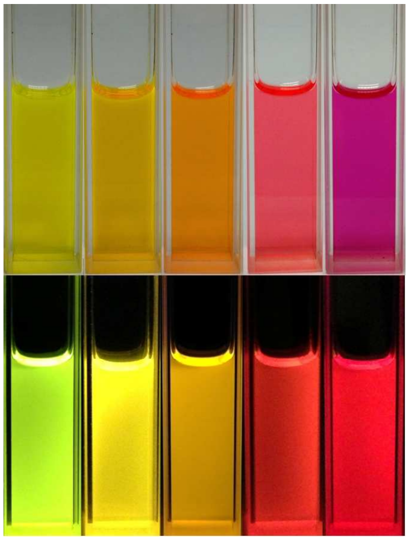
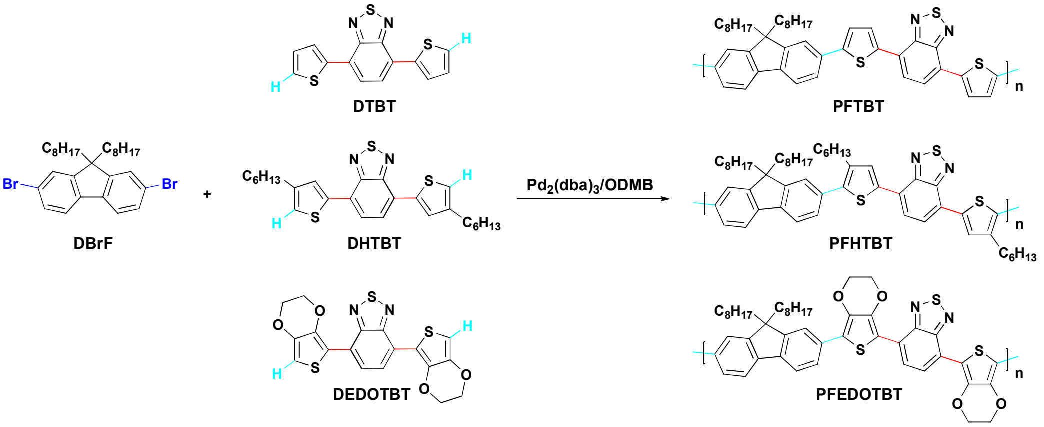


Figure 2. Photographs of solutions of **DTBTs** and selected polymers in *p*-xylene taken under ambient (top) and 365 nm UV light (bottom). From left to right: **DTBT**, **DHTBT**, **DEDOTBT**, **PFHTBT**, **PFTBT**.



Scheme 4. Synthesis of alternating polymers **PFTBTs** *via* direct arylation coupling.

Synthesis of Alternating Copolymers. The **DTBTs** obtained by direct arylation couplings were further used to synthesize conjugated polymers by polycondensation with **DBrF** (**Scheme 4**). The direct arylation polymerizations were carried out at 100 ^{o}C for 24 h, based on our previously reported conditions.[28] The polymerization results are listed in **Table 2**. After a general procedure of purification (more details are described in Experimental Section), both **PFTBT** and **PFHTBT** were obtained with high yields. Unfortunately, **PEDOTBT** was soluble neither in chloroform nor in tetrahydrofuran (THF), and could not be characterized further. Compared to that of **PFTBT**, the solubility of **PFHTBT** was dramatically improved by addition of hexyl groups on the thiophene units. As a result, the polymer **PFHTBT** could be partially dissolved even in hot hexane. Therefore, isopropanol instead of hexane was used in Soxhlet extraction to avoid unnecessary discarding of the target polymers. This phenomenon also suggested that the molecular weight of **PFHTBT** could be increased without sacrifice of its solubility. So we performed the polymerization under optimized condition and extended the reaction time to 72 h to obtain the polymer with higher molecular weight. General procedure of purification resulted in **PFHTBT2** with a higher M_n of 31.4 kg/mol. The decrease of the yield could be attributed to the solubility of the polymer in hot hexane in Soxhlet extraction (mainly lower molecular weight part).

Table 2. Polymerization Results and Photophysical Properties of the Alternating Copolymers.

	Yield (%)	M_n (kg/mol)	M_w (kg/mol)	PDI	λ_{abs} (nm)	λ_{onset} (nm)	λ_{em} (nm)
PFTBT	82	13.8	43.1	3.1	390, 546	617	612
PFHTBT[a]	91	17.6	33.9	1.9	365, 511	580	601
PFHTBT2[b]	72	31.4	55.3	1.8	366, 512	581	602

[a] In Soxhlet extraction, isopropanol was used instead of hexane.

[b] Reacted in a 100 ^{o}C oil bath for 72 hours.

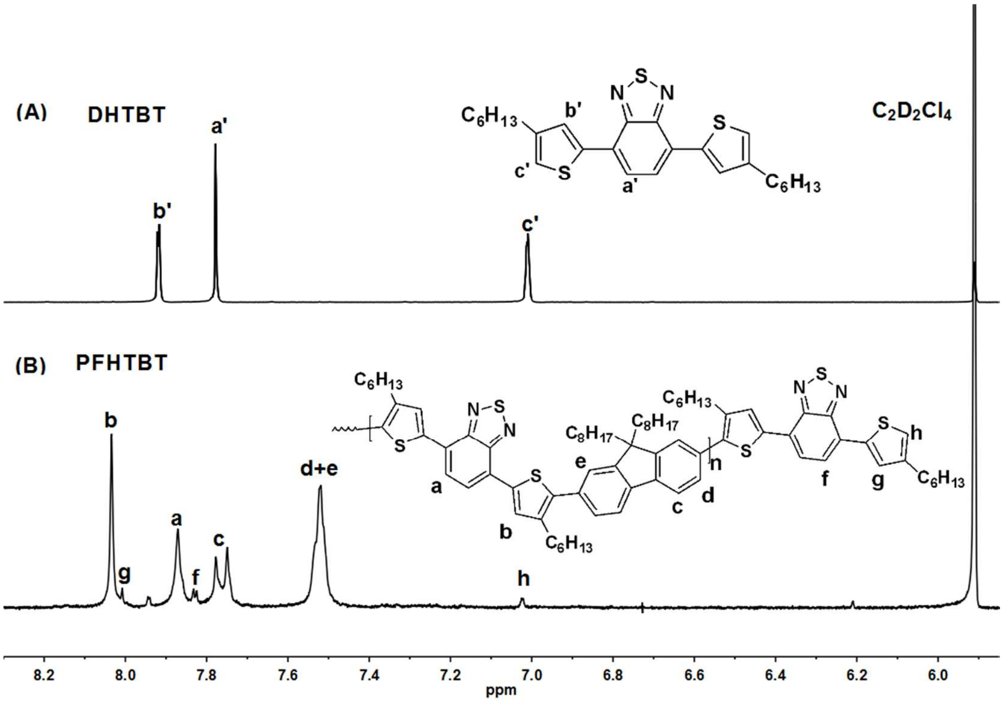


Figure 3. Aromatic range of ^{1}H NMR (300 MHz) spectra of (A) **DHTBT** and (B) **PFHTBT** in $C_2D_2Cl_4$ at 100 °C.

To examine any potential structural defects in the alternating copolymers synthesized by Pd_2dba_3-catalyzed DAP in ODMB, we employed high-temperature NMR to analyze the chemical structures of the resulting polymers (**Figure 3 and Figures S6-7**). **Figure 3** shows the aromatic part of the ^{1}H-NMR spectrum of PFHTBT in comparison to that of DHTBT in $C_2D_2Cl_4$ at 100 °C. The relatively sharp and well resolved peaks in the aromatic region, which was also observed in other polymers with similar chemical structures,[33, 34] offer us the opportunity to analyze the chemical structures of PFHTBT. One can see that all of the major peaks attributed to the backbone of the polymer are clearly resolved in the aromatic region. In addition, the small peaks at 8.01, 7.82 and 7.02 ppm are attributed to the protons (g, f, h, respectively) from the chain-end moieties, mainly DHTBT, of the polymers (**Figure 3B**). These results clearly demonstrate that there are negligible structural defects in the polymer PFHTBT that we synthesized via Pd_2dba_3-catalyzed DAP. For example, the homocoupling observed by Sommer and coworkers[33] in $Pd(OAc)_2$-catalyzed DAP between 4,7-bis(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole and

2,7-dibromo-9-(1-octylnoly)-9H-carbazole under certain catalytic conditions was not observed in our polymerizations described above. These results suggest that our Pd_2dba_3-catalyzed DAP enabled synthesis of nearly defect-free PFHTBT with good C-H selectivity. Similarly, the ^{1}H-NMR spectrum (**Figure S6**, Supporting Information) of the PFTBT copolymer that we synthesized via Pd_2dba_3-catalyzed DAP also shows that there were few structural defects in the resulting polymer, which further proves the good C-H selectivity in our catalytic conditions.

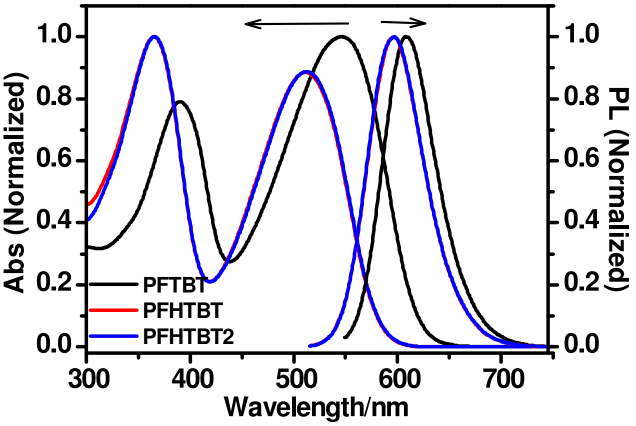
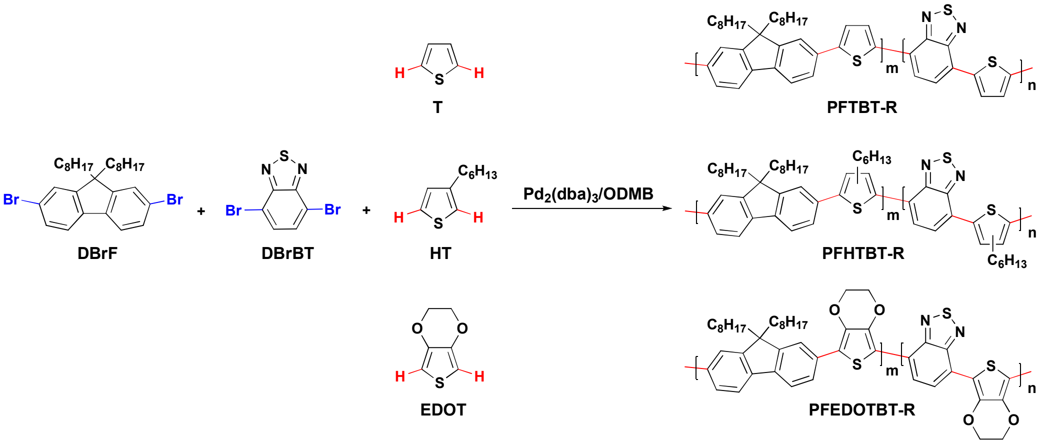


Figure 4. Normalized absorption and PL emission spectra (excited at the maximum absorption wavelength in the visible region) of the alternating copolymers.

The absorption and PL spectra of the alternating copolymers are shown in **Figure 4**. The maximum absorption and emission wavelengths are summarized in **Table 2**. Similar to thiophene-flanked benzothiadiazole derivatives, these alternating polymers exhibited two absorption bands. The absorption peaks of the corresponding polymers bathochromic shifted compared to those of **DTBTs**. At the same time, the relative absorption intensity of the peak at the longer wavelength increased. These phenomena implied the extension and enhancement of the conjugation from **DTBTs** monomers to the corresponding polymers. **PFHTBT2** showed almost the same absorption and PL spectra as **PFHTBT**, indicating the same effective conjugation length. In other words, **PFHTBT** with M_n of 17.6 kg/mol (the number-average degree of polymerization (DP) of about 20) reached the maximum effective conjugation length. So the further increase of the molecular weight (DP) did not affect the optical properties significantly.

Compared with **PFTBT**, **PFHTBT** showed hypsochromic shifted absorption spectrum accompanied with a decrease in relative intensity of the long-wavelength absorption band. This should be attributed to the increase of dihedral angles between thiophene unit and fluorene unit resulting from steric hindrance of hexyl substituents on the thiophene ring, which could interfere the π-conjugation in **PFHTBT**.[35] A digital photograph of the solutions (**Figure 2**) showed that the alternating polymers appeared highly fluorescent in *p*-xylene under UV (365 nm) irradiation.



Scheme 5. Synthesis of random polymers **PFTBTs-R** *via* one-pot direct arylation coupling.

Table 3. Polymerization Results and Photophysical Properties of the Random Copolymers.

	Yield (%)	M_n (kg/mol)	M_w (kg/mol)	PDI	λ_{abs} (nm)	λ_{onset} (nm)	λ_{em} (nm)
PFTBT-R	26	10.1	18.3	1.8	-	-	-
PFTBT-R[a]	54	10.2	22.2	2.2	425, 546	650	621
PFHTBT-R	65	10.1	17.7	1.8	367, 514	595	613

PEDOTBT-R	62	13.6	29.7	2.2	322, 443, 465, 588	692	660

[a] The reaction vial was shaken from time to time during being heated in an oil bath.

Synthesis of the Random Copolymers. The random copolymers were synthesized by one-pot direct arylation polycondensation between **DBrF**, **DBrBT** and the corresponding thiophene derivatives under the optimized conditions, similar to that used in preparation of the alternating copolymers (**Scheme 4**). Polymerization results are listed in **Table 3**. After general procedure of purification, **PFTBT-R**, **PFHTBT-R** and **PEDOTBT-R** were obtained with yields of 26%, 65% and 62%, respectively. The low yield of **PFTBT-R** should be mainly due to the low boiling point of thiophene. While being heated in oil bath, the thiophene evaporated out of the reaction mixture and condensed on the inner surface of the top of the reaction vial. According to **Equation 1**[36]:

$$\bar{X}_n = \frac{1+r}{1+r-2rp} \quad (1)$$

Number-average degree of polymerization ($\bar{X}_\mathrm{n}$) is determined by the stoichiometric ratio of functional groups (r) (the excess reactant is conventionally the denominator so that $r < 1$) and the extent of reaction (p). In the limit of complete conversion of the limiting reagent monomer, $p \rightarrow 1$ and

$$\bar{X}_n \rightarrow \frac{1+r}{1-r} \quad (2)$$

The absence of stoichiometric thiophene resulted in the unbalance of the functional group (C-H and C-Br), and led to the decrease in r and therefore limited the degree of the polymerization. As a result, a large amount of low-molecular-weight oligomers formed in the polymerization. In the subsequent purification, low molecular weight species were removed by Soxhlet extraction, so the yield was obviously decreased. For the same reason, all of the random polymerization gave lower reaction yield than the alternating polymerization described in the earlier section. We tried to improve the polymerization of **PFTBT-R** by shaking the reaction vial up and down every hour at the beginning six hours to flush the thiophene condensed at the top of the vial back to the reaction mixture. As a consequence, the polymerization yield was doubled. This result validated the hypothesis described above.

While we tried to characterize the three random copolymers described above using NMR spectroscopy, the obtained spectra (**Figure S8-10**) in $C_2D_2Cl_4$ at 100 °C showed broad and significantly overlapped peaks in the aromatic region. Thus further detailed analysis of the structural information of these polymers was difficult to obtain from the NMR spectra.

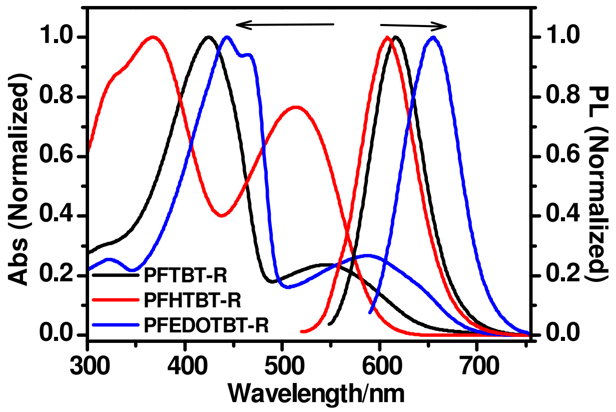
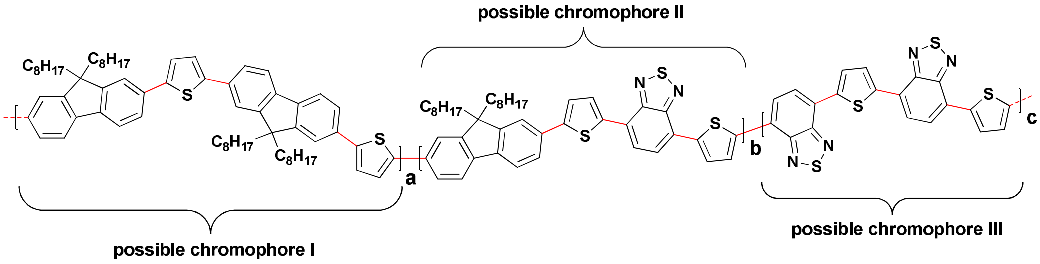


Figure 5. Normalized absorption and PL emission spectra (excited at the maximum absorption wavelength in the visible region) of the random copolymers.

The random copolymers showed much different absorption spectra from the alternating copolymers, as shown in **Figure 5**. For random copolymers, the relative absorption intensities in the long wavelength range decreased dramatically compared to those of the alternating copolymers shown in **Figure 4**. A close inspection of the absorption spectra revealed red shifts of onset absorption wavelengths (λ_{onset}) of the random copolymers. The detailed optical data are summarized in **Table 3**. In the random conjugated copolymers, repeating units are difficult to define because many different monomer sequences are possible. As a consequence, multiple chromophores can be expected depending on the actual effective conjugation length.[37] Taking **PFTBT-R** as an example, three types of chromophores with different monomer sequences are illustrated in **Scheme 6**. Chromophore II shared the same monomer sequences with **PFTBT**, so they should have the same absorption characteristics.

Compared to Chromophore II, Chromophore I consisting of dioctylfluorene and thiophene may absorb at shorter wavelengths. Chromophore Ⅲ consisting of benzothiadiazole and thiophene may result in a lower band gap and thus absorption of low-energy photons.



Scheme 6. Multichromophoric structure in random polymer **PFTBT-R**.

The absorption spectrum of **PFTBT-R** was taken as an example to further analyze the optical characteristics of the random copolymers, as illustrated in **Figure 6**. The absorption spectrum of the alternating copolymer **PFTBT** was also included for comparison. It is clear that the strong absorption band covered from 350 to 480 nm was mainly contributed by Chromophore I. This peak agreed well with the absorption of poly(9,9-di-*n*-octylfluorene-alt-thiophene) (F8T1).[38] The absorption in the range of 480-600 nm may correspond to Chromophore II and Ⅲ. The absorption over 600 nm could be mainly attributed to the Chromophore Ⅲ. The random copolymers thus had broader absorption than the alternating copolymers (which mainly contained a single chromophore) because they contained multiple distinct chromophores, which could cover different regions of the absorption spectra.

The decrease of band gaps in random copolymers consisting of the multiple chromophores caused the red shifting of the PL spectra. The emitting peak wavelengths of the random polymers bathochromic shifted about 10 nm, compared with the corresponding alternating copolymers. In multiple chromophores system, the energy transfers from higher energy photon emitter to lower ones.[39] In **PFTBT-R**, when excited, the energy may transfer from Chromophore I to Chromophore II and then to Chromophore Ⅲ, resulting in light emission at longer wavelength. Of course, in this process, the energy transfer efficiency in each step should be considered.

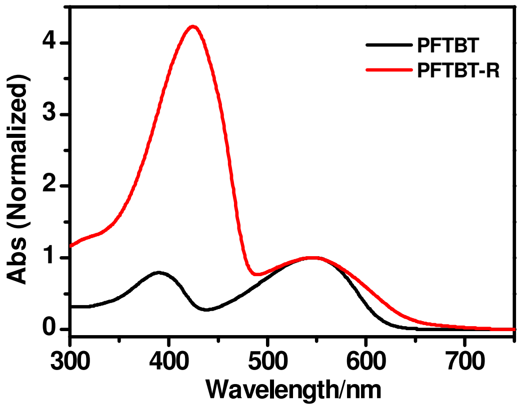


Figure 6. Comparison of normalized UV-Vis absorption spectra of the alternating copolymer **PFTBT** and the random copolymer **PFTBT-R**.

CONCLUSION

We have synthesized thiophene-flanked benzothiadiazole derivatives and the corresponding conjugated copolymers by direct arylation coupling reactions. After optimization, Pd_2dba_3-catalyzed direct arylation coupling gave **DTBTs** with yields comparable to that of Suzuki or Stille coupling reaction. **DTBTs** were further used to synthesize well-defined alternating polymers by direct arylation polycondensation. One-pot direct arylation polymerizations were also carried out between benzothiadiazole dibromide, fluorene dibromide and thiophene derivatives to form random **DTBTs** containing polymers. This synthetic strategy enabled facile and efficient synthesis of thiophene-flanked benzothiadiazole derivatives and corresponding conjugated copolymers with good C-H selectivity. The resulting small molecular building blocks and copolymers showed UV-vis absorption and fluorescence properties comparable to those of molecules and polymers synthesized by Suzuki coupling or Stille coupling. From a broad perspective, this work expanded the scope of direct arylation coupling reactions to synthesize thiophene-flanked π-conjugated molecular building blocks, and enabled the synthesis of high-quality conjugated polymers by exclusive direct arylation coupling reactions via fewer synthetic steps and without using flammable, nonstable and toxic organometallic reagents such as BuLi and Me_3SnCl.

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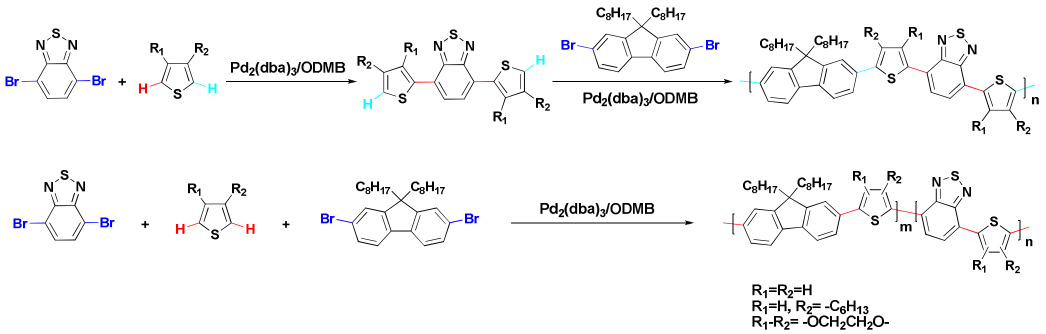
For Table of Contents Only

Synthesis of Conjugated Polymers *via* Exclusive Direct-Arylation Coupling Reaction: A Facile and Straightforward Way to Synthesize Thiophene-Flanked Benzothiadiazole Derivatives and Their Copolymers

Xiaochen Wang, Kai Wang, Mingfeng Wang*



Thiophene-flanked benzothiadiazole derivatives and their copolymers were synthesized *via* exclusive direct-arylation coupling reactions.