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Access to small molecules semiconductor via C-H activation for photovoltaic applications

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The first methodology of ruthenium carboxylate-catalysed single step oxidative cross coupling that challenges the conventional Stille and Suzuki coupling reactions, affording BT and MFBT derivatives in absence of protecting groups. Both mono and biarylated derivatives are formed in moderate to high yields (30-75%). Innately high selectivity, low catalyst loading and lack of formation of regio-isomers ensures the large-scale synthesis of various photonic and electronic materials employing this method.

Heteroarenes containing benzothiadiazole(BT) moieties possess a range of unique optical properties showing outstanding characteristic of functional materials.¹ The use of fluorinated benzothiadiazole (FBT) has gained immense interest in the recent past because of the small size and high electronegativity of the fluorine atom that imparts good system.² optoelectronic properties to the The benzothiadiazole-thiophene motif based on donor-acceptor assembly developed for high performance optoelectronic materials³. Substitution of the BT moieties with strong electron withdrawing groups helps in lowering the Highest Occupied Molecular Orbital (HOMO) energy levels and thereby increasing power conversion efficiency (PCE). The PCE of FBT found to increase manifold compared to that of simple benzothiazole⁴ because of the presence of the electron withdrawing fluorine atom. Several transition metal catalysed reactions have been developed for the coupling of benzothiadiazole molecules, where either one of the coupling partner has been pre-functionalised with a metal and the other with halides⁵. However, the atom economical C-C crosscoupling reactions are attractive and sustainable approach towards the synthesis of functional materials. The traditional

route to synthesize these donor-acceptor motifs includes the Suzuki and Stille coupling reaction with substituted benzothiadiazoles and their stannyl or boronyl thiophene counterpart.⁶ Although, the method is widely established one, it suffers several drawbacks. Firstly, stannyl derivatives are highly toxic and leave behind environmentally hazardous byproducts. Secondly, in case of the boronic acid derivatives reaction procedure involves a number of steps including the halogenation and boronylation of benzothiadiazole and its coupling partner. It is in fact a challenging task to perform controlled halogenation as always a mixture of mono and bi halogenated compounds obtained that further on treatment with the stannyl or boronyl derivative leads to different products. Thirdly, the scope of this method is restricted mainly to symmetrical products thereby limiting its diverse applications.⁷

Recent report by Zhang et.al on the selective thienylation on fluorobenzothiadiazole derivatives requires the blocking of every active site of the FBT keeping only one C-H bond available for reaction.⁸

The selectivity of the catalytic system not seemed to be sufficient to react at one particular active site in presence of others. This reaction can also be performed in absence of blocking groups using main group catalysts along with bis(dibenzylideneacetone)Pd⁰ as reported by Paul and co-workers⁹. However, one of the major drawbacks like synthesis and stability of main group metal catalysts makes the process less suitable for a large-scale synthesis¹⁰. Grignard reagents used in this process are highly moisture sensitive and requires immense care while maintaining an intense inert condition. In order to overcome these drawbacks, we have tried to use catalysts that are moderately reactive, less sensitive but more selective in nature as depicted in Fig 1.

Earlier our group had studied the effect of bulky $Ru(MesCO_2)_2p$ -cymene on the alkenylation of nitrogen directing inactivated aryl moieties¹¹ and we further wanted to explore the catalytic capability of $Ru(MesCO_2)_2p$ -cymene on inactivated benzothiadiazoles. As ruthenium catalysts are less reactive but more selective in nature compared to other

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shown in ESI Table 1.

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transition or main group metals generally used as catalyst, the addition of bulky acid group however enhanced its reactivity manifold. The present work reports the sp^2-sp^2 coupling between the unsubstituted benzothiadiazole and thiophene counterpart in the presence of catalyst and oxidant.



Fig.1 Summary of the previous reports in contrast to the present work

The initial screening reaction was performed with benzothiadiazole (1) and 2-bromothiophene (2a) with catalyst $[Ru(p-cymene)Cl_2]_2$, oxidant AgOAc and toluene as solvent. However, the negative result for the above reaction motivated us to change the solvent from non-polar to highly polar and high boiling solvents like DMF, DMSO etc. (Fig 2). Change in solvent from toluene to DMF increased the yield of 3a to 32% and a remarkable hike to 56% was found on using DMSO as a solvent.¹²



Fig.2 Representative optimisation reaction

The product 3a emphasizes the fact that reaction is tolerant to bromo group and therefore the coupling involved H-H removal instead of H-Br removal. The yield of this product was further improved to 65% on changing the catalyst to Ru(pcymene)(MesCO₂)₂.The detailed optimization table is mentioned in the ESI as Table 1. The carboxylic acid based ruthenium catalyst sets off the attack of the coupling partner directly to the ortho-position of the directing group¹³. The bulkiness of the acid group helps in the easy formation of a thermodynamically favoured 6-membered transition state¹⁴. Although silver acetate, a renowned oxidizing agent for orthoarylation¹⁵, we found better results on using silver oxide, a milder oxidizing agent. Surprisingly enhanced yield of 3a (70%) was found on increasing the catalyst loading to 20 mol%. However excess catalyst loading upto 25 mol%, diminished the



yield of 3a (67%) probably due to catalyst deactivation as

Fig.3 Representative examples of the synthetic schemes with heteroarenes

Further rise in the yield of 3a to 74% was observed when the oxidant loading was increased to 15 mol%. Combination of DMSOpiperidine as a solvent leads to higher yields when piperidine a base is added in minimal amount (1-2 drops). Addition of a catalytic amount of piperidine in DMSO (pk_a= 0.5) helps in the easy abstraction of the less acidic C-H bond of the BT and FBT¹⁶. Scale up reaction was carried out for 3a derivative in order to affirm the applicability of this methodology in commercial grounds. The reaction for 3a was performed on a scale of 2 mmol, 5 mmol, 8 mmol and 10 mmol, where the yields ranged from 65% to 75% (see ESI). This confirms the availability of this reaction on a few milligram scales for the large scale synthesis. Formation of 3b, 3j and 3i required around 12hr for completion along with residual starting material. Further prolonging the reaction time for these derivatives did not help in any improvement of their respective yields. Substrates containing fluorine 3p, 3q, 3r and 3x required less reaction time (4hrs) than their non-fluorine counterparts. This may depend on the lability of the C-H bond adjacent to the nitrogen atom. The homo-coupling product of 1 in Fig 2 was not observed under the above reaction conditions thereby making this method a Published on 05 June 2018. Downloaded by California State University at Fresno on 05/06/2018 20:07:09

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more versatile one. Coupling of a range of thiophenes and substituted thiophenes under the optimised reaction conditions resulted in mono-substituted derivatives with high yields. Thiophenes with variety of substitutions like bromides, acids, aldehydes, cyano showed excellent functional group tolerance resulting in products (3a, 3c, 3g-3i, 3m-3o, 3r) with moderate to high yields as shown in Fig. 3. The products with aldehyde and acid at the terminal end (3c, 3h, 3n, 3o, 3r) utilized as potential cosensitizer precursor for Dye Sensitized Solar Cells (DSSC). Similarly, bisthiophene and thienothiophene (3b, 3e, 3j), obtained in good yields can be useful in Bulk Heterojunction (BHJ) solar cells and field effect transistors¹⁷.Compounds like 3e, 3g, 3t can be easily synthesized in one-step using excess amount (4eqv) of the thiophene partner. The unreacted thiophene or thiazole was recovered from the reaction mixture through column chromatography.

Further exploration, observed the selective synthesis of monothienvlated product required the use of excess amount of BT (3-4 eqvs). The tuning of the ratio of 1 and 2a (as depicted in Fig. 2) can lead to successful formation of mono (3a) and bi coupled (3g) products. In this process, we observed around 62% of bi-arylated compound and 12% of mono arylated compound. This significantly contrasts to the other traditional methods where 4,7-diiodoFBT¹⁸ is reacted with the stannyl thiophene, followed by bromination¹⁹. We can overcome the demerits of the conventional methods like toxicity, harsh conditions and increased number of steps using the previously mentioned procedure. This can also be useful for the synthesis of unsymmetrical FBT derivatives in one pot provided the addition of the second thiophene partner was made after assuring the complete reaction with the first thiophene (see ESI synthesis of 3ac). The unreacted BT if any was easily separated using column chromatography and hence there is no loss of starting material.

Since benzothiadiazole-dibenzene, structural motifs have found immense application as optoelectronic materials; their synthesis was performed under the developed reaction conditions. Upon optimisation, it was realised that the standardised reaction conditions mentioned earlier in this paper was not favourable for the coupling of benzothiadiazole with benzene. The reason may be the lesser reactivity of the unsubstituted benzene in comparison to other heterocycles.



Fig.4 Synthetic scheme for the reaction of BT or FBT with benzene

Another set of reactions were performed using 1.0 eqv of BT or FBT and 4-8 eqv of benzene in 1ml of DMSO along with 0.2ml of piperidine were found to be the facile reaction condition for mono and di-arylation (Fig 4). Unlike thienylation, arylation using benzene required excess of piperidine because of the unavailability of acidic hydrogen's on either of the coupling partner. The yields of the final products (3v-3y) dramatically improved from low to moderate on replacing Ag_2O with AgOAc.

The plausible mechanism of the reaction is illustrated in Fig 1-ESI, where it is expected that the initial hydrogen abstraction from the benzothiadiazole takes place with the help of the catalytic amount of piperidine that is added in the reaction mixture and the electron rich benzothiadiazole species is attacked by the ruthenium complex that is electron deficient thereby forming a 16e⁻ species which undergoes oxidative addition. Earlier reports on the mechanistic studies of ruthenium(p-cymene) catalyst by Fabre et.al have clearly mentioned that the oxidative addition takes place on the 16e⁻ ruthenium species.²⁰ The addition of thiophene leads to the formation of the complex C that is indicated in the HRMS spectra. In the later stage the complex undergoes reductive elimination to give the desired product and a ruthenium complex that undergoes one electron reduction in presence of silver to regenerate the catalyst.

Upon synthesis of the above molecules we explained its possible application in DSSC as co-sensitizer. The metal free organic sensitizers are an exemplary candidate for the co-sensitized DSSCs,²¹ because of its high molar extinction coefficients, easy structural modification, and facile synthetic process. Earlier, some groups have reported small organic dyes highlighting a simple donor- π -acceptor structure using benzothiadiazole as a core moiety, which successfully enhanced the incident photon-to-current conversion efficiency (IPCE) of black dye (BD) in the UV region in a co-sensitized DSSC.²² However, improvements in the spectral response require to harvest the maximum light matching the commercial needs. Therefore, synthesis of several organic dyes employed, showed a reasonable absorbance in the UV-Vis region successfully to increase the photocurrent in co-sensitized DSSCs.²³



Fig.5 Scheme for the synthesis of cyanoacetic acid co-sensitizers Based on the above strategy, syntheses of a series of light harvesting dyes were conducted for application in dye-sensitized solar cells. Here we have shown few different applications of the synthesized derivatives in solar cell. Co-sensitization is one of the most prominent techniques to enhance the PCE of DSSCs. Research groups across the globe including ours have been working on this technique to achieve higher PCE²⁴⁻³⁰. In addition to our efforts in the coupling of FBT or BT with heteroarenes, we also derivatized the products 3c and 3r to their respective cyanoacetic acids (FBT-CAA and BT-CAA) (Fig 5). These molecules used as co-sensitizers

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with ruthenium complex N749 (Black dye) as a base dye to construct the DSSC devices.

These molecules (3c and 3r) showed very high PCE of 11.55% with high J_{sc} of 23.41mA/cm² (detailed in the ESI Fig. 4 table 4). It is noteworthy to mention that our aim was not to achieve high efficiency but just to confirm that our catalytic protocol may be utilized for more appropriate and highly efficient organic compounds. Finally, this methodology could also be employed to develop several small molecules having thienothiophene³¹ and thienogermoles³²moeities for their various solar cell applications.

In summary, we have accomplished highly selective one-step cross thienylation and arylation of the benzothiadiazole and fluorobenzothiadiazole using ruthenium as a catalyst. The reaction pathway ended up with high regio and chemo selectivity. The coupling with selenophene as well as benzoselenadiazole afforded high yields, which also proves to be tolerant with diverse functional groups in good efficacy. Even coupling with thieno[3,2b]thiophene gave better results which otherwise is difficult to synthesis following the conventional methods. On extending the derivatives for further applications in DSSC, high efficiency was observed. These inspiring results helps us to conclude that, use of the studied methodology as a replacement for the conventional techniques leads to synthesis of complex molecules for solar cell applications thereby, making this method versatile for large-scale production.

Conflicts of interest

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Authors declare no conflict of interest.

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