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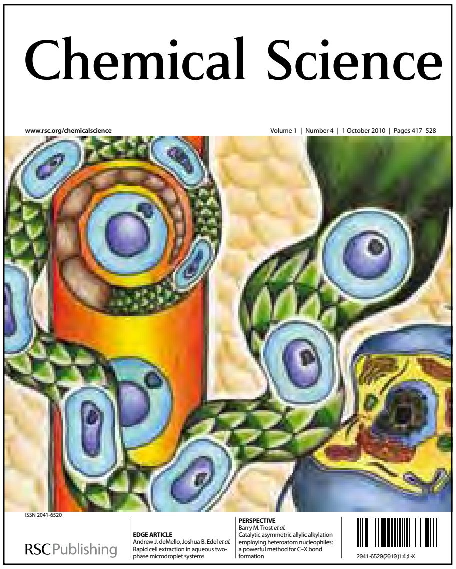

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PERSPECTIVE
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EDGE ARTICLE

Selective thienylation of fluorinated benzothiadiazoles and benzotriazoles for organic photovoltaics

Chun-Yang He,[b] Cai-Zhi Wu,[b] Yan-Lin Zhu,[a] and Xingang Zhang*[a]

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An unprecedented example for the selective and efficient synthesis of FBT-thiophene structural motif via dual C-H functionalization catalyzed by palladium has been developed. Fluorinated benzotriazole was also applicable to the reaction. This protocol provides a facile access to unsymmetrical and symmetrical thienylated FBTs that can be applied in the development of high performance photovoltaics, in particular in bulk heterojunction (BHJ) solar cells.

Fluorinated organic compounds play an important role in functional materials owning to the unique characteristics of fluorine atom, such as small size between hydrogen and oxygen, the strongest electronegativity and so on,[1] which often lead to profound changes of functional materials in their physical and other unprecedented characteristics.[2] In particular, the use of fluorinated benzothiadiazole (FBT)-thiophene structural motif based on donor (electron-rich aromatics)-acceptor (electron-deficient aromatics) system has received great attention, and become an important strategy in the development of high performance optoelectronic materials.[3] Because of the strong electron-withdrawing effect of fluorine atom(s), such a structural unit has brought about great improvements in devices performance through lowering the HOMO energy level of conjugate molecules and improving the morphology and structure in films.[4] For example, the power conversion efficiency (PCE) of bulk heterojunction (BHJ) solar cell[5] could be improved to >7% by employment of FBT, while lower PCE was observed for its nonfluorinated counterpart.[3b] The classical synthetic routes toward such structural motif are palladium catalyzed cross-coupling between halogenated FBTs and stannyl thiophenes.[6] Despite its reliability, this method suffers from several intrinsic drawbacks. Firstly, the stannanes are toxic, expensive, and difficult to handle or require several steps to prepare, and often produce toxic and environmentally risky stannyl-containing byproducts. Secondly, the halogenation of FBTs often generates symmetrical dihalogenated products that often lead to symmetrical dithienylated FBTs.[3] To date, it remains challenging to selectively prepare unsymmetrical thienylated FBTs via this method, thus limiting its structural diversity for further wide-spread synthetic applications. Thirdly, important functional groups, such as halides, are incompatible with this method. Hence, to meet the increasing demand in the development of high performance optoelectronic materials, developing efficient and environmentally benign methods to access such prominent structural motif are highly desirable.

As part of ongoing study in transition-metal-catalyzed direct functionalization of electron-deficient arenes,[7] herein, we demonstrate the feasibility of selective thienylation of electron-deficient FBT with simple thiophenes via dual C-H functionalization,[8] which would pave the way for efficient and environmentally benign synthesis of optoelectronic materials. In this communication, we focus on three difficult issues for our study, including (1) *chemo*-selectivity, desired cross-coupling products between FBTs and thiophenes *vs* undesired homo-coupling byproducts of each coupling partner; (2) *regio*-selectivity, unsymmetrical thienylation of FBTs *vs* symmetrical thienylation of FBTs; (3) efficient catalytic system that can undergo reaction under mild reaction conditions with broad substrate scope and high functional group compatibility. As a result, we disclose an unprecedented example of selective C-H thienylation of FBTs with simple thiophenes.[9] The reaction can also be extended to fluorinated benzotriazoles (FTAZ). Several notable advantages can be featured for this protocol: (1) synthetic simplicity via dual C-H functionalization with the omission of toxic stannanes; (2) high efficiency, broad substrate scope, and excellent functional group compatibility even bromide; (3) controllable catalytic system to produce unsymmetrical or symmetrical FBT-thiophene structures under mild reaction conditions. To demonstrate the usefulness of this protocol, some important monomers in the development of high performance BHJ solar cells were also efficiently prepared.

To begin this study, a new compound, mono bromide substituted difluorinated BT (DFBT) **1** was designed as a coupling partner for the reaction (Table 1). We considered that if the C-H thienylation of **1** was feasible, the resulting DFBT-thiophene structure would be a useful and versatile building block for further transformations or polymerization. Accordingly, compound **1** and 2-bromo-3-hexylthiophene **2a**, a common unit for the electronic and optoelectronic materials, were chosen as model substrates. Compound **1** can be easily prepared from commercially available 4,5-difluoro-2-nitroaniline[10] (for details, see Supporting Information). Initially, a negative result was obtained when the reaction was carried out in the presence of $Pd(OAc)_2$ (5 mol %) and AgOAc in DMF at 80 ^{o}C, in which AgOAc was supposed to functionalize both as an oxidant and base (Table 1, entry 1). Further investigation of the solvent effect revealed that DMSO benefited the reaction efficiency,[11] providing **3a** in 50% yield (Table 1, entry 4). Other solvent, such

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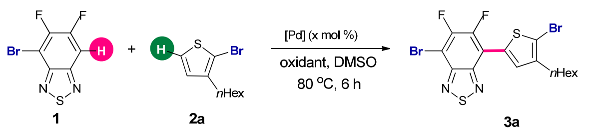
as toluene and dioxane, failed to give **3a** either (Table 1, entries 2 and 3). Switching AgOAc to Ag_2O dramatically improved the yield to 76% (Table 1, entry 7). The choice of palladium sources also influenced the reaction efficiency, and a slightly higher yield (82%) of **3a** was provided when $Pd(TFA)_2$ was employed (Table 1, entry 8). To our delight, a comparable yield (81%) still could be obtained by increasing the reaction concentration with utilization of 2.5 mol % of $Pd(TFA)_2$ (Table 1, entry 10). No product was generated in the absence of $Pd(TFA)_2$ or Ag_2O, thus demonstrating that a palladium redox catalytic cycle is involved in the reaction (Table 1, entries 11 and 12). It was noteworthy that no homo-coupling of **1** was observed under these optimal reaction conditions (Table 1, entry 10).

Table 1. Representative results for optimization of thienylation of DFBT **1** with **2a**.[a]



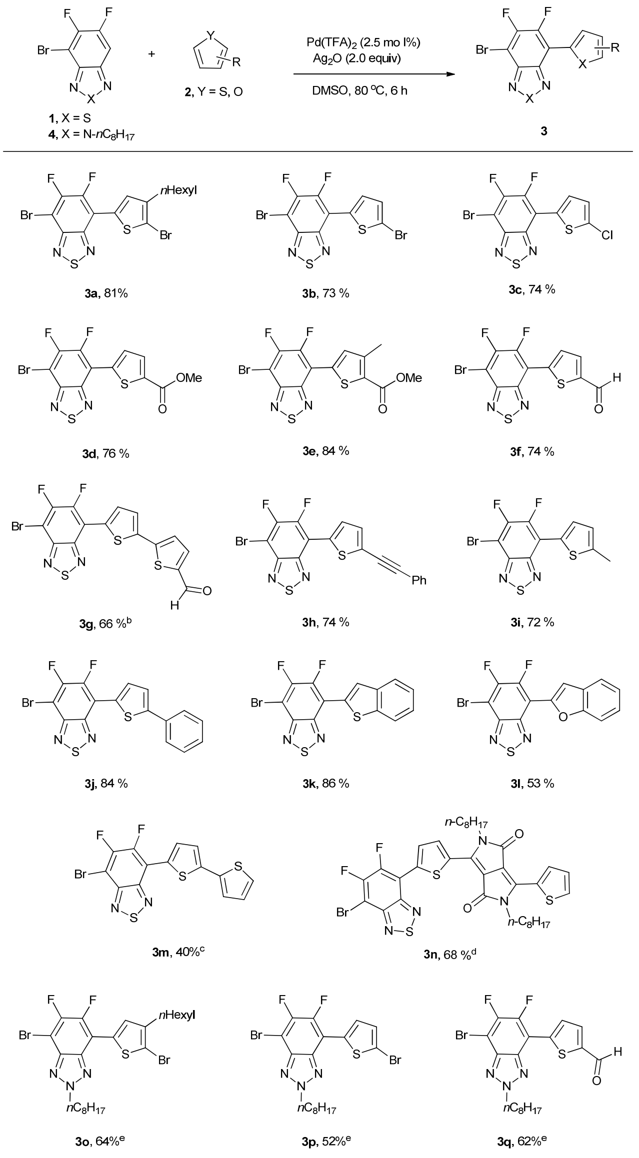
entry	[Pd] (x)	oxidant (equiv)	solvent	yield (%)[b]
1	$Pd(OAc)_2$ (5)	AgOAc (3)	DMF	trace
2	$Pd(OAc)_2$ (5)	AgOAc (3)	dioxane	NR
3	$Pd(OAc)_2$ (5)	AgOAc (3)	toluene	NR
4	$Pd(OAc)_2$ (5)	AgOAc (3)	DMSO	50
5	$Pd(OAc)_2$ (5)	Ag_2O (1.5)	DMSO	60
6	$Pd(OAc)_2$ (5)	Ag_2CO_3 (1.5)	DMSO	45
7	$Pd(OAc)_2$ (5)	Ag_2O (2)	DMSO	(76)
8	$Pd(TFA)_2$ (5)	Ag_2O (2)	DMSO	(82)
9	$Pd(TFA)_2$ (2.5)	Ag_2O (2)	DMSO	(76)
10[c]	$Pd(TFA)_2$ (2.5)	Ag_2O (2)	DMSO	(81)
11	$Pd(TfA)_2$ (2.5)	---	DMSO	NR
12	---	Ag_2O (2)	DMSO	NR

[a]Reaction conditions (unless otherwise specified): **1** (0.2 mmol), **2a** (2 equiv), solvent (2 mL). DMSO should be stored with the powder of 4 Å MS. [b]NMR yield determined by ^{19}F NMR using fluorobenzene as internal standard and number in parentheses is isolated yield. [c]1 mL of DMSO was used.

The reaction allowed thienylation of DFBT **1** with a variety of thiophenes in high efficiency (Table 2). Thiophenes bearing versatile functional groups, such as bromide, chloride, ester, aldehyde, and alkynl group, all showed good tolerance to the present reaction conditions, and afforded their corresponding products in good to high yields (**3a-h**), thus featuring the advantages of present method. 2-Phenylthiophene and benzothiophene were also applicable to the reaction, with high yields obtained (**3j-k**). In addition, benzofuran was also a suitable substrate, affording **3l** in moderate yield. Most remarkably, compounds **3m** and **3n** could be easily prepared via this strategy in only one step, thus offering us a unique opportunity to use such compounds as monomers for polymerization through direct arylation approach.[12] This would be useful for the development of high performance BHJ solar cells and field-effect transistors.[13] However, it is difficult to access these unsymmetrical FBT-thiophene structural motifs via traditional methods. It should be mentioned that although 4 equiv of **1** was used in the preparation of **3n**, it can be easily recovered after the reaction. While, only poor yield of **3n** was obtained under standard reaction conditions.

Since the difluorinated benzotriazole (FTAZ)-thiophene structural motif also has important applications in optoelectronic materials,[3c] the reaction of FTAZ **4**[10] with thiophenes was then investigated. It was found that the standard reaction conditions were not ideal for FTAZ. To further improve the reaction efficiency by addition of 1.0 equiv of HOAc with utilization of 5 mol % of $Pd(OAc)_2$ afforded **3o-q** in good yields.

Talbe 2. Selective thienylation of DFBT **1** and FTAZ **4** with thiophenes.[a]



[a]Reaction conditions (unless otherwise specified): **1** (0.2 mmol), **2** (2 equiv), DMSO (1 mL). All reported yields are isolated yield. [b]1.5 equiv of **2** was used. [c]5 mol % of $Pd(TFA)_2$ was used. [d]**1a** (4 equiv), **2** (0.1 mmol), $Pd(TFA)_2$ (5 mol %), Ag_2O (4 equiv), DMSO (1.5 mL), 10 h. [e]$Pd(OAc)_2$ (5 mol %), HOAc (1.0 equiv), 8 h.

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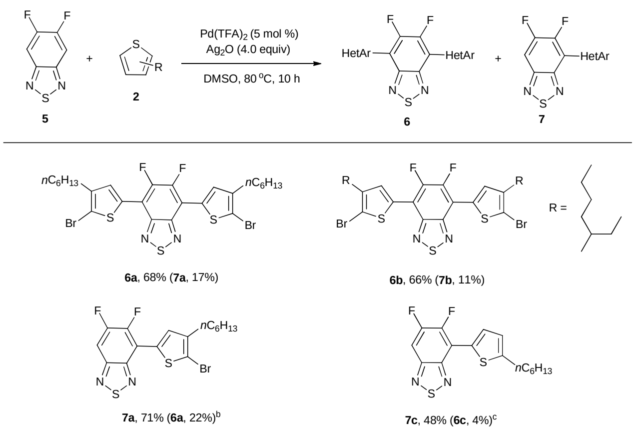
The importance and utility of the method can also be featured by rapid access to the prominent FBT-thiophene monomers. As shown in Table 3, a symmetrical monomer **6a** used for improvement of PCE of BHJ solar cells up to 8.3%[14] was easily synthesized between unfunctionalized DFBT **5** and **2a** in good yield (68%) via only one step, albeit with formation of 17% yield of mono-thienylated product **7a**.[15] This is in sharp contrast to the traditional techniques in the synthesis of **6a** from **5**, which required 4 steps,[14] including preparation of unstable 4,7-diiodo-DFBT[16] and toxic stannyl thiophene, Stille cross-coupling, and finally bromination of thiophene. In addition, harsh reaction conditions (110 °C) were required for the Stille coupling. Thus, compared to the traditional method, this approach featured several advantages, such as mild reaction conditions and synthetic efficiency and simplicity. Similarly, another useful monomer **6b** for the development of BHJ solar cells[3b, 14] was also obtained in a highly efficient manner. The selective synthesis of mono-thienylated DFBT **7** was also possible by reaction of **5** with thiophenes in high concentration through tuning the ratio between **5** and **2** (**7a** and **7c**). To our delight, even the reaction was run in 2 mmol scale, good yield (71%) of mono-thienylated product **7a** was still obtained. A synthetically useful yield of **7c** was also afforded under similar reaction conditions in 1 mmol scale synthesis. Although 3.0 equiv of **5** was used to suppress the formation of bi-thienylated product **6**, compound **5** can be easily recovered after the reaction.

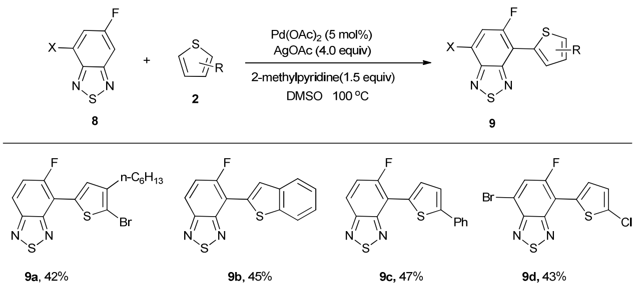
Table 3. Selective thienylation of DFBT **5** with thiophenes.[a]



[a]Reaction conditions (unless otherwise specified): **5** (0.2 mmol), **2** (4 equiv), DMSO (1 mL), 10 h. All reported yields are isolated yield. [b]**5** (3 equiv), **2** (2 mmol), Pd(TFA)$_2$ (2.5 mol %), Ag$_2$O (2.0 equiv), DMSO (6 mL), 10 h. [c]**5** (3 equiv), **2** (1 mmol), Pd(TFA)$_2$ (2.5 mol %), Ag$_2$O (2 equiv), DMSO (2.5 mL), 10 h.

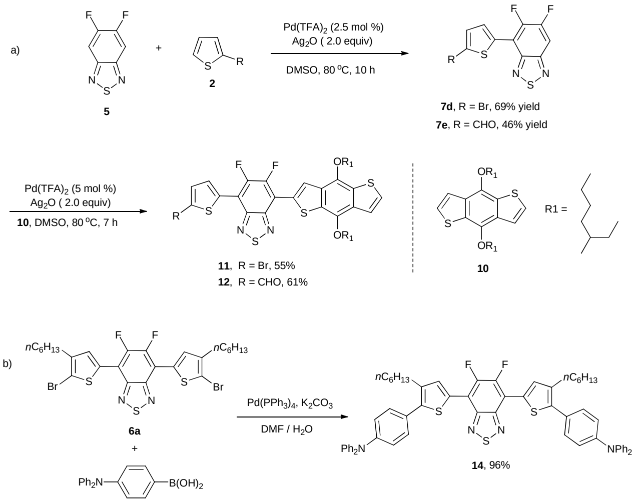
The substrate scope with respect to FBTs was not restricted to difluorinated substrates, mono-fluorinated BT (MFBT)[17] **8** were also examined. It was found that compounds **8** were less reactive than their difluorinated counterparts due to the low acidity of C-H bond that was to be activated.[18] Increasing the reaction temperature by using 5 mol % Pd(OAc)$_2$ in conjunction with 1.5 equiv of 2-methylpyridine as additive could afford products **9** in synthetically useful yields, in which the most acidic C-H bonds located between fluorine and C=N are primary reaction site (Table 4). It should be pointed out that although moderate yields of compound **9** were obtained, compared to the traditional methods, it is still an efficient method to access these useful building blocks for the photovoltaics studies.

Table 4. Selective thienylation of MFBT **8** with thiophenes.[a]



[a]Reaction conditions (unless otherwise specified): **8** (3 equiv), **2** (0.2 mmol), DMSO (2 mL), 9 h. All reported yields are isolated yield.

It was also possible to prepare unsymmetrical dithienylated DFBT via sequential C-H bond functionalization strategy. As shown in Scheme 1a, after selective C-H mono-thienylation of DFBT **5**, the resulting compounds **7d** and **7e** were directly thienylated with **10**, respectively, leading to unsymmetrical DFBT derivatives **11** and **12** in a highly efficient manner, which is difficult to prepare otherwise. It is noteworthy that compound **11** can be itself as a useful monomer for the polymerization through direct arylation approach, thus again demonstrating the advantages of the present method in the development of optoelectronic materials.[3] In addition to the demonstrated usefulness of this protocol, symmetrical DFBT derivative **14**, a new red light-emitting dye, was also synthesized from **6a** in high efficiency (Scheme 1b) (For the UV-vis absorption spectra of **14** see Supporting Information Figure S1).[19] Actually, on the basis of this strategy, a series of light-emitting dyes can be efficiently prepared, which may be used for dye sensitized solar cells.



Scheme 1. Synthesis of unsymmetrical dithienylated DFBT via sequential C-H bond functionalization and red light-emitting dye **14**.

In conclusion, we have demonstrated an unprecedented example of selective Pd-catalyzed thienylation of FBT with simple thiophenes via dual C-H functionalization. The reaction proceeds under mild reaction conditions, providing a series of unsymmetrical and symmetrical FBT-thiophene structures in high efficiency with excellent functional group compatibility. The

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reaction can also be extended to FTAZ. Application of the method led to important and useful FBT-thiophene monomers that can be applied in the development of high performance photovoltaics, in particular in BHJ solar cells. Because of the synthetic simplicity as well as high *chemo*- and *regio*-selectivity of this protocol, we believe that it should be useful for the atom/step-economical synthesis of new FBT-thiophene based photovoltaic materials. Further studies to extend the substrate scope and its application in the development of photovoltaics are underway in our laboratory and will be reported in due course.

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, and analytical data for all new compounds.. For ESI or other electronic format see DOI: 10.1039/b000000x/

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