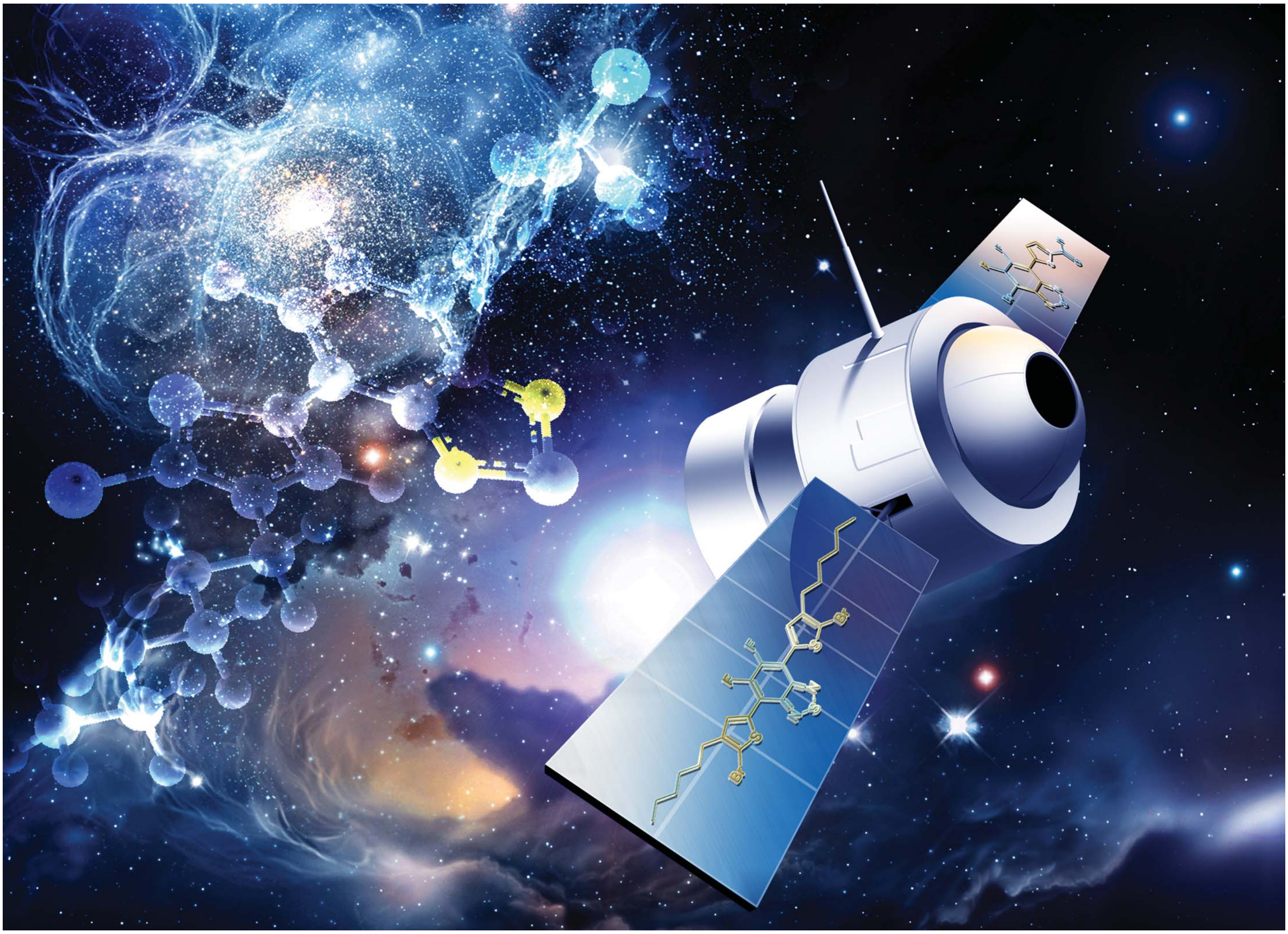

Showcasing research from Prof. Xingang Zhang's Laboratory at Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China.

Selective thienylation of fluorinated benzothiadiazoles and benzotriazoles for organic photovoltaics

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Selective thienylation of fluorinated benzothiadiazoles and benzotriazoles for organic photovoltaics†

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An unprecedented example for the selective and efficient synthesis of an FBT–thiophene structural motif *via* dual C–H functionalization, catalyzed by palladium, has been developed. Fluorinated benzotriazole is also applicable to the reaction. This protocol provides 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 owing to the unique characteristics of fluorine atom, such as its small size, between that of hydrogen and oxygen atoms, being the most electronegative atoms and so on,[1] which often lead to profound changes in the physical and other unprecedented characteristics of functional materials.[2] In particular, the use of a fluorinated benzothiadiazole (FBT)–thiophene structural motif based on a 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 device performance by 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 a bulk heterojunction (BHJ) solar cell[5] could be improved to >7% by employment of an FBT, while a lower PCE was observed for its nonfluorinated counterpart.[3b] The classical synthetic route towards such structural motifs is 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 motifs is highly desirable.

As part of an ongoing study of 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 paves the way for efficient and environmentally benign synthesis of optoelectronic materials. In this communication, we focus on three difficult issues in our study, including (1) *chemo*-selectivity, desired cross-coupling products formed 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) developing an efficient catalytic system that can undergo a 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 exist 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 with bromide; (3) it is a controllable catalytic system which produces unsymmetrical or symmetrical FBT–thiophene structures under mild reaction conditions. To demonstrate the

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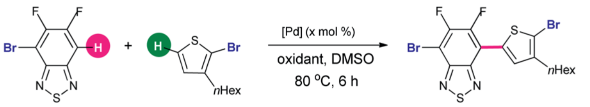
† Electronic supplementary information (ESI) available: Detailed experimental procedures, and analytical data for all new compounds. See DOI: 10.1039/c3sc53119h

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, monobromide 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 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 ESI†). 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 °C, in which AgOAc was supposed to act as both an oxidant and base (Table 1, entry 1). Further investigation of the solvent effect revealed that DMSO increased the reaction efficiency,[11] providing **3a** in 50% yield (Table 1, entry 4). Other solvents, such as toluene and dioxane, also failed to produce **3a** (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 source also influenced the reaction efficiency, and a slightly higher yield (82%) of **3a** was obtained when $Pd(TFA)_2$ was employed (Table 1, entry 8). To our delight, a comparable yield (81%) could still be obtained by increasing the reaction concentration using 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]



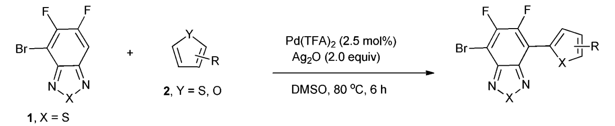
1 2a 3a

Entry	[Pd] (*x* mol%)	Oxidant (equiv.)	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$ (5)	AgOAc (3)	DMF	Trace
2	$Pd(OAc)_2$ (5)	AgOAc (3)	Dioxane	No reaction (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

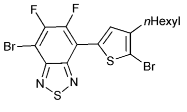
[a] Reaction conditions (unless otherwise specified): **1** (0.2 mmol), **2a** (2 equiv.), solvent (2 mL). DMSO should be stored with 4 Å MS powder. [b] NMR yield determined by ^{19}F NMR using fluorobenzene as the internal standard. Number in parentheses is the isolated yield. [c] 1 mL of DMSO was used.

The reaction allowed thienylation of DFBT **1** with a variety of thiophenes with high efficiency (Table 2). Thiophenes bearing versatile functional groups, such as bromide, chloride, ester, aldehyde, and alkynl groups, all showed good tolerance to the given reaction conditions, and afforded their corresponding products in good to high yields (**3a–h**), thus exhibiting the advantages of the 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

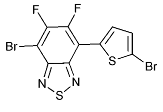
Table 2 Selective thienylation of DFBT **1** and FTAZ **4** with thiophenes[a]



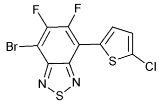
1, X = S
4, X = N-nC_8H_{17}
2, Y = S, O
3



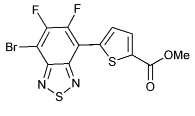
3a, 81%



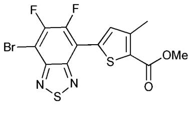
3b, 73 %



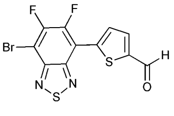
3c, 74 %



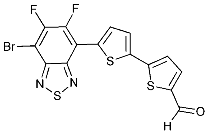
3d, 76 %



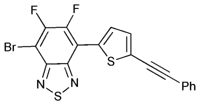
3e, 84 %



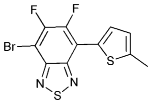
3f, 74 %



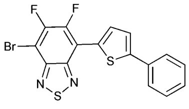
3g, 66 %[b]



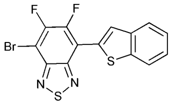
3h, 74 %



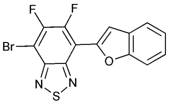
3i, 72 %



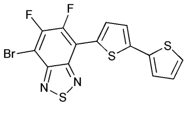
3j, 84 %



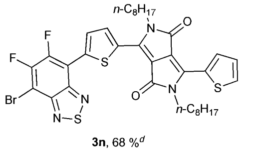
3k, 86 %



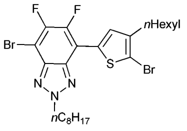
3l, 53 %



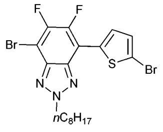
3m, 40%[c]



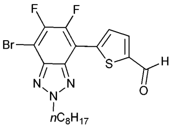
3n, 68 %[d]



3o, 64%[e]



3p, 52%[e]



3q, 62%[e]

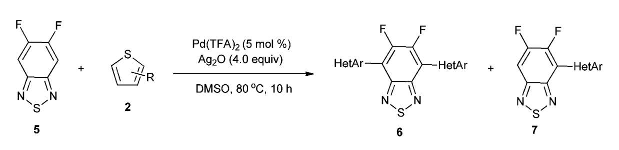
[a] Reaction conditions (unless otherwise specified): **1** (0.2 mmol), **2** (2 equiv.), DMSO (1 mL). All reported yields are isolated yields. [b] 1.5 equiv. of **2** was used. [c] 5 mol% of $Pd(TFA)_2$ was used. [d] **1a** (4 equiv.), **2** (0.1 mmol), $Pd(TFA)_2$ (5 mol%), Ag_2O (4 equiv.), DMSO (1.5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

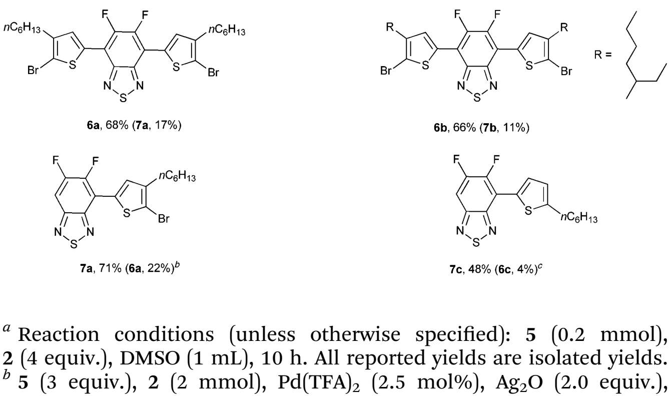
in only one step, thus offering us a unique opportunity to use such compounds as monomers for polymerization through a direct arylation approach.[12] This would be useful for the development of high performance BHJ solar cells and field-effect transistors.[13] However, it is difficult to form these unsymmetrical 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, whereas only a 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** (ref. 10) with thiophenes was then investigated. It was found that the standard reaction conditions were not ideal for FTAZ. The reaction efficiency was further improved by addition of 1.0 equiv. of HOAc with 5 mol% of $Pd(OAc)_2$, which afforded **3o–q** in good yields.

The importance and utility of the method can also be exhibited by the rapid formation of the prominent FBT–thiophene monomers. As shown in Table 3, a symmetrical monomer **6a** used to improve the PCE of BHJ solar cells up to 8.3% (ref. 14) was easily synthesized between unfunctionalized DFBT **5** and **2a** in good yield (68%) *via* only one step, albeit with the formation of 17% yield of mono-thienylated product **7a**.[15] This is in sharp contrast to the traditional techniques used 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 methods, 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 concentrations by tuning the ratio between **5** and **2** (**7a** and **7c**). To our delight, even when the reaction was run on a 2 mmol scale, a high yield (71%) of mono-thienylated product **7a** was still obtained. A synthetically useful yield of **7c** was also afforded under similar reaction conditions on a 1 mmol scale synthesis. Although 3.0 equiv. of **5** was used to suppress the formation of bi-thienylated product **6**, compound **5** was easily recovered after the reaction.

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





6a, 68% (**7a**, 17%)

6b, 66% (**7b**, 11%)

7a, 71% (**6a**, 22%)[b]

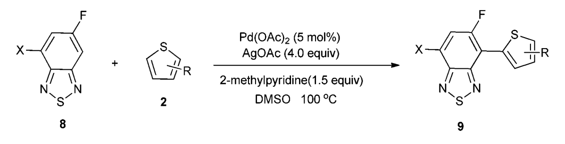
7c, 48% (**6c**, 4%)[c]

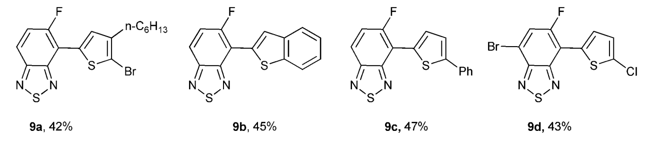
[a] Reaction conditions (unless otherwise specified): **5** (0.2 mmol), **2** (4 equiv.), DMSO (1 mL), 10 h. All reported yields are isolated yields. [b] **5** (3 equiv.), **2** (2 mmol), $Pd(TFA)_2$ (2.5 mol%), Ag_2O (2.0 equiv.), DMSO (6 mL), 10 h. [c] **5** (3 equiv.), **2** (1 mmol), $Pd(TFA)_2$ (2.5 mol%), Ag_2O (2 equiv.), DMSO (2.5 mL), 10 h.

The substrate scope with respect to FBTs was not restricted to difluorinated substrates; mono-fluorinated BTs (MFBTs)[17] **8** were also examined. It was found that these compounds **8** were less reactive than their difluorinated counterparts due to the low acidity of the 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 an additive could afford products **9** in synthetically useful yields, in which the most acidic C–H bonds located between fluorine and C=N were the primary reaction sites (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 photovoltaic studies.

It was also possible to prepare unsymmetrical dithienylated DFBT *via* a 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**, leading to unsymmetrical DFBT derivatives **11** and **12** respectively, which are otherwise difficult to prepare, in a highly efficient manner. It is noteworthy that compound **11** can be a useful monomer for polymerization through a 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, the symmetrical DFBT derivative **14**, a new red light-emitting dye, was also synthesized from **6a** with high efficiency (Scheme 1b) (for the UV-vis absorption spectrum of **14** see ESI Fig. S1†).[19] 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.

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





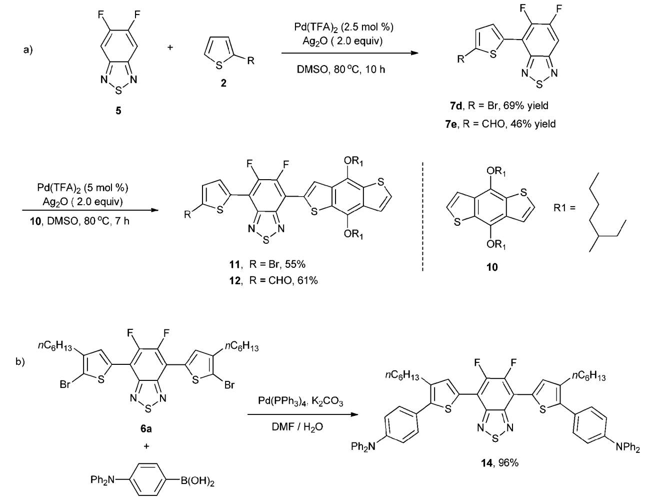
9a, 42%

9b, 45%

9c, 47%

9d, 43%

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



Scheme 1 Synthesis of unsymmetrical dithienylated DFBT *via* sequential C–H bond functionalization and synthesis of 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 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 the 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.

Acknowledgements

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