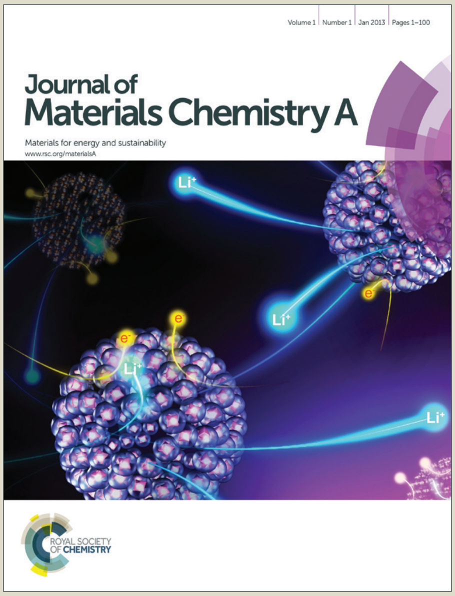
Journal of Materials Chemistry A

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Direct Access to 4,8-Functionalized Benzo[1,2-b:4,5-b']dithiophenes with Deep Low-lying HOMO Levels and High Mobilities

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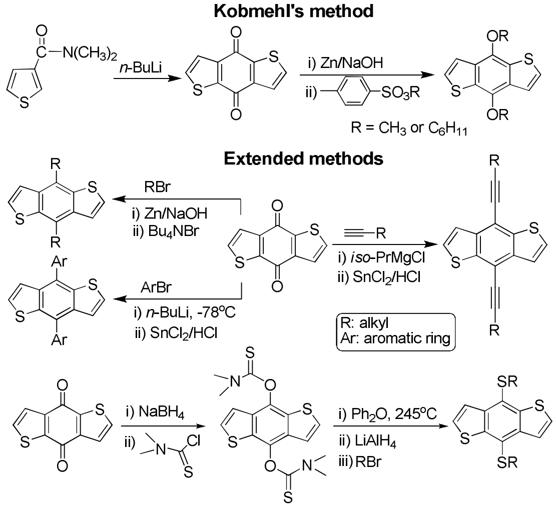
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A general methodology has been proposed for the straightforward access of 4, 8-functionalized benzo[1,2-b:4,5-b']dithiophene (BDT)s via Pd mediated coupling reactions including Suzuki/Sonogashira coupling and carbon-sulfur bond formation reactions. This versatile platform can be used to construct a library of BDT core centred conjugated systems, featuring large fused-ring structure and good charge mobility, where hole mobility of 0.061 cm^{2}V^{-1}s^{-1} is demonstrated. With energy level fine-tuned with functionalization, the charge transporting BDTs show great potential for donor-acceptor polymers.

To date, benzo[1,2-b:4,5-b']dithiophene (BDT) has been proved to be one of the most important fused-ring structured building blocks in the design of conjugated polymers donors for bulk heterojunction (BHJ) solar cells due to its high mobility and lower the highest occupied molecular orbital (HOMO) level.[1-4] As a donating moiety, BDT has been chosen for the following merits: a) the fused BDT ring structure allows the incorporation of substituents on the central benzene core, while also maintaining the planarity of the two thiophene units; b) its structural symmetry and the rigid fused aromatic system could enhance the electron delocalization and interchain interactions to improve the charge mobility and eliminate the need to control the regioregularity during the polymerization process;[5] c) it would maintain a low HOMO energy level of the resulting polymers as demonstrated by donor-strong and acceptor-weak polymers.[6] Kobmehl et al. firstly synthesized 4,8-dimethoxybenzo[1,2-*b*:4,5-*b′*]dithiophene with benzo[1,2-*b*:4,5-*b′*]dithiophene-4,8-dione as the precursor using a two-step reaction protocol (Scheme **1**).[7] Several extended methods were then explored for the synthesis of alkyl, alkenyl and aromatic ring substituted BDT derivatives.[8,9]

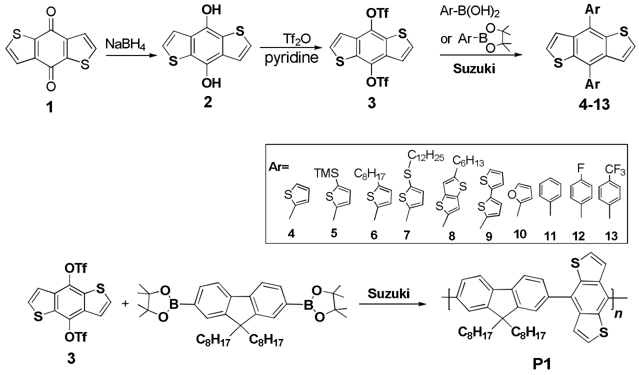
The BDT derived polymers were first developed as donors for BHJ solar cells by Hou et al. in 2008.[9] In the meantime, many research groups showed strong interest in this fascinating building blocks, and a large spectrum of BDT derived donors have been developed since then by introducing various substituents including alkyl, alkylthienyl, and alkyl phenylethynyl to the benzene core of BDT.[3b,10] Particularly, the ethynylene and thienyl-substituted BDT derived linear or two-dimensional (2D) small molecules and conjugated polymers exhibited promising performance in BHJ solar cells. For example, small molecules and polymers based ethynylene-containing benzo[1,2-b:4,5-b']dithiophene derivatives displayed low HOMO levels and excellent hole mobility up to 1.1-1.2 cm^{2}V^{-1}s^{-1} (on/off current ratio ~ 10^7) in field-effect transistors (FETs).[2b,2d] The blend of 4,8-triisopropylsilylethynyl functionalized BDT polymer and PC$_{71}$BM in 1:2 weight ratio delivered a power conversion efficiency (PCE) of 6% in BHJ cells.[11] A PCE of 8.13% was even achieved from 2D small molecules with bithienyl-substituted BDT donor, which performed much better than its thiophene-substituted BDT analogues.[12] Open circuit voltage (V_{oc}) is directly proportional to the HOMO level of electron donor.[13] The lower the HOMO level of the donor, the higher the V_{oc}. Thus, high mobility and low HOMO level are prerequisite to achieve high-performance solar cells.[6a,13,14]



Scheme 1 Synthetic routes for BDT derivatives in literature.

To achieve air-stable and high charge-transporting donor materials, the design and preparation of 2D BDTs by attaching conjugated substituents onto the central benzene core to fine-tune the energy levels and facilitate for regular π-π stacking of conjugated molecules and polymer backbones is considered to be a critical issue in the development of high-performance solar cells.[12,15] However, the previous methods have certain drawbacks: i) the synthesis of BDT derivatives with *n*-BuLi/SnCl$_2$ method has a limited scope for the substituents that may be introduced;[9] ii) the use of Grignard method[16] for the preparation of acetylene-substituted BDTs instead of lithiation only work for limited phenyl substituents with low yields; iii) larger fused aromatic substituents like thio[3,4-b']thiophene could not be accessed with any methods in literature, probably due to steric hindrance.

In conjunction with development of new donors for solar cells, we are keen to search for more general synthesis approaches to expand novel π-extended BDT-based donor materials. Herein we report a versatile method (Scheme **2**) for the synthesis of a library of amazing compounds using 4,8-triflated BDT as the precursor for the first time. Aryl triflates have frequently been used as electrophiles in coupling reactions.[17] By introducing trifluoromethanesulfonyloxy groups on 4,8-positions of BDT as leaving group, a library of 4, 8-functionalized BDT derivatives have been successfully prepared via Pd mediated coupling reactions including Suzuki and Sonogashira coupling. Importantly, the straightforward access of dialkylthio BDTs can be easily achieved with high yields ($\geq$ 90%) through one-step palladium-catalyzed coupling reaction. Dialkylthio substituted BDTs were reported to be synthesized with a two-step protocol, where a Newman-Kwart rearrangement under 245°C heating is the key step.[18] Excitingly, the Suzuki coupling can be successfully extended for the synthesis of conjugated polymers. This effective strategy provides a versatile platform to construct 2D conjugated systems centred on BDT core, featuring large fused-ring structure and good planarity. The new BDT derivatives developed with this approach, we believe, will find great potential in the design of new molecular/polymeric semiconductors for organic electronics.

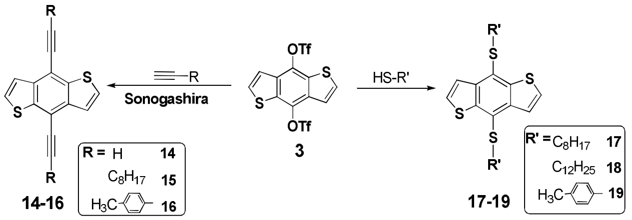


Scheme 2 Access to 4,8-difunctionalized BDT monomers/polymer via BDT triflate involved Suzuki coupling.

As shown in Scheme **2**, 4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione **1** was readily synthesized according to the reported procedure with thiophene-3-carboxylic acid as starting material.[9] A reduction of **1** with sodium borohydride in ethanol afforded **2** in 99% isolated yield under heating at 85°C.[18] Ensuing treatment of **2** with Tf$_2$O and pyridine in CH$_2$Cl$_2$ provided the key intermediate, 4,8-bis(trifluoromethanesulfonyloxy)benzo[1,2-b:4,5-b']dithiophene **3,** in 85% yield. It should be noted that reaction with DMF as solvent instead of CH$_2$Cl$_2$ was not successful. The structure of the as-obtained **3** was confirmed by ^{13}C NMR spectrum (Figure S4). The coupling constant of the characteristic peak (δ = 118.6 ppm) corresponding to trifluoromethanesulfonyloxy groups was shown as 319 Hz, which was in good agreement with literature.[17b] With the key precursor triflate **3** at hand, Suzuki cross-coupling between **3** and arylboronic acids or esters (Table 1, entries 1-10) proceeded smoothly in the presence of Pd(PPh$_3$)$_4$ and Na$_2$CO$_3$ to afford a new library of 4,8-diaryl-BDT monomers in 50-90% yields. The scope of thiophene analogues was extended from single thiophene unit to fused thio[3,4-b']thiophene and bithiophene. The coupling reaction with 2-thienylboronic acid afforded **4** with a yield of 80% (entry 1), while the couplings with 5-(trimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-thiophene,[14] 5-(octyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-thiophene and 5-(dodecyl-thio)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-thiophene[19a] were explored to prepare **5-7** (entries 2-4) with ~ 70% yields.

To the best of our knowledge, the larger the conjugated ring directly linked to the core in the cross-coupling, the more difficult it is to achieve it. Hence, the coupling with fused thio[3,4-b']thiophene (TT)[19] and bithiophene gave **8** and **9** (entries 5-6) in relatively low yields (55% and 60%). It should be noted that **8** was first prepared with BDT triflate, since the incorporation of TT ring using *n*-BuLi was found to be inaccessible. The results indicated the applicability of this protocol for the incorporation of relatively large substituents to 4,8-position of BDTs. We extended this approach to other aromatic rings. For instance, the coupling with 2-furanboronic acid afforded **10** (entry 7) in 81% yield. And the synthesis of BDTs with phenyl or its analogues with fluorine and trifluoromethyl substituent (**11-13**) was successfully achieved with a yield of 90, 81 and 82% (entries 8-10), respectively. It should be noted that aryl boronic acids were more reactive than the corresponding Bpin esters in Suzuki cross-coupling reactions and the electron-withdrawing strength of substituents had positive effect on the yield of couplings with phenyl analogues.

The BDT triflate was also explored for Sonogashira cross-coupling reactions with acetylene substituents **(Scheme 3)**. The reaction proceeded smoothly with 10 mol% [PdCl$_2$(PPh$_3$)$_2$] and 20 mol% CuI as catalyst in DMF/Et$_3$N (2:1, v/v) mixture solvent under heating at 100°C for 16 h. The coupling between **3** and 2.5 equiv. of 1-octyne, or 4-methyl-phenyl-acetylene gave the corresponding products **15**, **16** (entries 12 and 13) with a yield of 80 and 88%, respectively. Due to desilylation under the condition of excess base, however, the coupling with trimethylsilylacetylene only gave **14** as the product with a yield of 55%.

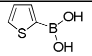
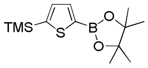
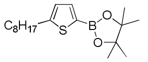
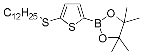
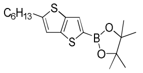
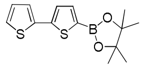
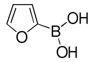
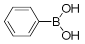
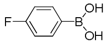
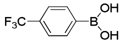
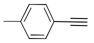
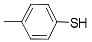


Scheme 3 Access to 4,8-difunctionalized BDT monomers via BDT triflate involved Sonogashira coupling and carbon-sulfur formation.

We were pleased to note that our protocol can also be used for the preparation of BDT thiols from the alkyl/aryl thiols substrates with BDT triflate (entries 14-16). The BDT sulfides **17-19** (Scheme 3) were successfully prepared via transition-metal-catalyzed cross-coupling transformation using Pd$_2$(dba)$_3$ and Xantphos phosphine ligand without formation of their disulfide compounds.[20] Octylmercaptan, dodecylmercaptan and benzylmercaptan were S-arylated in excellent yields of 90%, 91% and 90%, respectively.

We are also interested in the developing protocols that allow the preparation of conjugated polymers from BDT triflate **3** and aryl boronic ester. Fluorene is the most frequently used moiety for organic electronics.[14,21] Hence, a Suzuki cross-coupling between BDT triflate **3** and fluorene diboronic ester was explored in a biphasic mixture of aqueous K_2CO_3 and toluene with $Pd(PPh_3)_4$ as the catalyst and tetrabutylammonium bromide as the phase transfer catalyst (Scheme 3). The polymer **P1** was obtained with good solubility in organic solvents (ca. $CHCl_3$, THF, dichlorobenzene) and a high molecular weight (M_w = 21.4 kDa, M_w/M_n = 1.81), a value comparable to those of polyfluorenes prepared with arylbromide.[19b]

Table 1 Coupling reactions between BDT triflate **3** and different coupling reagents

Entry	Coupling reagent	Product	T (°C)	Yield (%)
1		**4**	85	80
2		**5**	85	70
3		**6**	85	68
4		**7**	85	69
5		**8**	85	55
6		**9**	85	60
7		**10**	85	81
8		**11**	85	90
9		**12**	85	81
10		**13**	85	82
11	$TMS-\equiv$	**14**	100	55
12	$C_8H_{17}-\equiv$	**15**	100	90
13		**16**	100	88
14	$C_8H_{17}SH$	**17**	reflux	90
15	$C_{12}H_{25}SH$	**18**	reflux	91
16		**19**	reflux	90

Conditions: $Pd[PPh_3]_4$ (5 mol%), THF/ Na_2CO_3 (aq. 1 M) (4/1, v/v), 85°C, 16 h for entries 1-10; $Pd(PPh_3)_2Cl_2$ (10 mol%), CuI (20 mol%), DMF/Et_3N (2/1, v/v), 100°C, 16 h for entries 11-13; $Pd_2(dba)_3$ (2.5%), Xantphos (5%), *i*-Pr_2NEt (2.3 equiv), toluene, reflux, 12 h for entries 14-16.

In order to evaluate the applicability of the as-prepared BDT monomers as donating units in the development of donor-acceptor (D-A) alternating narrow bandgap polymers for solar cells, the optical and electrochemical properties of the as-prepared BDT monomers (**4-19**) were further studied. The UV-vis absorption spectra of monomers **4-19** in both $CHCl_3$ solutions and thin films are shown in Figure **S39**. All spectra feature two distinct absorption peaks, with the one at 300~450 nm assigned to the delocalized π–π* transition between BDT core and the attached side chains and the other beyond 300 nm corresponding to the incorporated side chains. For electron-rich thiophene analogues (**4-9**), a relatively large red-shift absorption was observed for the films as compared to the solutions. Interestingly, in the case of **4** and **9**, by changing the single thiophene unit to bithiophene unit vertical to core of BDT, the low-energy absorbance increased in intensity and larger red-shift was observed. The reason was that resonance structure in BDT increased the double-bond character of the single bonds in **9** and this consequent reduction of the bond-length alternation effectively modified the absorption behaviours of BDT.[22] When comparing the UV-vis spectra of **8** with that of **4**, the larger planar structure of thio[3,4-b']thiophene unit was the so-called "prequinoid" monomer and the quinoid resonance form is lower in energy than the single thiophene form. The stabilized quinoid form effectively reduces the bandgap of related conjugated systems.[3a,21,23] As expected, thio[3,4-b']thiophene substituted BDT monomer **8** exhibited red shifted absorptions than **4** in both solution (15 nm) and film (nearly 20 nm). By attaching trimethylsiyl or octyl thiophene, the resulting BDT monomers **5** and **6** exhibited the similar absorption spectra with **4**, indicating that alkyl chains had negligible effect on the electronic structures of BDT.[24]

For **10**, the film with onset absorption (λ_{edge}) of 490 nm displayed 55 nm bathochromic shift than its solution, indicating an increased degree of BDT aggregation in solid state. Compared with monomer **11**, it was found that the anchoring of fluorine or trifluoromethyl group at 4,8-positions of BDT core for **12** and **13** had no distinct effect on the electronic structures. The phenylacetylenated **16** exhibited the widest absorption band, with a λ_{edge} extended to 500 nm. And a remarkable red-shifted absorption (~ 80 nm) was observed in film when comparing with its dilute solution, suggesting *J*-aggregation as the dominant packing mode in the solid state.[25] Monomers **17**, **18** and **19** exhibited about 5 nm red-shifted absorption than the reference 4,8-didodeoxyl BDT (**BDT-O-$C_{12}H_{25}$**). This indicates that stronger π-π stacking between BDT and diarylthio or dialkylthio substituent occurs than that in dialkoxy substituted BDT analogue.

The optical and electrochemical data of the BDT monomers are summarized in Table **S1**. The alignment of HOMO and LUMO energy levels of BDT monomers are further plotted in Figure **1**. The HOMO energy level of BDT monomers is found to be dependent upon the electron-donating substituents on the BDT core. For monomers with relatively electron-deficient phenyl analogues, the HOMO energy levels were estimated to be -5.55, -5.56 and -5.58 eV, respectively, for **11-13**. Phenyl substituent beaing six π-electrons on BDT core introduced a relatively larger perturbation to the conjugated backbone, further lowering the LUMO level. The HOMO energy levels of ethynylene-containing BDTs (**14-16**) were estimated to be -5.47, -5.48 and -5.51 eV, respectively, which indicated that the introduction of triple bonds led to increased conjugation length and good planarity to give the low HOMO energy level.

For electron-rich thiophene analogues, the HOMO energy levels estimated for **4-9** were -5.41, -5.45, -5.43, -5.42, -5.43 and -5.38 eV, respectively, indicating the incorporated 2-functionalized thiophene had negligible effect on the HOMO energy level when comparing **5-7** with **4**. The thio[3,4-

b']thiophene substituted **8**, with so-called "pre-quinoid" unit, showed low HOMO energy level due to the enforced planarity and more effective π-electron delocalization than single thiophene.[24] Monomer **9** showed the highest HOMO level among all thiophene analogues (**4-9**), due to the existence of more π-electrons with two 5-membered rings in comparison to other thiophene substituents. The HOMO level of furan-substituted **10** was calculated to be -5.42 eV, similar to that of **4**. The HOMO energy levels of **17-19** were calculated to be -5.41, -5.41 and -5.42 eV, respectively, much deeper than that of BDT-O-$C_{12}H_{25}$ (-5.18 eV). This can be explained with the poorer electron-donating ability of sulfur atom than oxygen atom due to the poorer overlap of its orbitals with the π-system of BDT backbone.

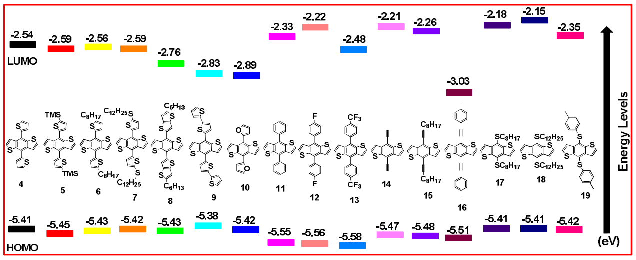


Fig. 1 The alignment of HOMO and LUMO energy levels of BDT monomers.

According to the electrochemical studies discussed above, the electron-deficience of the screened substituents can be arranged by the order: thiophene analogues < ethynylene analogues < phenyl analogues. The poorer the aryl substituent, the lower HOMO level. Amazingly, most of BDT monomers exhibit a HOMO level close to the HOMO of "ideal" polymers for high-efficiency solar cells (ca. -5.4 eV)[13]. Though there are argument on the inheretance of HOMO of D-A polymers from the electron-rich monomers,[28] the closeness of the HOMO level of BDT monomers to that of the "ideal" polymer donors in a necessarily disarable situation will help in finding matachable electror-deficient monomers to obtain new D-A polymers for high-performance solar cells.

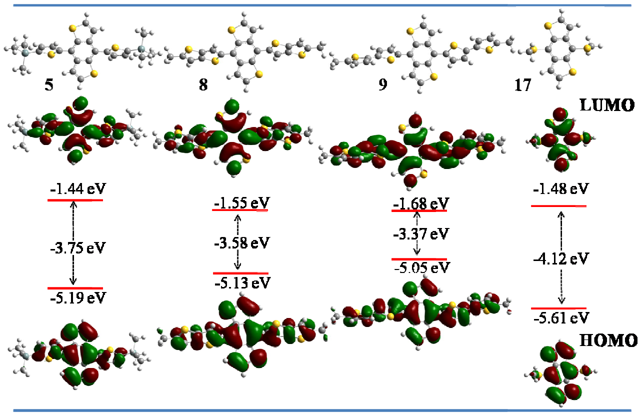


Fig. 2 Calculated HOMOs and LUMOs of **5**, **8**, **9** and **17** with the TDDFT B3LYP/6-31(d) level.

In order to demonstrate the electronic structures as well as molecular energy levels of the BDT monomers, quantum chemistry calculations were performed by using the density functional theory (DFT) on the B3LYP/6-31G level.[26] As shown in Figure **2**, these four units show planar structures and the π-electrons are well delocalized along their backbones, however, the HOMO and LUMO levels are different. The bandgaps of **5**, **8** and **9** are 3.75 eV, 3.58 eV and 3.37 eV, respectively, indicating that the bandgap becomes smaller with increasing of the conjugation length of substituents. The HOMO level of **17** is -5.61 eV, implying that the introduction of sulfur as hetero atom affects the molecular energy levels of fused aromatic systems distinctly.[27] The results from DFT calculations clearly show the similarity/difference of the energy levels of the frontier orbitals as well as the molecular electronic structures among **5**, **8**, **9** and **17**.

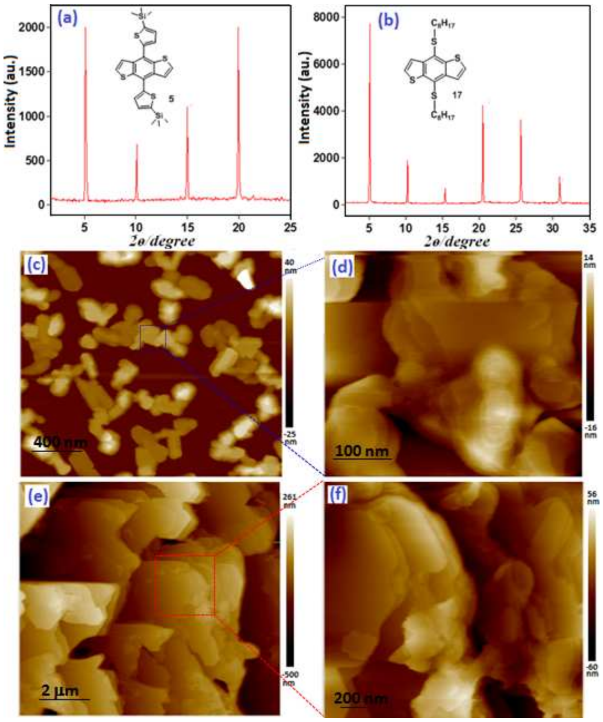


Fig. 3 X-ray reflection diagrams of **5** (a) and **17** (b) thin films on OTS-treated Si/SiO_2 substrate at 25°C. AFM Images of **5** (c, d) film on OTS-treated Si/SiO_2 substrate and **17** (e, f) film on glass substrate

The ordered-structure and crystallization features of BDT monomers were investigated by film X-ray diffraction (XRD) and atomic force microscopy (AFM). As depicted in Figure **3a-b**, the films of **5** and **17** displayed a series of equidistant peaks in XRD spectra,[24] indicating highly crystalline property of the thin films. The d-spacing of 1.73 nm for **5** and 1.74 nm for **17**, corresponding exactly to the strong primary diffraction peak at 5.11° and 5.08°, respectively, suggested that the molecules oriented normal to the substrate surface with certain extent of tilt.[26] Interestingly, no peaks were observed for the other BDT monomers, indicating the poor crystalline nature of their films. As illustrated in Figure **2c-f**, AFM images of **5** and **17** also showed ordered thin-film morphology. Both films of **5** and **17** exhibited terrace structures, which is generally favorable for high charge transport in FET.[19a]

Bottom-gate top-contacted transistors were further fabricated to investigate the charge transport properties. Among all BDT monomers, only **5** and **17** exhibited *p*-channel performance with the mobility calculated from the saturation regime, which agreed well with the results of the XRD and AFM. Figure **4** shows the typical current-voltage characteristics of **5** and **17** device made by vacuum deposition at room temperature on octyltrichlorosilane (OTS)-treated Si/SiO$_2$ substrate.

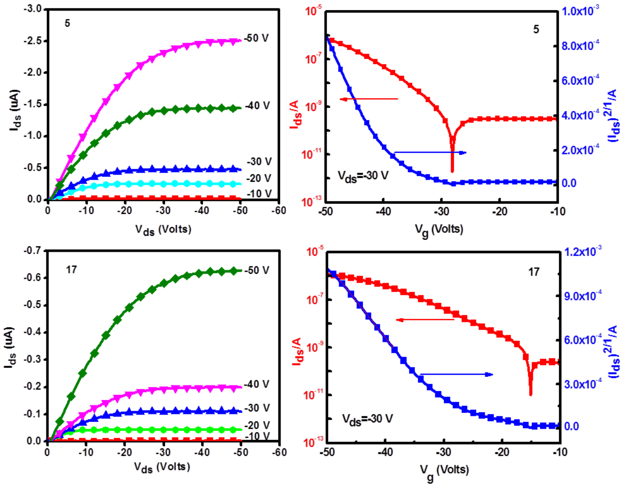


Fig. 4 The output (left) and transfer (right) curves of **5** and **17** FETs

The representative FET results for monomers **5** , **8**, **9**, **16** and **17** are summarized Table **2** (with the FET data for all monomers listed in Table S2). The vacuum-deposited device of **5** based on polymethyl methacrylate (PMMA) spin-coated on Si/SiO$_2$ substrate showed the relatively good average mobility, i.e., the thin film transistors demonstrated a maximum hole mobility of 0.025 cm^{2}V^{-1}s^{-1} and on/off current ratios of 1.2×10^5 (Figure **S40**). When adopting OTS-treated Si/SiO$_2$ substrate, the device of **5** achieved much improved average mobility up to 0.045 cm^{2}V^{-1}s^{-1} with the highest mobility of 0.06 cm^{2}V^{-1}s^{-1} and on/off current ratios of 4×10^5. The vacuum-deposited device on OTS-treated Si/SiO$_2$ substrate of **17** also demonstrated the average mobility of 0.015 cm^{2}V^{-1}s^{-1}. The highest mobility was up to 0.025 cm^{2}V^{-1}s^{-1}, with an on/off current ratio of 2.0×10^6.

Table 2. The FET data for monomers **5** , **8**, **9**, **16** and **17**

Monomers	μ (cm^{2}V^{-1}s^{-1})^c	on/off ratio	V$_{th}$ (V)
5^a	0.013 (0.016)	10^5-10^6	-25.60
5^b	0.045 (0.061)	10^4-10^5	-37.01
8^a	0.013 (0.015)	10^5-10^6	-26.93
9^a	0.012 (0.014)	10^5-10^6	-27.16
12^a	0.009 (0.011)	10^5-10^6	-36.45
16^a	0.007 (0.009)	10^7-10^8	-41.25
17^b	0.016 (0.025)	10^4-10^6	-40.68

^{a}PMMA-modified Si/SiO$_2$ substrate, ^{b}OTS-treated Si/SiO$_2$ substrate, ^{c}the average mobility and the maximum in parenthesis out of six samples

It was amazing that negligible variation in structures of monomers led to prodigious differences in the XRD, AFM and FETs devices. The correlation study of structure-property is still under progress and the optimized FETs data will be reported in due course. The as-prepared BDTs exhibited low HOMO levels close to that of "ideal" polymer as well as high hole mobilities. According to the strategy of weak donor-strong acceptor to design ideal polymers for organic solar cells,[28a] if suitable strong acceptors, such as diketopyrrolopyrrole,[29] benzooxadiazole[30] and naphtho[1,2-c:5,6-c]bisthiadiazole,[31,32] would be selected to constructe alternating low band gap copolymers via internal charge transfer with as-developed BDT monomers, we believe, new D-A polymers with suitable energy level alignment and high hole mobilities would be developed to achieve high-performance solar cells with optimized deveice engineering.

In summary, we have presented here a versatile method for the 4,8-functionalization of benzo[1,2-b:4,5-b']dithiophene via palladium-catalyzed Suzuki and Sonogashira couplings as well as carbon-sulfur bond formation reaction. Using this methodology, a library of 4,8-functionalized benzo[1,2-b:4,5-b']dithiophene monomers have been developed with aryl, ethynyl, arylethynyl, alkylthio and arylthio substituents. The absorption and energy levels of BDT monomers can be fine-tuned by adjusting the donating strength of the incorporated substituents. The as-prepared BDT monomers exhibit a bandgap ranging from 2.48 to 3.34 eV and a relatively low HOMO energy level. The high crystalline nature and hole mobility of BDT monomers demonstrated for **5** and **17** shows manipulating the functionalization of BDT core can result in prodigious differences in charge transport properties. High FET mobility of 0.061 cm^{2}V^{-1}s^{-1} and 0.025 cm^{2}V^{-1}s^{-1} was readily achieved for **5** and **17**. The as-developed BDT monomers may be promising donating units for constructing D-A narrow bandgap polymers for high-performance solar cells and *p*-type FETs if high mobility co-monomers are used and the resulted polymers have highly ordered structures.

This work is supported by the National Natural Science Foundation of China (Grant No. 21074055), Program for New Century Excellent Talents in University (NCET-12-0633), The Jiangsu Province Natural Science Fund for Distinguished Young scholars (BK20130032), Doctoral Fund of Ministry of Education of China (No. 20103219120008), and the Fundamental Research Funds for the Central Universities (30920130111006). The authors thank Dr. Baojing Zhou for the theoretical calculation.

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† Electronic Supplementary Information (ESI) available: details of synthesis and characterization data as well as both ^{1}H and ^{13}C NMR spectra of all products. See DOI: 10.1039/b000000x/

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A methodology for versatile and direct access to 4,8-functionalized benzo[1,2-b:4,5-b']dithiophenes with high mobility is developed.