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Ferrocene catalysed heteroarylation of BODIPy and reaction mechanism studies by EPR and DFT methods

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Abstract: The C-H heteroarylations of BODIPy using heteroaryl diazoniumtetrafluoroborate and ferrocene (Fc) as catalyst were carried out. Mono and di heteroaryl BODIPy derivatives (**1-8**) were obtained in a cost-effective way. This method gives easy access to 4-pyridyl substituted BODIPy (**7-8**) which are useful to synthesize water soluble derivatives for biological applications. Reaction pathway for this reaction was studied by carrying out the spin cross-over experiments using electron paramagnetic resonance (EPR) technique. A strong signal in EPR was obtained in the presence of ferrocene and heteroaryldiazonium salt which indicates the formation of radicals during the initial steps of reaction. In addition, we have also performed the computational investigations on different steps of reaction to elucidate the role of ferrocene as a radical initiator in this reaction.

Introduction

4,4'-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPy) is one of the most popular dye family and has been studied extensively in past few years.[1-3] BODIPy dyes are known for their rich optical properties, photostability etc. Photophysical, electrochemical and

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morphological properties of these dyes can be tuned, almost at will, which makes BODIPy an important fluorophore for applications in different areas.[4-6] A variety of substituted BODIPys with variable degree of conjugations, multimeric BODIPy, conjugates of BODIPy with other fluorophores, such as porphyrins, substitution with variety of aryl groups have been synthesized to alter the photophysical properties.[7] Heteroarylation of BODIPy, has also been well explored as substitution of heteroaryls changes the optical properties drastically.[8] Even though many BODIPy derivatives bearing various heteroaryl substituents have been reported, methods of their synthesis are rather challenging. In general, to synthesize the heteroaryl derivatives of BODIPy one can start with the heteroaryl substituted pyrrole. A few reports are available for the synthesis of 3,5-diheteroaryl BODIPy in multiple steps.[9] In some of these methods, 2-heteroaryl substituted pyrroles were first synthesized and further used in the synthesis of heteroaryl BODIPy. In other approaches, transition metal catalysed coupling reactions (Suzuki Miyaura, Stille coupling etc.) were used to synthesize the aryl BODIPy derivatives.[10] These coupling reactions require expensive transition metal catalyst, heteroaryl coupling partners and halogenated BODIPy. In these methods, purification of desired heteroaryl BODIPy is quite tedious.

The transition-metal-free processes have been realized as alternative choices to perform various aryl C-C cross-coupling reactions. Several such reactions have been suggested, such as, base promoted coupling reaction between unactivated arenes and aryl halides have been used in the presence of nitrogen heterocyclic ligands.[11] In situ, metal complex formation with ligand facilitates the single-electron-transfer (SET) from metal tert-butoxides to ligands on heating or in the presence of light.[12] Light absorbing metal

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complexes (Ir-ppy complex) or other chromophores have been used as active photoredox catalyst in C-H arylation.

Recently, Dehaen et al. showed a very useful, convenient, efficient and cost-effective method for C-H arylation of BODIPy.[13] In this, phenyl BODIPy derivatives were synthesized by the reaction of phenyldiazoniumtetrafluoroborate with BODIPy in presence of ferrocene as catalyst. Later, alkylated BODIPy derivatives were synthesized using alkyltrifluoroborate or boronic acids and manganese acetate as catalyst.[14] Herein, we further extend the method developed by Dehaen et al to synthesize heteroaryl substituted BODIPy derivatives **(1-8)** by using convenient and cost-effective way. Heteroaryl diazoniumtetrafluoroborate and ferrocene along with BODIPy were reacted in acetone at room temperature. To get the insight on the possible reaction mechanism the electron paramagnetic resonance (EPR) experiments were carried out. Spin cross-over experiments with 5,5-dimethyl-pyrroline N-oxide (DMPO), in presence of ferrocene, helped in trapping the radicals formed in reaction. Furthermore, reaction mechanism is investigated using density functional theory (DFT) methods. The comparison of free energies of different steps of reaction, using ferrocene and other catalysts such as CuCl and ascorbic acid, helped to understand the role of ferrocene in this reaction. At this stage we believe that reaction proceeds with radical formation. Absorption and emission properties of heteroaryl BODIPys are also reported.

Results and Discussion

The heteroaryl BODIPys **(1-8)** were synthesized by the reaction of heteroaryl diazoniumtetrafluoroborate and BODIPy precursor with ferrocene as catalyst (Scheme 1).

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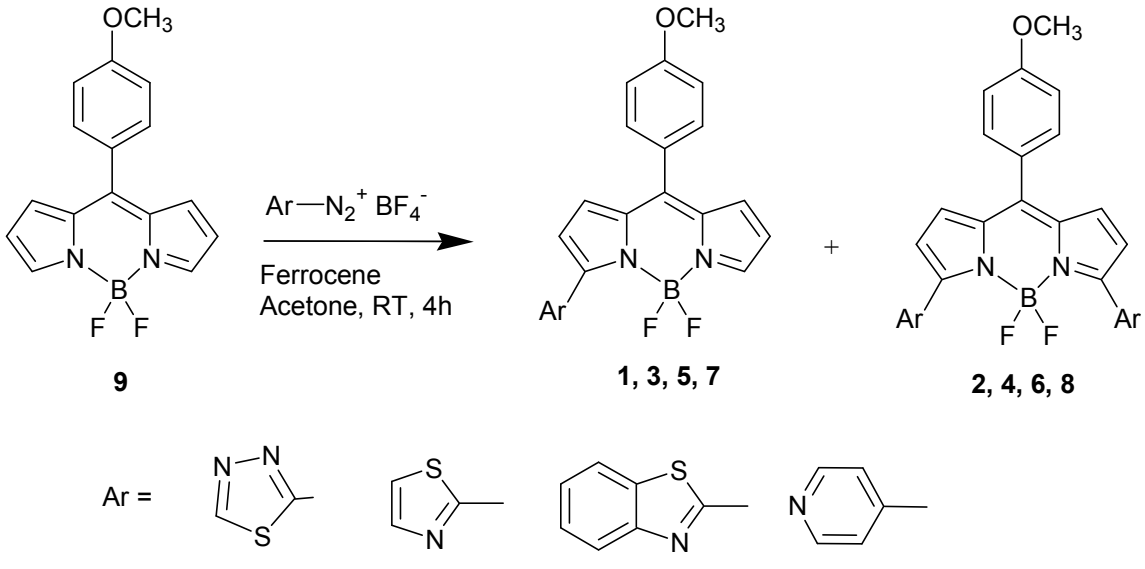
The precursor 8-anisyl BODIPy was synthesized by the literature method[15] whereas the diazonium salts of heteroaryls were synthesized by slightly modified classical method. The unsubstituted BODIPy was reacted with 2-thiadizole diazoniumtetrafluorborate, 2-thiazole diazoniumtetrafluorborate, 2-benzothiazole diazoniumtetrafluorborate, and 4-pyridyl diazoniumtetrafluoroborate in the presence of ferrocene to get the compounds **1-8**. All these reactions produced a mixture of mono and di-heteroaryl substituted BODIPys. The exclusive synthesis of di-heteroaryl BODIPy could not be achieved, irrespective of the number of equivalents of diazonium salts. All these reactions were monitored by thin layer chromatography and absorption spectroscopy. After about 4 h all the starting BODIPy was found to be consumed. Purification by column chromatography afforded the pure **1-8** in 40-70 % yields except for compound **2**. For compound **2** only 4-5% yield was observed even in the excess of 2-thiadizole diazonium salt. Compounds **1-8** were characterized by several spectroscopic techniques which include ^{1}H-NMR, ^{13}C-NMR, MALDI-mass etc. Compounds **1-8** are fairly soluble in common organic solvents.



Scheme 1: Ferrocene catalysed synthesis of BODIPy derivatives, **1-8**.

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Figure 1 shows the ^{1}H-NMR and ^{13}C-NMR of compound **6**. Two doublets were obtained for pyrrolic protons between 8.0-8.2 ppm in ^{1}H-NMR. These two doublets show the substitutions at -3,5 positions only and not at 2,6 positions in which case we expect two singlets for pyrrolic protons. Substitutions at 3,5 positions was further confirmed with the help of correlation spectroscopy (COSY) (see SI information). Other peaks in aromatic region were assigned to aryl substituents.

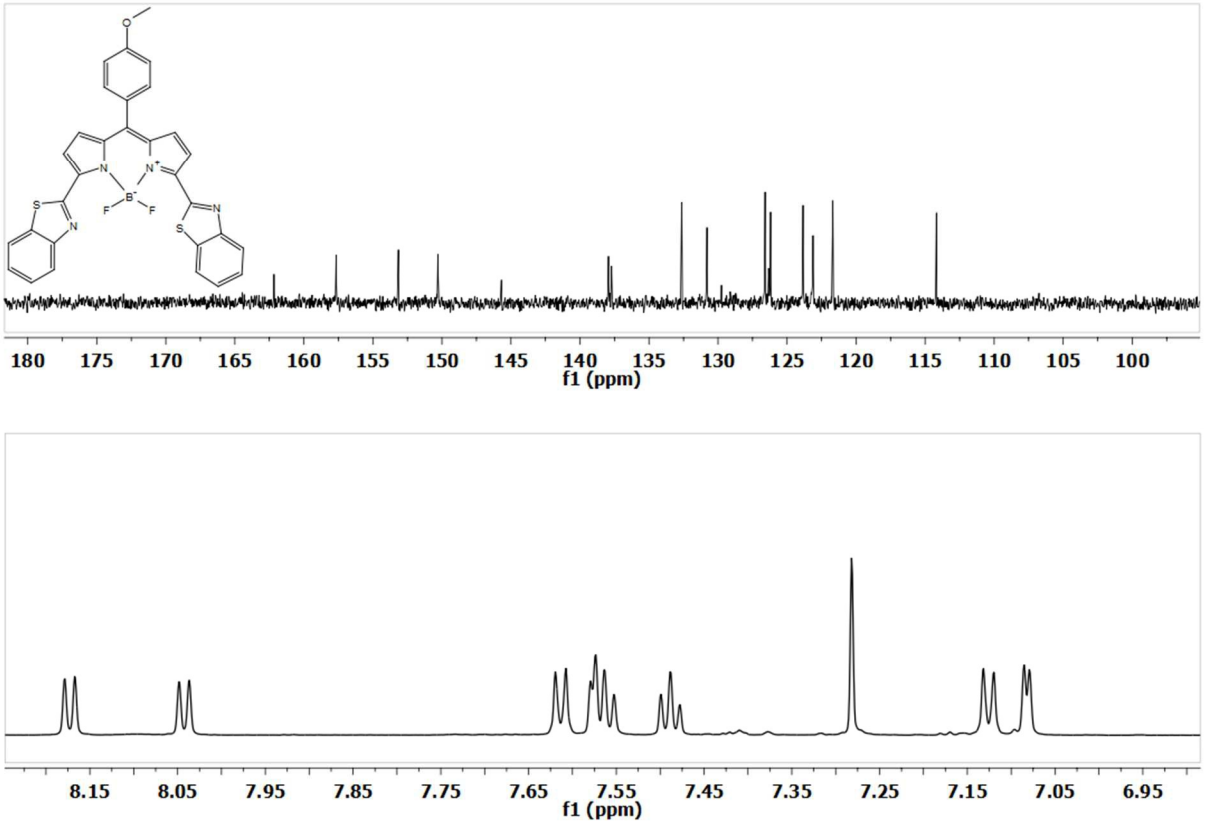

Figure 1: ^{13}C-NMR and ^{1}H-NMR of BODIPy derivative **6** (only aromatic region is shown for better clarity)

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To get an insight on the reaction mechanism we carried out a set of electron paramagnetic resonance (EPR) experiments. The EPR spectra were recorded on X band spectrometer (Bruker EMX series) at room temperature. Samples were degassed by passing high purity N_2 gas before recording EPR. No signal was observed when diazonium salt and ferrocene mixture was used. This does not rules out the absence of aryl radicals as it may be short lived or efficiently relaxing. It is well known to use 5,5-dimethyl-pyrroline N-oxide (DMPO) as spin trapping agent for aryl radicals in spin cross-over experiments.[16] Reaction mixture of diazonium salt and DMPO produced a weak signal in EPR which shows the presence of radical formation. A sharp increase in intensity of this signal was observed when EPR was conducted with diazonium salt, DMPO and Fc together (Figure 2). A sharp increase in the intensity in EPR spectrum in presence of Fc indicates the catalytic behaviour of Fc in the radical formation. Weak signal obtained in the absence of ferrocene was attributed to the self decomposition of diazonium salt. It will be worth to note that reaction of diazonium salt and BODIPy gives desired product even in absence of ferrocene albeit in lesser yield and more reaction time.

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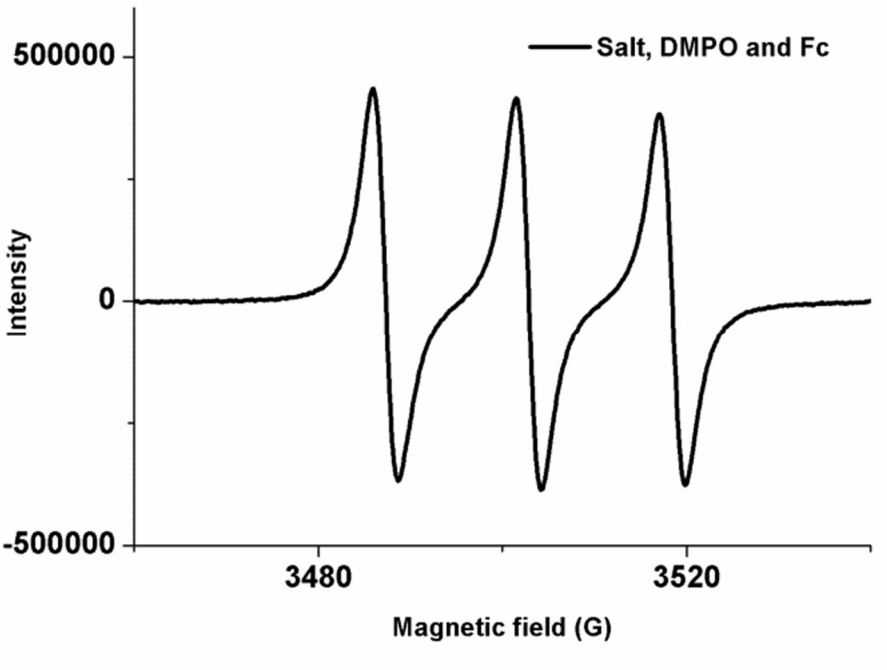

Figure 2: Electron paramagnetic resonance spectrum of 2-benzothiazolediazonium salt, ferrocene and DMPO in acetone.

Having established the formation of radical intermediate in these reactions, we further investigated the mechanism of reaction using the density functional theory (DFT) calculations to establish the role of Fc in the reaction. The proposed steps involved in the reaction mechanism are shown in Scheme 2. All calculations were performed using Gaussian 09 suite of programs.[17] The geometries of the reactants, intermediate structures and transition states were optimized in the solvent phase using the M06-2X functional[18] (UM06-2X functional for open shell systems) with 6-311G** basis set. The solvent effect of acetone was taken into account by the polarizable continuum model (PCM).[19] The free energy changes of each step of the reaction are calculated and provided in table 1.

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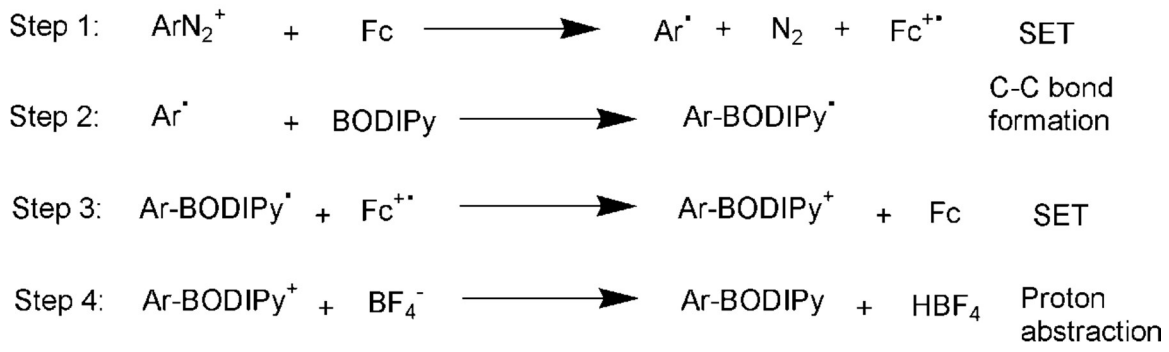

Scheme 2: Proposed reaction steps involved in the radical mechanism.

The reaction commences with a single electron transfer (SET) from ferrocene to the aryl diazonium salt which splits aryl diazonium salt into aryl radical and nitrogen molecule. The 2-thiazole diazoniumtertrafluroborate was taken as a model aryl diazonium salt in the calculations. A SET from ferrocene to thiazole diazonium salt is found to be exoergic by 10.3 kcal/mol. In the next step, thiazole radical adds to BODIPy to form radical σ complex Ar-BODIPy•. This step is predicted to be exoergic by 35.1 kcal/mol. The transition state for the addition thiazole radical to BODIPy was also located at the M062X/6-311G** level of theory. The addition of thiozole radical to the BODPy requires an activation barrier of 9.5 kcal/mol. The resulting Ar-$BODIPy^\bullet$ radical transfer an electron to the $Fc^{+\bullet}$ to generate cationic σ complex Ar-$BODIPy^+$, this step is also found to be exoergic by 7.1 kcal/mol. In final step, the Ar-$BODPy^+$ loses its proton to BF_4^- to provide heteroaryl BODIPy.

It is quite evident from these results that the ferrocene plays crucial role in electron transfer steps (Step-I and Step-III) since these steps are found to be fairly exoergic. To gain better insights on the role of ferrocene in electron transfer steps, free energies of

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these steps were calculated by replacing ferrocene with other reducing agents such as CuCl and ascorbic acid. The free energy changes of step-I and step-III involving CuCl and ascorbic acid are provided in Table 1. Interestingly, electron transfer from CuCl and ascorbic acid to thiazole diazonium salt is found to be endoergic by 13 kcal/mol. Thus, it is clear that ferrocene ensure a facile electron transfer to the diazonium salt and helps to initiate aryl radical from diazonium salt.

Table 1: The free energies (kcal/mol) of steps involved in heteroarylation of BODIPy calculated using DFT

Step	Fc	CuCl	L-Ascorbic acid
Step-I (ΔG1)	-10.3	13.3	13.8
Step-II (ΔG2)	-35.1	-	-
Step-III (ΔG3)	-7.1	-30.4	-31.2
Step-IV (ΔG4)	-12.1	-	-

BODIPy derivatives **1-8** were studied by absorption and emission spectroscopies in solution. The Figure 3 shows the absorption and emission spectra in toluene. Compounds **1-8** showed strong S_0-S_1 ($\pi-\pi*$) absorption maxima in the range of 524-632 nm. This band is assigned to diisoindolomethene core of compounds **1-8**. The absorption maxima of this band are directly dependent on the extent of de-localization of π electrons of heteroaryl substituents on BODIPy core. The broad band observed in the high energy region 414-461 nm of spectrum corresponds to the S_0-S_2 transition of the boradiazaindacene. Substitution of heteroaryl groups produced large bathochromic shift

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of around 20-130 nm in absorption maxima in comparison to un-substituted BODIPy.[15] Molar absorption coefficients for **1-8** were high and are summarized in Table 2.

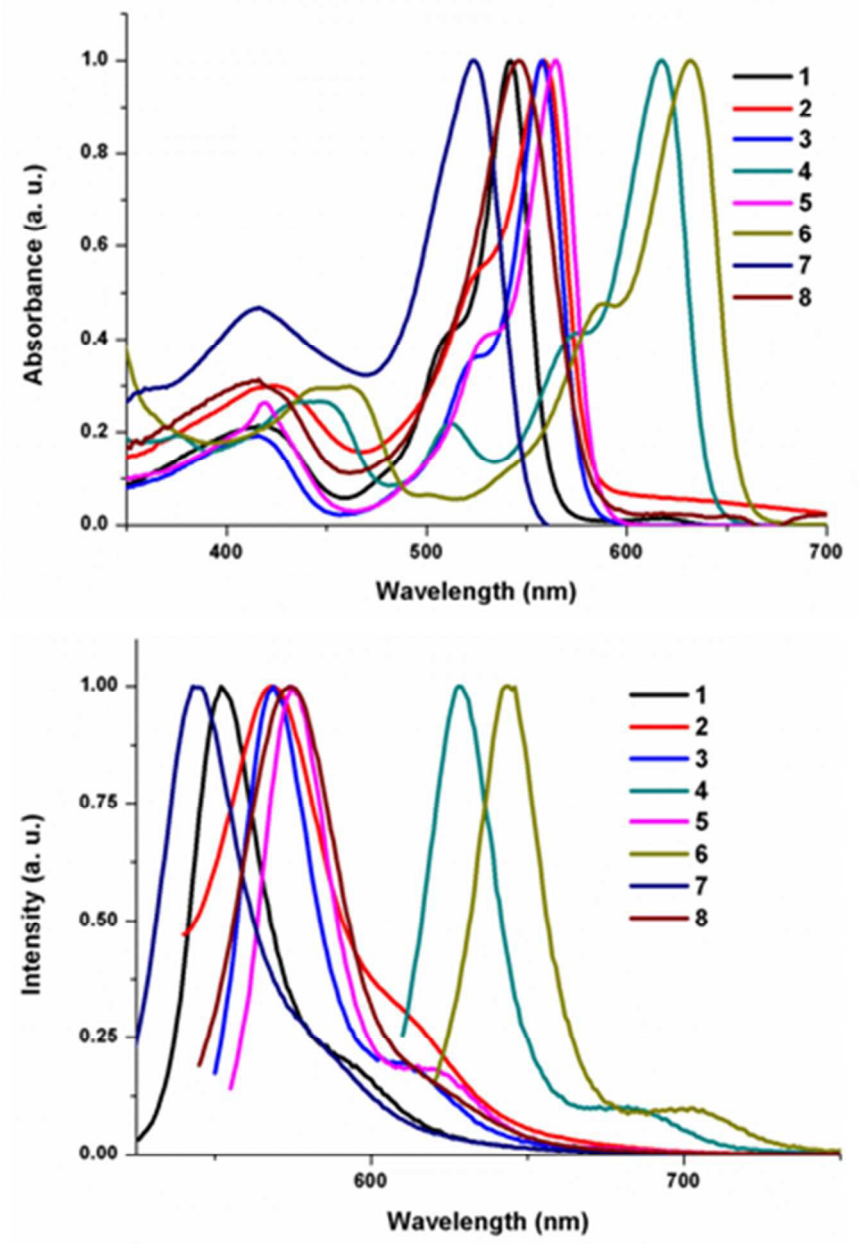

Figure 3: Absorption (above) and emission (below) spectra of **1-8** in toluene.

Emission spectra of compounds **1-8** recorded in toluene are shown in Figure 3. Compounds **1-8** showed emission peak at 544 -644 nm with a low intensity shoulder in

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further low energy region. Compounds **1-8** showed bathochromic shifts in emission spectra and upto 110 nm red shifts were observed in comparison to un-substituted BODIPy. A very small Stoke shift of ~10 nm for **1-6** was observed while for **7-8** Stoke shift of ~ 25 nm was observed, which suggests the change occurred in the ground and excited state geometry is minimal in **1-6**. Fluorescence quantum yields of compound **1-8** were calculated with respect to either Rhodamine B ($\phi = 0.68$ in ethanol) or tetraphenyl porphyrin (TPP)[20] (Table 2). Fluorescence life time studies of **3-6** were carried out in toluene and data are presented in Table 2.

Table 2: Photophysical properties of **1-8** in toluene.

Compounds	λ_{abs} & ε [nm] (log)	λ_{em} [nm]	Φ	τ [ns]
Std.[15]	503 (4.73)	521		
1	542 (4.76), 509 (4.37), 414(4.08)	552, 594	65[a]	-
2	559 (4.52), 523, 421	568	60[a]	-
3	558 (4.87), 522 (4.42), 416(4.15)	568, 610	55[a]	7.7
4	617 (4.83), 572 (4.45), 448(4.26)	628, 681	370[b]	1.8
5	565 (4.95), 527 (4.54), 419(4.33)	575, 618	71[a]	9.5
6	632 (4.85), 586 (4.52), 461(4.32)	644, 704	410[b]	9.1
7	524 (4.67), 414 (4.46)	544	22[a]	-
8	546 (4.22), 414 (3.6)	574	10[a]	-

[a]w.r.t. Rhodamine B; [b]w.r.t. tetraphenyl porphyrin

Conclusion

The heteroarylation of BODIPy is achieved in moderate to good yields using diazonium tetrafluoroborate and ferrocene as a catalyst. Furthermore, the reaction mechanism was investigated using electron paramagnetic resonance (EPR) experiments and DFT calculations. Spin cross over experiments on the ferrocene mediated reaction showed sharp signals in EPR

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spectrum indicating the formation of radical intermediate in the initial step of the reaction. We also elucidated the role of ferrocene as a radical initiator in this reaction using the DFT calculations. EPR experiments and DFT calculations support the radical mechanism for the ferrocene mediated heteroarylation of BODIPy using diazonium salt. The absorption and emission properties upon heteroaryl substitutions on BODIPy were studied. To the best of our knowledge a conclusive proof for this mechanism is being reported here for the first time. We strongly believe that knowledge on the pathway of reaction mechanism of this C-H arylation will help in designing the advanced materials for various applications.

Experimental section

Chemicals and instrumentation

All general chemicals and solvents were procured from S D. Fine Chemicals, India and Sigma-Aldrich. Column chromatography was performed using silica gel of 100-200mesh size. The ^{1}H and ^{13}C-NMR (δ in parts per million) spectra were recorded using a Bruker 500 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal reference for recording ^{1}H-NMR spectra (residual proton; δ = 7.26 ppm) in CDCl3. The MS spectra were recorded on Bruker MALDI-TOF. UV–vis spectra were acquired on Shimadzu 1800. Fluorescence measurements were carried out using Horiba Fluoromax 4. For emission, compounds **1-8** were excited at 380 nm. Photophysical studies were carried out in toluene (~1 X 10^{-6} M). The EPR spectra were recorded on X band spectrometer (Bruker EMX series) at room temperature. Samples were degassed by passing high purity N_2 gas before recording EPR.

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Synthesis and characterization of BODIPys (1-8)

A round bottom flask was charged with BODIPy (1 eqv.), respective aryl diazonium tetrafluoroborate (4 eqv.) and acetone. Ferrocene (0.1 eqv.) solution in acetone was added dropwise and slowly in 15 min time at room temperature. Reaction mixture was further stirred for 4h. A noticeable colour change of reaction mixture was observed. Reaction mixture was extracted with dichloromethane and organic layers were washed with brine and water. Solvents were removed and crude product obtained was purified by column chromatography using hexane and dichloromethane to afford the compounds **1-8** (~ 40-70% except for **2**) as purple or greenish solids.

3-(2-thiadizolyl)-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-s-indacene, **1:** Purification by silica gel column chromatography using hexane and dichloromethane (2:8) produced **1** as brown solid. Yield: (15 mg, 40 %); M.P.: 132 ^{o}C; ^{1}H-NMR (500 MHz, $CDCl_3$)): δ 9.32 (s, 1H), 8.03 (s, 1H), 7.60 (d, 2H, J = 8.55 Hz), 7.50 (d, 1H, J = 4.3 Hz), 7.11 (d, 2H, J = 8.5 Hz), 7.08 (t, 2H, J = 6.9 Hz), 6.68 (d, 1H, J = 3.6 Hz), 3.90 (s, 3H, OCH_3); ^{13}C-NMR (500 MHz , $CDCl_3$):δ 154.05, 153.34, 145.45, 144.64, 139.27, 132.57, 132.49, 130.70,126.01, 121.08, 114.27, 114.21; MALDI-TOF mass for $C_{18}H_{13}BF_2N_4OS$ calcd.382.09, found 363 $(M-F)^+$.

3,5-Bis(2-thiadizolyl)-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-s-indacene, **2**: Purification by silica gel column chromatography using hexane and dichloromethane (2:8) produced **1** as brown solid. Yield: (2 mg, 4 %); M.P.: 168 ^{o}C; FT-IR (KBr, cm^{-1}): ν 3090.6, 2920.7, 2851.4, 1706.9, 1525.6, 1546.3, 1503.5, 1395.9, 1370.9, 1297.2, 1253.2,

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1176.8, 1127.3, 1069.4, 1021.2, 979.2, 879.4, 795.4, 739.9, 708.4, 608.1; MALDI-TOF mass for $C_{20}H_{13}BF_2N_6OS_2$ calcd.466.63, found 446.63 $(M\text{-}F)^+$.

3-(2-thiazolyl)-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-s-indacene, **3:** Purification by column chromatography using hexane and dichloromethane (2:8) produced **3** as brown solid. Yield: (20 mg, 52 %); M.P.: 184 ^oC; FT-IR (KBr, cm^{-1}): ν 3113.5, 2956.2, 2917.4, 1602.3, 1525.0, 1505.0, 1297.0, 1251.1, 1170.2, 796.8, 734.5; ^{1}H-NMR (700 MHz , $CDCl_3$): δ 8.04 (s , 1H), 7.97 (s, 1H), 7.66 (d, 1H, J = 3.85 Hz), 7.57 (d, 2H, J = 11.7 Hz) , 7.35 (d, 1H, J = 5.3 Hz), 7.09 (d, 2H, J = 11.9 Hz), 7.04 (d, 1H, J = 5.2 Hz), 6.99 (s, 1H), 6.61 (s, 1H), 3.94 (s, 3H OCH_3); ^{13}C-NMR (600 MHz , $CDCl_3$): δ 162.04, 157.41 , 149.75, 144.55, 143.80, 137.26, 132.35, 130.55, 126.32, 123.74, 121.83, 113.98, 29.58; MALDI-TOF mass for $C_{19}H_{14}BF_2N_3OS$ calcd. 381.2, found 381 $(M)^+$, 361.7 $(M\text{-}F)^+$.

3,5-Bis(2-thiazolyl)-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-s-indacene, **4:** Silica gel column chromatography using hexane and dichloromethane (2:8) produced **4** as brownish purple solid. Yield: (25 mg, 54 %); M.P.: 204.2 ^oC; FT-IR (KBr, cm^{-1}): ν 3076.5, 2922.4, 2850.1, 1538.3, 1454.4, 1250.0, 1066.0, 853.6, 791.3, 734.5; ^{1}H-NMR (700 MHz , $CDCl_3$): δ 8.02 (d, 2H, J = 2.3 Hz), 7.64 (d, 2H, 2.85 Hz), 7.55 (d, 2H, J = 8.4 Hz), 7.37 (d, 2H, J = 3.9 Hz), 7.07 (d, 2H, J = 3.9 Hz), 6.98 (d, 2H, J = 8.4 Hz), 3.94 (s, 3H); ^{13}C-NMR (500 MHz , $CDCl_3$):δ 161.93, 157.48, 149.60, 146.16, 143.80, 143.49, 137.18, 134.76, 134.76, 132.36, 131.26, 130.70, 126.29, 123.42, 121.06, 118.83, 113.99,

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29.57; MALDI-TOF mass for $C_{22}H_{15}BF_2N_4OS_2$ calcd. 464.32, found 463.9 $(M)^+$, 444.9 $(M-F)^+$.

3-(2-benzothiazolyl)-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-s-indacene, **5** Column chromatography using hexane and dichloromethane (2:8) produced **5** as brown-purple solid. Yield: (29 mg, 67 %); M.P.: 179 ^oC; FT-IR (KBr, cm^{-1}): ν 3116.4, 2918.3, 2844.5, 1548.4, 1496.3, 1392.8, 1128.3, 910.4, 838.4, 781.3, 723.7; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.15 (d, 1H, J = 7.5 Hz), 8.02 (s , 1H), 7.97(d, 1H, J = 7.3 Hz), 7.55–7.57 (m, 3H), 7.44 (s, 2H), 7.02–7.07 (m, 4H), 6.63 (s, 1H), 3.92 (s, 3H,-OCH_3); ^{13}C-NMR (700 MHz , $CDCl_3$): δ 162.12, 157.82, 153.10, 149.04, 146.80, 144.73, 137.54, 137.26, 135.13, 132.50, 131.58, 130.76, 126.47, 126.25, 125.98, 123.73, 121.78, 121.53, 119.47, 114.10, 29.67; MALDI-TOF mass for $C_{23}H_{16}BF_2N_3OS$ calcd. 431.11, found 431.1 $(M)^+$ and 411.9 $(M-F)^+$.

3,5-Bis(2-benzothiazolyl)-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-s indacene, **6**: Purification by silica gel column chromatography using hexane and dichloromethane (2:8) produced **6** as brown solid. Yield: (37 mg, 66 %); M.P.: 254 ^oC; FT-IR (KBr, cm^{-1}): ν 3058.9, 2917.8, 2850.4, 1702.8, 1596.7, 1571.0, 1532.8, 1496.3, 1254.4, 1118.4, 1080.3, 1022.8, 879.1, 832.1; ^{1}H-NMR (700 MHz, $CDCl_3$): δ 8.17 (d, 2H , J = 8.12 Hz) , 8.05 (d, 2H , J = 7.98 Hz) , 7.62 (d, 2H , J = 8.33 Hz), 7.57-7.58 (m, 4H), 7.49 (t, 2H , J = 7.56 Hz) , 7.12 (d, 2H , J = 8.26 Hz) , 7.08 (d, 1H, J = 4.27 Hz) , 3.96 (s, 3H, OCH_3); ^{13}C-NMR (500 MHz, $CDCl_3$): δ 162.16, 157.66, 153.15, 150.29, 145.73, 137.94, 137.71, 132.63, 130.80, 129.75, 126.59, 126.20, 123.84, 123.11, 121.69, 114.19,

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29.6; MALDI-TOF mass for $C_{30}H_{19}BF_2N_4OS_2$ calcd. 564.11, found 564.11 (M^+) and 545.10 $(M\text{-}F)^+$.

3-(4-pyridyl)-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-s-indacene, **7**: Column chromatography was performed using dichloromethane to purify the compound **7**. Yield: (19 mg, 51%); FT-IR (KBr, cm^{-1}): ν 2920.9, 2850.9, 1710.9, 1631.6, 1598.3, 1571.7, 1539.4, 1509.8, 1462.5, 1279.2, 1175.0, 1145.5, 1069.8, 1021.6, 969.5, 810.75, 757.57, 740.03, 710.7, 683.4; ^{1}H-NMR (700 MHz, $CDCl_3$): δ 8.7 (d, 2H , J = 4.1 Hz) , 7.8 (d, 2H , J = 5.0 Hz) , 7.5 (t, 3H , J = 7.3, 8.5 Hz) , 7.0 (t, 3H J = 8.65, 6.45 Hz) , 6.9 (d, 1H, J =4.35 Hz), 6.6 (d, 1H, J =3.8 Hz) , 6.4 (d, 1H, J =5.3 Hz) , 3.9 (s , 3H, -OCH_3) ^{13}C-NMR (500 MHz, $CDCl_3$): δ 149.79, 144.28, 143.23, 139.81, 132.61, 132.49, 131.79, 131.51, 131.17, 129.68, 129.10, 126.25, 123.26, 119.82, 119.22, 117.39, 114.13, 113.15, 29.69; MALDI-TOF mass for $C_{21}H_{16}BF_2N_3O$ calcd. 375.14, found 375.82 $(M)^+$ and 355.94 $(M\text{-}F)^+$.

3,5-Bis(4-pyridyl)-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-s-indacene, **8:** A mixture of DCM and methanol (99:1) was used as eluent to get pure **8** as brownish purple solid. Yield: (18 mg, 46%); M.P.: 211 ^{o}C; ^{1}H-NMR (700 MHz, $CDCl_3$): δ 8.70 (d, 4H, J = 5.7 Hz), 7.70 (d, 4H, J = 5.75 Hz), 7.60 (d, 2H, J =8.45 Hz), 7.11 (d, 2H, J = 8.55 Hz), 7.00 (d, 2H, J = 4.25 Hz), 6.7 (d, 2H, J = 4.2 Hz), 3.9 (s, 3H, OCH_3); ^{13}C-NMR (500 MHz, $CDCl_3$): δ 155.43, 149.70, 139.65, 132.46, 131.75, 123.22, 120.76, 114.05, 107.44, 107.36, 96.11, 29.61; MALDI-TOF mass for $C_{26}H_{19}BF_2N_4O$ calcd. 452.26, found 452.34 $(M)^+$

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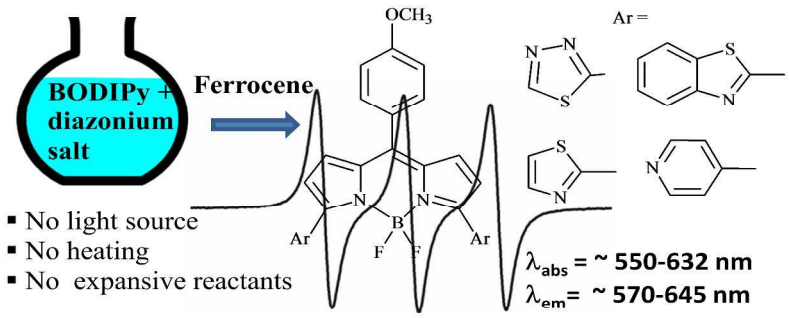
Graphical abstract



Spin cross-over experiment using EPR and DFT calculations show the radical formation