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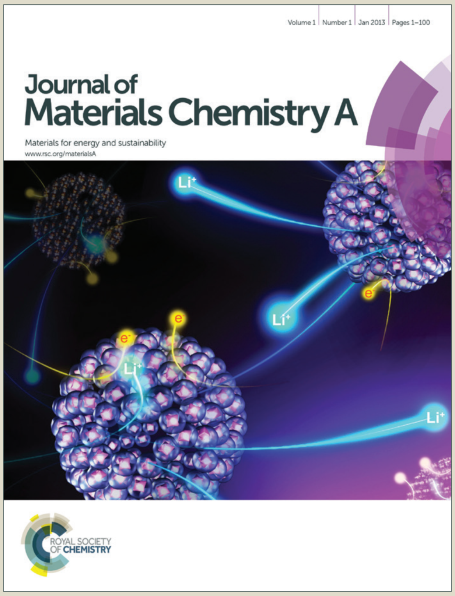

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ARTICLE TYPE

Versatile strategy to direct access 4,8-functionalized benzo[1,2-b:4,5-b’]difurans for organic electronics

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The direct access to 4,8-functionalized benzo[1,2-b:4,5-b′]difurans (BDFs) is developed. By fine-tuning the energy levels with different 4,8-functionalities or incorporating with electron-accepting units, BDFs show great potential as organic electronic materials, as demonstrated with 4.61% power conversion efficiency for polymer solar cells.

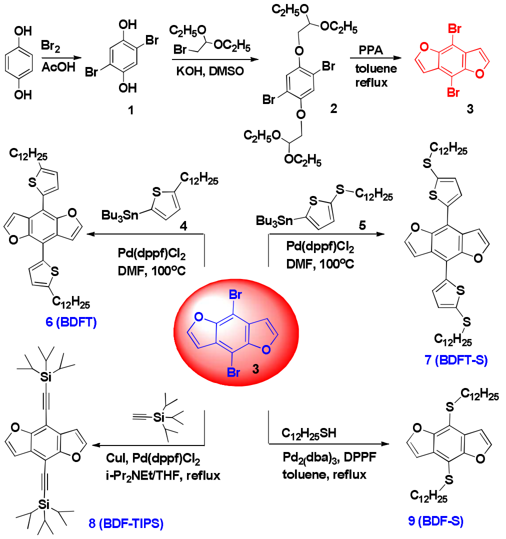
Organic semiconductors are gaining considerable interest because of their flexibility and easy structural modifications.[1-4] As one of the most important fused-ring structures, benzo[1,2-b:4,5-b']dithiophene (BDT) is most commonly explored as π-electron donors in organic electronics such as organic field effect transistors, organic light-emitting diodes as well as dye-sensitized and bulk heterojunction (BHJ) solar cells.[5,6] For example, BDT-based single-layer BHJ solar cells achieved a landmark power conversion efficiency of 9.2%.[6f] The BDT-based small molecule exhibited a hole mobility up to 0.81 $cm^2V^{-1}s^{-1}$ in single crystal transistor.[5]

In comparison to thiophene-based BDT, benzo[1,2-b:4,5-b′]difuran (BDF) has attracted much less attention for organic electronics. However, BDF counterparts can harvest deeper HOMO and LUMO levels due to the smaller diameter but higher electronegativity of oxygen atom has than sulfur atom. BDF-based donor-acceptor (D-A) type copolymers have shown tighter packing and smaller reorganization energy than their BDT counterparts, which could lead to higher charge mobility and smaller energy bandgap in coupling with higher HOMO energy levels.[7] Furthermore, furan based materials also show improved solubilities, weaker steric hindrance, biodegradable and biorenewable properties.[8,9] Several BDF D-A copolymers were reported to deliver PCEs of 4~6% in BHJ solar cells when used as donors.[8-12] New interests in constructing structural hybrid of BDF and BDT, i.e., thieno[2,3-f]benzofuran (TBF), even emerge for their promising photovoltaic properties.[13] BDF unit has thus been regarded as an attractive building block in constructing D-A conjugated systems for various optoelectronic applications.

To date, the 4,8-functionalization of BDF has been explored by adopting the similar approaches as for BDT with its 4,8-dione as the precursor.[14,15] Starting from benzo[1,2-b:4,5-b']difuran-4,8-dione, BDF monomers with alkyl, alkoxy, and aromatic ring to substituted onto the benzene core were developed as donor units for D-A polymers.[17-21] However, the reported methods have certain drawbacks: i) the methods employing either *n*-BuLi/$SnCl_2$[15] and Grignard reagents[16] have quite limited options for substrates and always accompanied by low yields; ii) larger fused aromatic substituents could hardly be incorporated onto the benzene core due to steric hindrance.

In light of the ever-increasing interest in developing 2-dimensional (2D) aromatic fused ring structure to fine tune the energy levels and facilitate regular π-π stacking of conjugated molecules and polymer backbones, our group have recently developed an efficient synthetic route for the direct access to 4,8-functionalized BDT monomers by using 4,8-triflated BDT as the key prescursor.[17] However, the ring-closure formation of precursors BDT/BDF-4,8-dione need undergo harsh reactions conditions with low yields.

In this work, we have herein present a general method for the direct access of 4,8-functionalized BDF building blocks under mild reaction conditions (Scheme 1). By adopting the acid-catalysed furan arylation, 4,8-dibromobenzo[1,2-b:4,5-b′]difuran, demonstrates its versatility for 4,8-functionalization of BDF to manipulate the energy levels of the resulted BDF monomers. This paved the way for further bandgap engineering of BDF-based D-A copolymers.



Scheme 1. Synthetic route to 4,8-functionalized BDF monomers with 4,8-dibromobenzo[1,2-b:4,5-b′]difuran as a versatile synthon.

A three-step protocol starting from hydroquinone facilely afforded the key synthon, 4,8-dibromobenzo[1,2-b:4,5-b′]difuran (dibromo BDF), with an overall yield of 32% (see Electronic

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Supplementary Information (ESI)). As illustrated, 1,4-dibromo-2,5-bis(2,2-diethoxyethoxy)benzene **2** was synthesized using Williamson-etherification between 2,5-dibromobenzene-1,4-diol **1** and 2-bromo-1,1-diethoxyethane with an overall yield beyond 80%. A further cyclocondensation of **2** using polyphosphoric acid (PPA) as acid catalyzed agent afforded 4,8-dibromobenzo[1,2-b:4,5-b′]difuran **3** with 60% yield. The replacement of PPA with Amberlyst-15 resin to increase the yield didn't work as expected, probably due to the slow reaction kinetics and the aromaticity.[18]

With dibromo BDF **3** at hand, a wide variety of 4,8-functionalized BDF monomers could thus be readily be prepared using palladium-catalyzed Stille and Sonogashira coupling as well carbon-sulfur formation reactions at high yields (≥ 86%). Dialkylthio substituted BDFs were prepared via straightforward carbon-sulfur bond formation reaction, which was previously afforded via high-temperature Newman-Kwart rearrangement reaction using irritant reagents.[19]

To demonstrate the versatility of this approach, both electron donating (alkylthio, aromatic ring) and accepting units (triisopropylsilylethynyl) were explored for the 4,8-functionalizatin of BDF. The Still cross-coupling between dibromo BDF and 2-dodecyl-5-tributyltinthiophene or 2-dodecylthio-5-tributyltinthiophene[20] proceeded efficiently to afford new BDF monomers **6** (BDFT) and **7** (BDFT-S) in 90% and 87% yield, respectively. The dibromo BDF was also explored for Sonogashira coupling with (triisopropylsilyl)acetylene in the presence of bis(triphenylphosphine) palladium(II) dichloride and cuprous iodide as catalyst to afford triisopropylsilyl ethynyl-substituted **8** (BDF-TIPS) with a yield of 90%. The dialkylthio **9** (BDF-S) was easily prepared via C–S cross-coupling[20] under the catalysis of $Pd_2(dba)_3$ and DPPF (1,1'-bis(diphenylphosphino)ferrocene) ligand with 95% yield.

The absorption spectra of BDF monomers in chloroform solution are plotted in Figure 1 (thin films shown in Fig. S1). In solution, four BDF monomers BDFT, BDFT-S, BDF-TIPS and BDF-S showed an absorption peak (λ_{max}) at 371 nm, 382 nm, 348 nm and 308 nm, respectively (Table 1). BDF-TIPS and BDF-S displayed two shoulder peaks at 331 nm and 321 nm. In solid state, BDF monomers displayed similar absorption profiles but extended absorption, indicating the increased intermolecular interactions and aggregation. The red-shifted absorption spectra followed the order of BDF-S<BDF-TIPS<BDFT<BDFT-S.

A close look at the optical results of BDF-TIPS and BDF-S, one would find that the introduction of a TIPS-ethynyl substituent to BDF core instead of alkthio leads to a ~40 nm red-shifted absorption spectra, mainly due to the expanded conjugated system and the electron-withdrawing effect of TIPS-ethynyl group. In comparison to BDF-S and BDF-TIPS, BDFT-S and BDFT show more red-shifted absorption, suggesting the enhanced electron delocalization over 2D conjugated BDF moieties when substituted with aromatic functionalities. BDFT-S exhibited ~11 nm red-shifted absorption than BDFT when substituted BDF with alkylthiothienyl instead of alkylthienyl group. As known, the longer wavelength domain corresponds to the π-π* transition, dominated by the electron excitation from HOMO to LUMO. Based on onset of the lowest energy absorption bands (λ_{onset}) of the films,[21] the corresponding optical bandgap (E_g^{opt}) of BDF monomers was estimated to be in the range of 2.58~3.50 eV (Table 1).

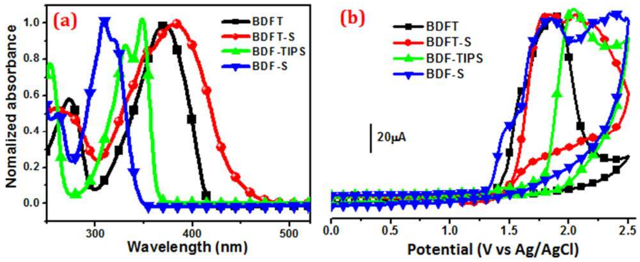

Fig. 1 (a) Normalized absorption spectra of BDF monomers in $CHCl_3$ solutions, (b) cyclic voltammogram of BDF monomers in solutions.

When comparing the λ_{max} values of three TIPS-ethynyl-substituted benzodichalcogenophenes, we can find that BDF-TIPS exhibits more blue-shifted λ_{max} (351 nm) than TBF-TIPS (366 nm)[13] and BDT-TIPS (384 nm).[29] This indicated that the lower energy transition was significantly shifted with the increasing number of heavier chalcogen atoms, probably due to the electronegativity of the heteroatom (O, 3.5; S, 2.5) playing a fundamental role in the absorption maxima location.[13] Compared the absorption peak of BDF-S with that of BDT-S,[17] obvious red-shift from 308 nm to 355 nm were found for their chloroform solutions. Similar phenomenon was also found for the optical spectra of BDFT and BDTT[17] films. The more S atoms were incorporated into the benzodichalcogenophenes, the more red-shift absorption.

Table 1 Optical and electrochemical properties of BDF monomers

	UV-vis					CV		
	λ_{max} (nm)[a]	λ_{onset} (nm)[a]	λ_{max} (nm)[b]	λ_{onset} (nm)[b]	E_g^{opt} (eV)[c]	E_{onset}^{ox} (V)	HOMO (eV)[d]	LUMO (eV)[e]
BDFT	371	414	375	419	2.96	1.36	-5.76	-2.80
BDFT-S	382	474	388	480	2.58	1.42	-5.82	-3.24
BDF-TIPS	348	367	351	369	3.36	1.35	-5.75	-2.39
BDF-S	308	351	312	354	3.50	1.28	-5.68	-2.18
P1	693	905	709	973	1.27	0.71	-5.11	-3.84
P2	712	951	744	1016	1.22	0.69	-5.09	-3.87
P3	701	906	708	942	1.32	0.78	-5.18	-3.86
P4	696	929	715	970	1.28	0.75	-5.15	-3.87
P5	902	-	945	-	-	0.47	-4.87	-
P6	851	-	947	-	-	0.60	-5.00	-
P7	795	-	853	-	-	0.76	-5.16	-
P8	945	-	981	-	-	0.62	-5.02	-
P9	559	666	570	730	1.70	0.91	-5.31	-3.61

[a]absorption in solution, [b]absorption in film, [c]E_g^{opt}= 1240/λ_{onset}, [d]HOMO = -e(E_{onset}^{ox} + 4.4) (eV), [e]LUMO = HOMO + E_g^{opt}.

Electrochemical properties of the as-prepared BDF monomers were investigated by cyclic voltammetry (Fig. 1b). All BDF monomers underwent an irreversible oxidation, similar to TBF and BDT monomers.[13,17] The onset potential for oxidation (E_{onset}^{ox}) was observed to be 1.36, 1.42, 1.35 and 1.28 V for BDFT, BDFT-S, BDF-TIPS and BDF-S, respectively. From E_{onset}^{ox}, the HOMO levels of derivatives were thus calculated (Table 1). The LUMO levels of BDF monomers were further determined in the range of -5.82 ~ -5.68 eV with their corresponding E_g^{opt} and HOMO energy levels. A close look at the data for BDFT and BDFT-S in Table 1, the 4,8-functionalization of BDF core with alkylthienyl and alkylthiothienyl substituent

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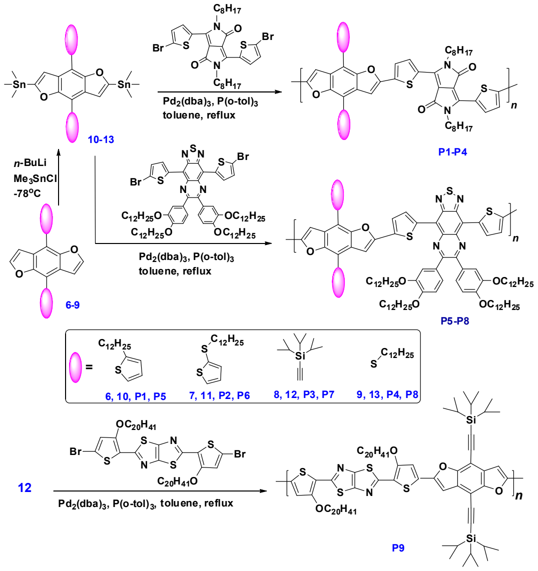
proved to be more effective in lowering both LUMO and HOMO energy levels, due to the incorporated aromatic moieties enhanced the planarity to induce more effective π-electron delocalized conjugated systems. Compared with BDFT, alkylthio-substituted BDFT-S maintained even lower energy levels and wider absorption region, due to the electron-donating effect of alkylthio group and enlarged conjugation.

Compared with BDF-S, BDF-TIPS displayed both lower LUMO and HOMO energy levels, which indicated increased conjugation length and planarity were induced with the introduced triple bonds. For TIPS-ethynyl-substituted benzodichalcogenophene anologues, the HOMO level increased in the order of BDF (-5.75 eV) < TBF (-5.70 eV)<BDT (-5.58 eV), as a result of higher electronegativity of oxygen atom.[10,13] Deeper HOMO level were also observed for BDF monomers, when comparing dialkylthio substituted BDF-S (-5.68 eV) with BDT-S (-5.41 eV) and BDFT (-5.76 eV) with BDTT (-5.42).[17]

To explore these energy level finely-tuned BDF monomers for optoelectronic applications, BDF-based D-A copolymers were prepared by alternating with diketopyrrolopyrrole (DPP),[4,22] thiadiazolo[3,4-g]quinoxaline (BTQx)[23] and thiazolo[5,4-d]thiazole (TTz)[24] via Still coupling reaction (Scheme 2). DPP and TTz were selected due to their moderate electro-withdrawing ability to build narrow bandgap conjugated materials (*ca,* 1.5~2.0 eV), while stronger accepting BTQx unit have been explored for organic semiconductors with extremely low bandgaps (*ca.* 1.0~1.5 eV) for near infrared optoelectronics.[25]



Scheme 2 Synthetic route to BDF-based D-A polymers.

With BDF tin reagents **10-13** (Scheme 2) in hand, structurally well-defined alternating polymers **P1-P9** were synthesized for BHJ solar cell application. All polymers showed excellent solubility in common organic solvents and exhibited relatively high molecular weights (M_n = 9.6~41.7 KDa) (Table S1). The thermogravimetric analysis (TGA) revealed the excellent thermal stability of polymers **P1-P9**, with T_d (temperature correspond to 5% weight loss) ranging from 320°C to 423°C (Fig. S2).

The BDF polymers **P1-P9** exhibited strongly acceptor-dependent photophysical and electronic properties (Table 1 and Fig. 2). DPP-based **P1-P4** exhibited strong absorption in 550~850 nm in films (Fig. S3), with E_g^{opt} calculated to be range from 1.22 eV to 1.32 eV. BTQx-based polymers **P5-P8** showed a typical two-absorption-band profile (Fig. S4), i.e., one at 300~600 nm and the other extending from 600 nm to the near-infrared region (>1100 nm), which endowed extremely narrow E_g^{opt} values (≤ 1.13 eV) for **P5-P8**. TTz-based **P9** exhibited one intensified absorption band at 400~650 nm. All polymers exhibited HOMO levels ranging from -4.87 to -5.31 eV and LUMO levels from -3.61 to -3.87 eV. As shown, the bandgaps as well and molecular electronic energy levels of BDF-cored polymers are readily tuned by copolymerizing with accepting units with different electron-withdrawing capability, with TTz<DPP<BTQx ranked in our case.

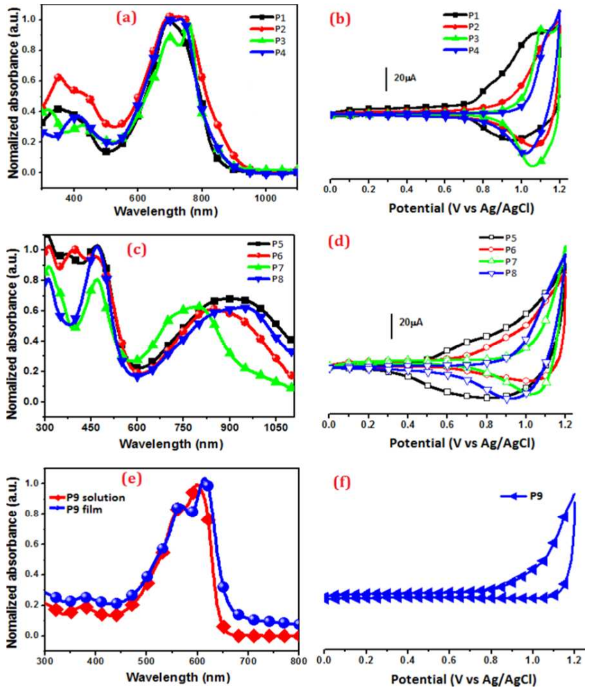


Fig. 2 Normalized absorption spectra of (a) **P1-P4**, (c) **P5-P8** and (e) **P9** in CHCl$_3$ solutions. CV traces of (b) **P1-P4**, (d) **P5-P8** and (f) **P9**.

The photovoltaic potential of BDF polymers were explored using the conventional single-layer device with a configuration of ITO/PEDOT:PSS/**P9**:PCBM (1:2, w/w)/LiF/Al (Table 2 and Fig. 3). Blend films of both **P9**:PC$_{61}$BM and **P9**:PC$_{71}$BM spin-coated from the corresponding chlorobenzene solutions were acted as the photoactive layers. The preliminary study has revealed that **P9**:PC$_{61}$BM device delivered power conversion efficiencies (PCEs) up to 2.29% under AM1.5 illumination (100 mW/cm^2). And **P9**:PC$_{71}$BM device exhibited a maximum PCE of 2.63%. The devices were further optimized by spin-coating **P9**:PC$_{71}$BM solution with the addition of 5% DIO. The best devices delivered a PCE of 4.61%, with a V_{oc} of 0.80 V, a J_{sc} of 9.81 mA/cm^2 and a FF of 58.7%. The photovoltaic performances of BDT counterpart polymer solar cells delivered a highest PCE of 4.33%, with a J_{sc} of 9.77 mA/cm^2, a V_{oc} of 0.89 V, a FF of 49.8%.[26] The higher FF may attribute to the smaller diameter but higher electronegativity of oxygen atom. Our model BDF polymers are very attractive for photovoltaic applications. The relatively lower J_{sc} and FF, we believe, can be optimized with device engineering. The characterization of photovoltaic properties for polymers **P1-P8** with stronger accepting units (BTQx and DPP) is in progress and

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will be reported at due time.

Table 2. Key photovoltaic parameters of polymer:PCBM (1:2, w/w) PSCs

Device	V_{OC} (V)	J_{SC} (mA/cm^2)	FF(%)	PCE (%)
P9:PC$_{61}$BM	0.83	6.12	45.4	2.29
P9:PC$_{71}$BM	0.80	7.51	43.8	2.63
P9:PC$_{71}$BM (with 5% DIO)	0.80	9.81	58.7	4.61

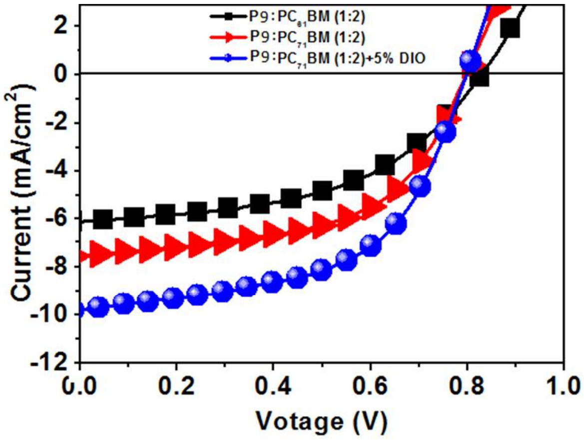

Fig. 3 *J-V* characteristics of ITO/PEDOT:PSS/**P9**:PCBM (1:2, w/w)/LiF/Al devices under the irradiation of AM 1.5 G (100 mW cm^{-2}).

In conclusion, we present a versatile synthetic strategy for 4,8-functionalized BDF building blocks using 4,8-dibromobenzo[1,2-b:4,5-b′]difuran as a versatile synthon. A platform is provided for feasible late-stage BDF derivatization. The chalcogen-property correlation study reveals a narrowing bandgap and lowing energy levels on going from sulfur to oxygen. BDF-based polymers with fine-tuned absorption and energy levels exhibit promising potential for solar cells with a PCE of 4.61% demonstrated in initial testing. As a consequence, the present work provides an insight on the structure-property relationship of BDF based conjugated materials and opens an avenue to develop new library of extended π-conjugated BDF molecules/polymers with high structural diversity for optoelectronic applications.

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† Electronic Supplementary Information (ESI) available: Experimental procedure and characterization for new materials, as well as device fabrication and characterization. See DOI: 10.1039/b000000x/

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Versatile strategy to direct access 4,8-functionalized benzo[1,2-b:4,5-b']difurans for organic electronics

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Direct access to 4,8-functionalized benzo[1,2-b:4,5-b′]difurans was developed for organic electronics, with 4.61% power conversion efficiency for polymer solar cells.