JOC The Journal of Organic Chemistry

Article

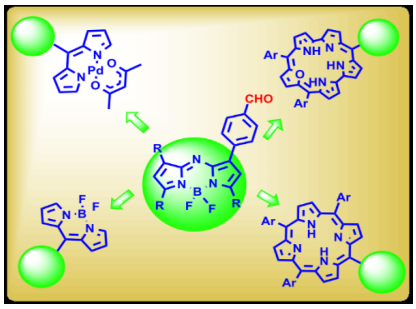
Mono-functionalized 1,3,5,7-TetraarylAzaBODIPYs and Their Application in the Synthesis of AzaBODIPY Based Conjugates

Angira Koch, and Mangalampalli Ravikanth

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b01311 • Publication Date (Web): 12 Aug 2019

Mono-functionalized 1,3,5,7-TetraarylAzaBODIPYs and Their Application in the Synthesis of AzaBODIPY Based Conjugates

Angira Koch and Mangalampalli Ravikanth*
Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India. E-mail: ravikanth@chem.iitb.ac.in



ABSTRACT:

A series of mono-functionalized 1,3,5,7-tetraarylazaBODIPYs containing functional groups such as *p*-hydroxymethyl phenyl, *p*-hydroxyphenyl, *p*-cyanophenyl, *p*-nitrophenyl and *p*-formylphenyl groups at 1-position of azaBODIPY core were synthesized by mixed condensation of two different nitrochalcones in *n*-butanol in the presence of CH_3COONH_4 at reflux followed by complexation with $BF_3{\cdot}OEt_2$. The mixed condensation of nitrochalcones resulted in the formation of three different dipyrromethenes, which was treated with $BF_3{\cdot}OEt_2$ to afford the desired mono-functionalized tetraarylazaBODIPYs in 30-35 % yields. To demonstrate the application of mono-functionalized tetraarylazaBODIPYs, we reacted mono-formyl functionalized tetraarylazaBODIPY with excess pyrrole to afford mono-dipyrromethanyl substituted tetraarylazaBODIPY, which was used as a key precursor to prepare novel covalently linked azaBODIPY based conjugates. The mono-dipyrromethanyl azaBODIPY was in situ oxidized with DDQ and either reacted with $BF_3{\cdot}OEt_2$ to afford azaBODIPY-BODIPY conjugate

or reacted with metal salt such as $Pd(acac)_2$ to afford azaBODIPY-Pd(II)dipyrrin conjugate. Alternately, the dipyrromethanyl-substituted azaBODIPY was condensed with dipyrromethane dicarbinol or 16-oxatripyrrane under mild acid catalyzed conditions followed by oxidation and chromatographic purification to afford azaBODIPY-porphyrin or azaBODIPY-oxasmaragdyrin conjugates, respectively. The photophysical studies on conjugates revealed that azaBODIPY is a good energy acceptor and invoked the possibility of energy transfer from donor to acceptor in covalently linked conjugates.

INTRODUCTION

4,4-Difluoro-4-bora-3a, 4a-diaza-s-indacenes (BODIPYs, **1**)[1] are one of the most attractive fluorescent dyes used as energy/electron donor/acceptor systems for various applications because of their favorable spectral and electrochemical properties viz., high photo stability, high extinction coefficients, decent quantum yields and redox properties.[2] BODIPY dyes have been used in several research fields including drug discovery, biomedical imaging and optical sensing. BF_2-chelated tetraarylazadipyrromethene derivatives (azaBODIPYs, **2**)[3] are the structural analogues of BODIPYs derived by replacing the *meso* "C" of BODIPYs with "N" and exhibits much better photophysical properties than BODIPYs. For example, BODIPYs show absorption and emission bands in the visible region with decent quantum yields whereas aza-BODIPYs absorb and emit in the NIR region with much better extinction coefficients and quantum yields. AzaBODIPYs have also been used in various applications such as photosensitizers in photodynamic therapy,[4] in sensing anions, cations[5] and as photosynthetic model systems capable of harvesting energy.[6] However, compared to BODIPYs, which have been investigated extensively over the years, the research on azaBODIPYs is relatively less because of the involvement of more number of synthetic steps and extensive purifications in

obtaining the intermediate precursors needed for the synthesis of azaBODIPYs. In fact, the azaBODIPYs were generally synthesized as symmetrical 1,3,5,7-tetraaryl azaBODIPYs and interestingly; there are very few reports available on unsymmetrical functionalized azaBODIPYs. A perusal of literature revealed that only few synthetic reports are available on difunctionalized azaBODIPYs where the functional groups were either introduced at the aryl groups present at the 3,5-positions of azaBODIPYs[7,8,9] **3** or at the direct 2, 6-positions of aza-BODIPY core **4** and **5** (Chart 1). The reports on functionalized azaBODIPYs where functional groups present at the 1,7-positions are very few and the mono-functionalized azaBODIPYs having one functionalized aryl group at 1 or 7 positions of azaBODIPY core is very scarce.

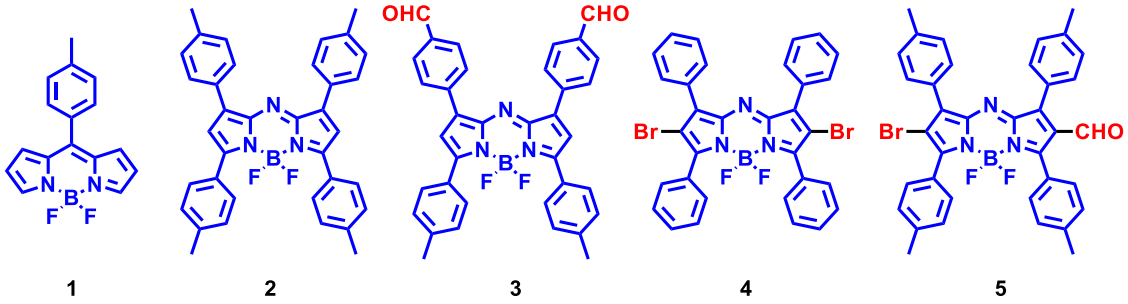
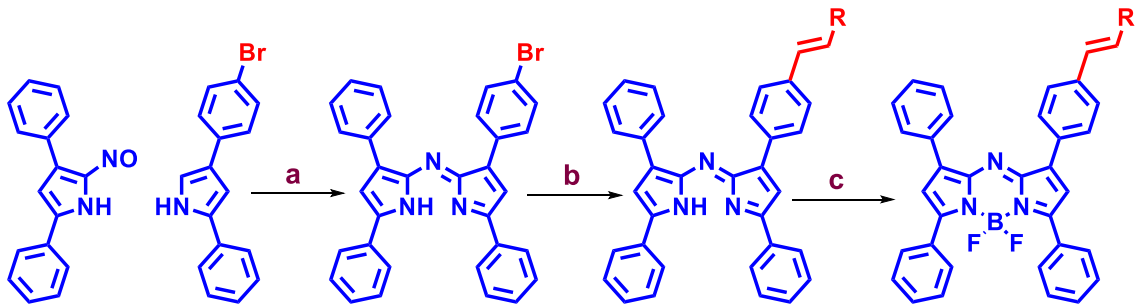


Chart 1: Structures of BODIPY (**1**) and aza-BODIPYs (**2-5**).

O'Shea and co-workers[10] reported the synthesis of unsymmetrical tetraarylazadipyrrins by cross condensation of nitroso derivatives of 2,4-diaryl pyrrole containing two different aryl groups with different 2,4-diarylpyrroles in acetic anhydride/acetic acid mixture at 100 ^{0}C. The research group of O'Shea successfully prepared one example of mono-functionalized aza-dipyrrin containing bromo-aryl group (Scheme 1) which was subsequently used by Parisotto et al.[11] to carry Heck coupling reactions and prepared a series NIR absorbing azaBODIPYs. Borisov and co-workers[12] adopted mixed condensation approach to prepare a series unsymmetrical azaBODIPYs by condensing two different nitro chalcones.



Scheme 1: Synthetic route for synthesis of unsymmetrical azaBODIPYs: (a) acetic anhydride/acetic acid, 100 ^{0}C, 1h; (b) aryl bromide, *t*-Bu acrylate, TBAB, DMF, 100 ^{0}C, stirring, 8 h; (c) CH_2Cl_2, TEA, $BF_3{\cdot}OEt_2$.

under base catalyzed conditions followed by BF_2 complexation. Except couple of these scattered reports, to the best of our knowledge, there is no report on tetraarylazaBODIPYs that are mono-functionalized on one of the four aryl rings. The mono-functionalized tetraarylazaBODIPYs, if easily accessible, can be used as building blocks to synthesize fluorescent azaBODIPY based systems and test their potential applications in various research fields. Herein, we report the synthesis of unsymmetrical mono-functionalized tetraarylazaBODIPYs **6-10** having the functionalized aryl group at the 1-position of azaBODIPY core by adopting mixed condensation approach. We have successfully introduced five different functional groups such as -CH_2OH, -OH, -CN, -NO_2 and -CHO groups at the aryl group present at 1-position of azaBODIPY core. The mono-functionalized tetraraylazaBODIPYs were used further to synthesize various novel azaBODIPY based systems such as azaBODIPY-BODIPY dyad **12**, azaBODIPY-metal dipyrrin dyad **13**, azaBODIPY-porphyrin dyad **14** and azaBODIPY-smaragdyrin dyad **15** (Chart 2). The spectral, electrochemical and photophysical properties of mono-functionalized azaBODIPYs and their dyads were also described.

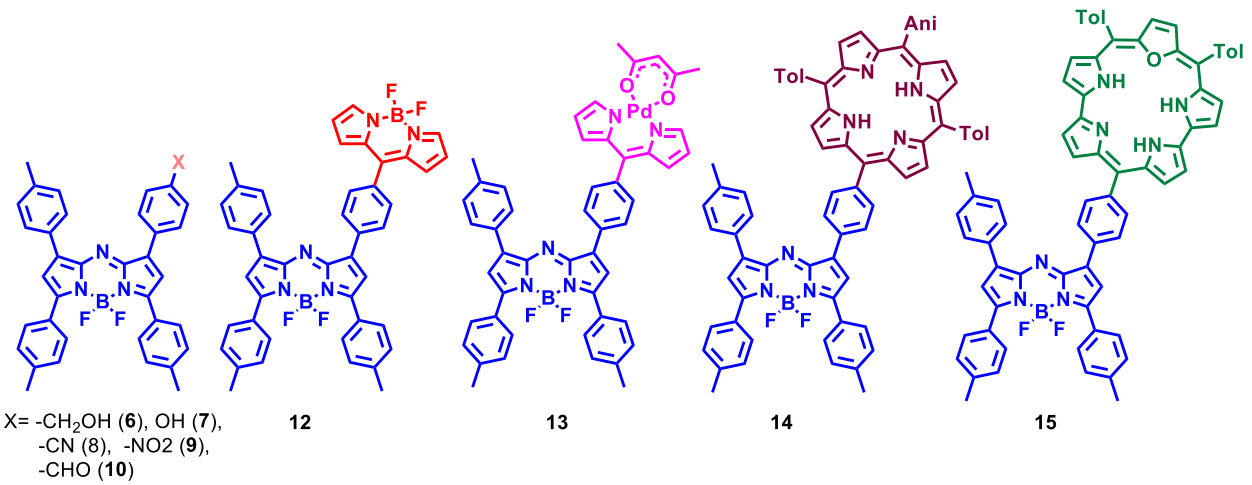
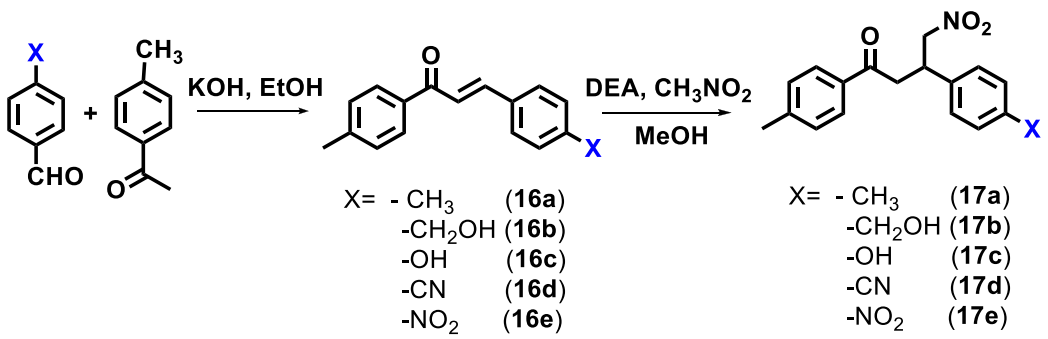


Chart 2: Structures of the monofunctional azaBODIPYs (**6 - 10**) and azaBODIPY-BODIPY dyads (**12**), azaBODIPY-Pd dipyrrin (**13**), azaBODIPY-porphyrin dyad (**14**) and azaBODIPY-oxasmaragdyrin dyad (**15**).

RESULTS AND DISCUSSION:

To synthesize the desired mono-functionalized azaBODIPYs, we need an access for various functionalized nitrochalcones, which were synthesized over a sequence of two steps as shown in Scheme 2. In the first step, aldol condensation of functionalized benzaldehyde and 4-methyl acetophenone under basic conditions in ethanol at room temperature followed by recrystallization afforded chalcones **16a-e** as off-white solids in 75-80 % yields. The chalcones were subjected to nitration under Michael addition conditions to afford nitrochalcones **17a-**e in 70-80 % yields. The mono-functionalized azaBODIPYs were prepared by mixed condensation method as shown in Scheme 3.

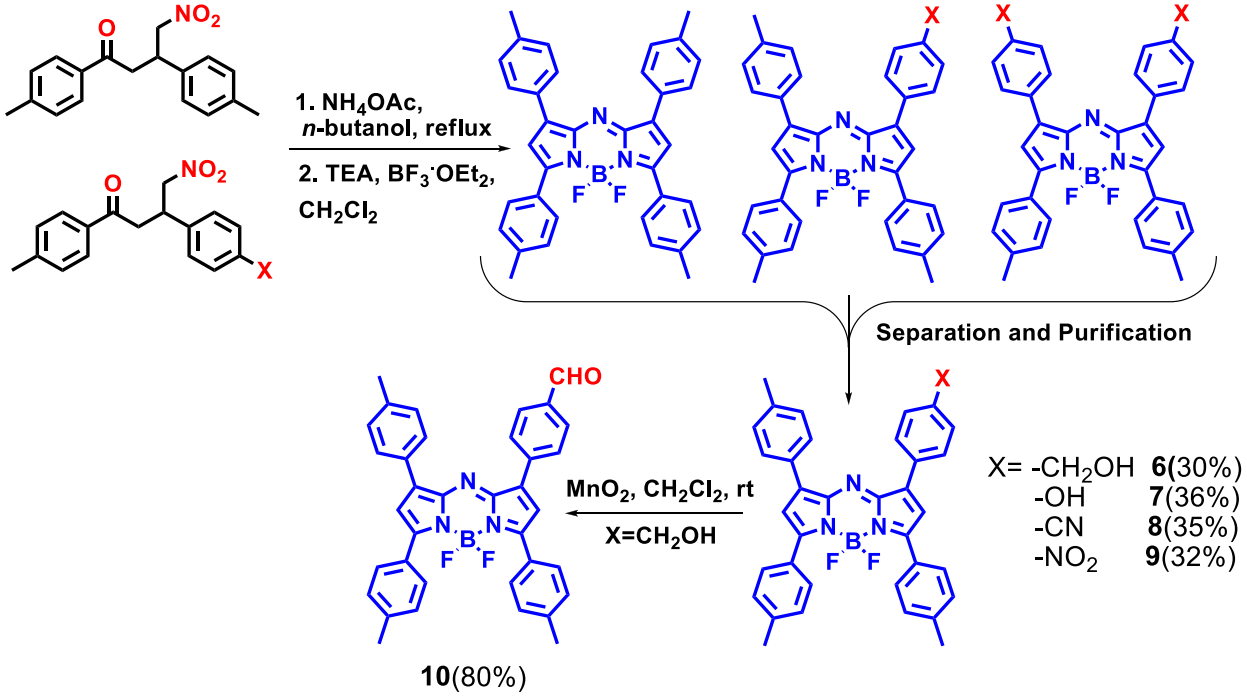
The condensation of desired functionalized nitrochalcones (**17b-17e**) with 3-(tolyl)-4-nitro-1-(*p*-tolyl)butan-1-one (**17a**) in *n*-butanol, in the presence of ammonium acetate at reflux temperature for 10 h resulted in the formation of a mixture of three dipyrromethenes as judged by TLC analysis.



Scheme 2: Synthesis of chalcones **16(a-e)** and nitrochalcones **17(a-e).**

The solvent was removed on rotatory evaporator under high vacuum and the resulted pasty solid was washed with water and filtered to obtain crude dark brown solid mixture of three azadipyrrins. Without further purification and separation, the crude solid in CH_2Cl_2 was treated with $BF_3{\cdot}OEt_2$ in the presence of triethylamine at room temperature in open air for 30 min followed by addition of water and left the reaction for overnight under stirring. The reaction mixture was subjected to standard work-up to afford the crude solid mixture of three azaBODIPYs: tetratolyl azaBODIPY, mono-functionalized azaBODIPY and difunctionalized azaBODIPY. TLC analysis clearly indicates the presence of three well-separated azaBODIPYs. The crude solid was subjected to silica gel column chromatographic purification and the desired pure mono-functionalized azaBODIPYs were separated from the other two azaBODIPYs and isolated as brown crystalline solids in 9-15 % yields. Thus, by following the mixed condensation approach, we have prepared four mono-functionalized azaBODIPYs containing functional groups such as $-CH_2OH$, -OH, -CN and $-NO_2$ groups at the aryl group present at 1-position of azaBODIPY core. The mono-formyl functionalized azaBODIPY was prepared by oxidizing compound **6** in CH_2Cl_2 with MnO_2 followed by column chromatographic purification. The mono-functionalized azaBODIPYs were found to be freely soluble in common organic solvents

and their identities were confirmed by molecular ion peak in HR-MS, 1D and 2D NMR techniques.



Scheme 3: Synthesis of monofunctionalized azaBODIPYs **6-10.**

The partial ^{1}H NMR spectrum along with ^{1}H-^{1}H COSY and NOESY spectra of compound **10** is shown in figure 1. The unsymmetrical nature of the functionalized azaBODIPYs was clearly noted in appearance of two sets of singlets for nine tolyl -CH_3 protons. The pyrrole *type a* and *type b* protons appeared as two singlets at 7.04 and 7.07 ppm. The ^{1}H NMR spectra of all mono-functionalized azaBODIPYs were clean and the meso-aryl protons showed cross-peak correlations in 2D NMR spectra.

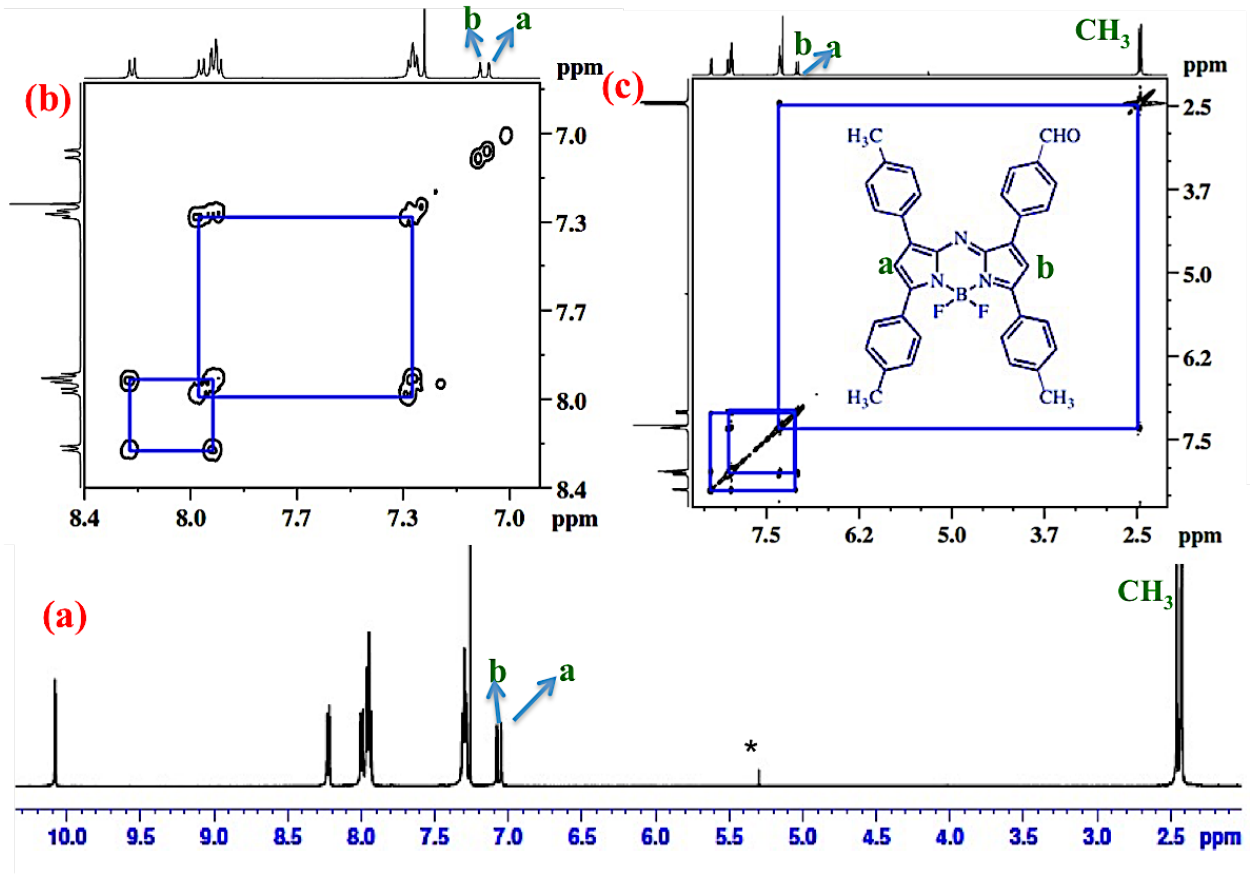
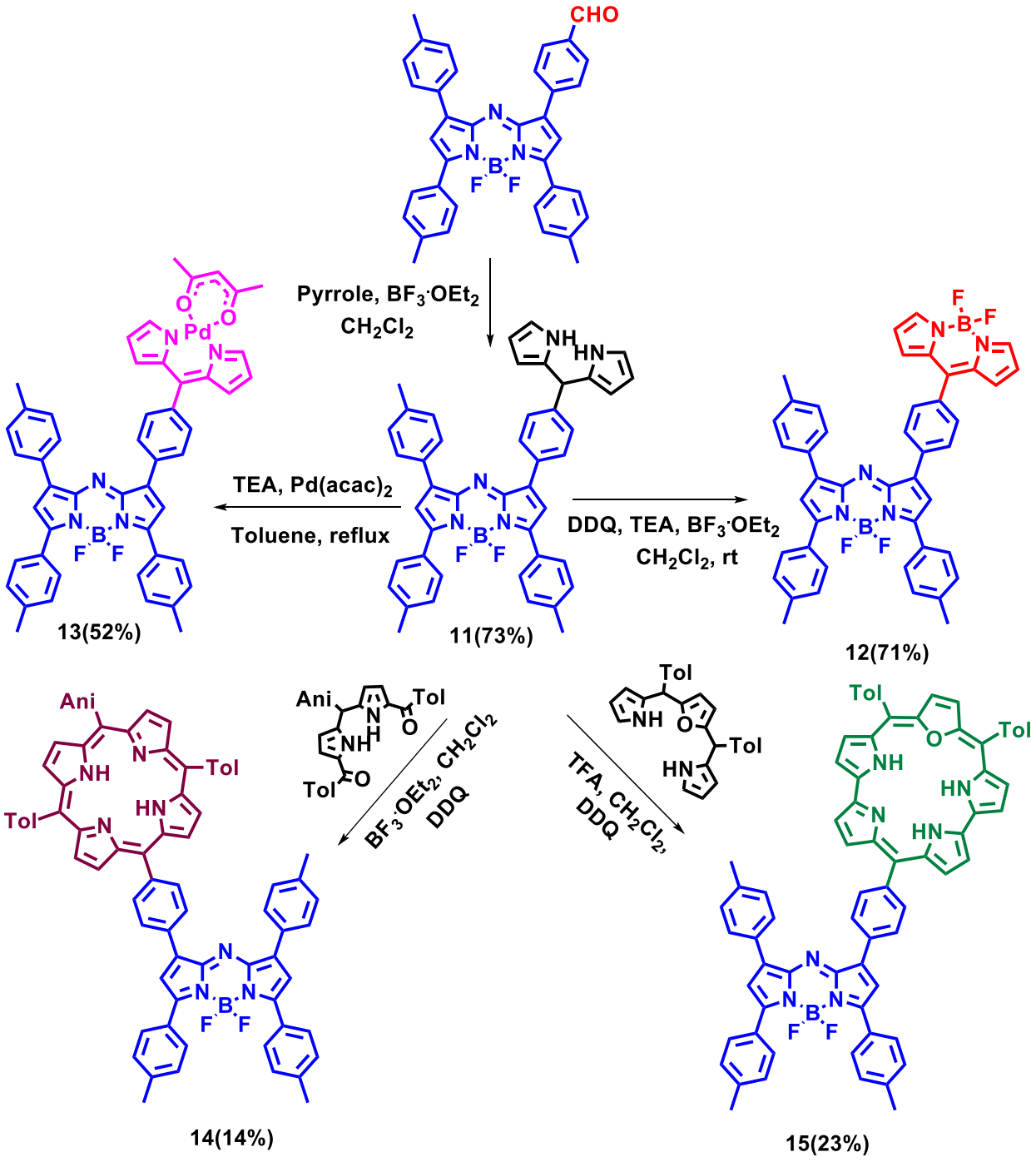


Figure 1. (a) ^{1}H, (b)^{1}H-^{1}H COSY and (c) ^{1}H-^{1}H NOESY NMR spectra of compound **10** recorded in $CDCl_3$.

The mono-functionalized azaBODIPYs are very useful synthons to prepare a range of fluorescent compounds which we have demonstrated here by taking mono-formyl functionalized azaBODIPY **10** as shown in Scheme 4.



Scheme 4: Synthesis of azaBODIPY conjugates **11-15**

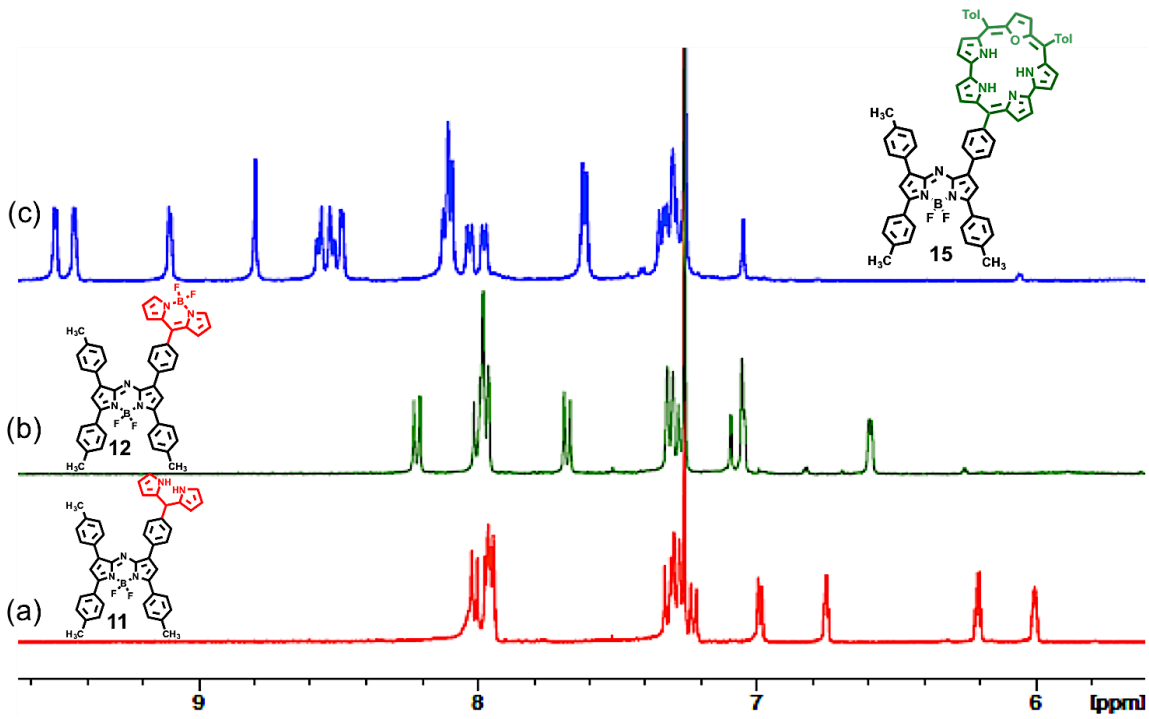


Figure 2. ^{1}H NMR spectra of compounds : (a) **11**, (b) **12** and (c) **15** recorded in $CDCl_3$

The compound **10** was treated with excess pyrrole in CH_2Cl_2 in the presence of catalytic amount of $BF_3{\cdot}OEt_2$ at room temperature for 30 mins followed by simple column chromatographic purification which afforded the mono-dipyrromethanyl azaBODIPY **11** in 80% yield. The molecular ion peak at 684.3117 and appearance of NMR resonances at 5.60 ppm (Figure 2c) corresponding to *meso* -CH proton and two sets of resonances in 5.90-6.30 ppm region corresponding to four pyrrole protons of dipyrromethanyl moiety along with other resonances corresponding to azaBODIPY moiety confirmed the identity of mono-dipyrromethanyl azaBODIPY **11**. The compound **11** was oxidized with DDQ in CH_2Cl_2 at room temperature in open air for 20 min and the resulted azaBODIPY appended with dipyrrin moiety, without isolating was treated with $BF_3{\cdot}OEt_2$ in the presence of Et_3N for additional 30 min at room temperature. The crude compound was subjected to silica gel column chromatographic purification to afford pure azaBODIPY appended with BODIPY unit **12** in 74% yield. The formation of **12** was confirmed by HR-MS, ^{1}H (Figure 2b), ^{11}B and ^{19}F NMR techniques. The

azaBODIPY appended with Pd(II) complex of dipyrrin **13** was prepared in two steps. In the first step, the compound **11** was oxidized with DDQ in CH_2Cl_2 followed by flash column chromatographic purification to isolate azaBODIPY appended with dipyrrin moiety. In the second step, the isolated azaBODIPY appended with dipyrrin moiety was treated with excess $Pd(acac)_2$ in toluene/Et_3N (5:1) at reflux temperature for 2 h. The crude compound, after standard work-up, was passed through celite bed followed by evaporation of solvent to afford azaBODIPY-Pd(II) dipyrrin conjugate **13** as blue solid in 52 % yield. The identity of compound **13** was confirmed by HR-MS and NMR spectroscopic techniques. The azaBODIPY-porphyrin conjugate **14** was prepared by condensing one equivalent of compound **11** with one equivalent of dipyrromethane dicarbinol **18** in CH_2Cl_2 in the presence of catalytic amount of $BF_3{\cdot}OEt_2$ for 2 h under an inert atmosphere followed by oxidation with DDQ at room temperature in open air for additional 30 min. The progress of the reaction was followed by TLC analysis and absorption spectroscopy. The crude compound was purified by silica gel column chromatography and afforded pure azaBODIPY-porphyrin conjugate **14** as bright purple coloued solid in 14% yield. The formation of **14** was also confirmed by HRMS, NMR and absorption spectroscopic techniques. We have also succeeded in synthesizing azaBODIPY-oxasmaragdyrin conjugate **15** by condensing **11** with 16-oxatripyrrane under mild acid catalyzed conditions followed by oxidation with DDQ to afford the conjugate **15** in 28% yield. The identity of compound **15** was also confirmed by molecular ion peak at 1082.4537 in HR-MS and a clean NMR spectrum presented in Figure 2.

PHOTOPHYSICAL AND ELECTROCHEMICAL STUDIES:

The azaBODIPYs strongly absorb and emit in the region of 650-670 nm. The mono-functionalized tetraarylazaBODIPYs **6**-**10** showed strong absorption and emission in the region

of 660-710 nm and the relevant data are tabulated in Table 1. The absorption band position and extinction coefficients were slightly varied depending upon the kind of functionalized aryl groups present at the 1-position of azaBODIPY core. For example, the mono-formyl functionalized tetraarylazaBODIPY **10** showed absorption band at 675 nm whereas it was observed at 678 nm in mono-nitro functionalized tetraarylazaBODIPY **9**. The mono-dipyrromethanyl azaBODIPY **11** showed slight hypsochromically shifted absorption band at 667 nm. The azaBODIPY-BODIPY conjugate **12** showed a moderately intense band with a shoulder at 506 nm corresponding to BODIPY moiety and one intense band at 677 nm corresponding to azaBODIPY moiety (Figure 3a). The compound **13** containing azaBODIPY and Pd (II) dipyrrin units showed one broad band 497 nm corresponding to Pd(II) dipyrrin moiety and a strong band at 670 nm due to azaBODIPY moiety (Figure 3b). The azaBODIPY-porphyrin conjugate **14** showed one strong Soret band at 421 nm corresponding to porphyrin unit, two weak Q-bands at 517 and 554 nm due to porphyrin unit and one broad intense band at 670 nm due to both azaBODIPY and porphyrin moieties (Figure 3c). The azaBODIPY-oxasmaragdyrin conjugate showed less number of bands due to strong interaction between azaBODIPY and oxasmaragdyrin moieties. The strong Soret band at 448 nm and weak Q-band at 556 nm are due to smaragdyrin moiety whereas moderately intense broad band at 666 nm is due to both azaBODIPY and smaragdyrin moieties (Figure 3d). Due to strong interaction between the two chromophoric moieties in compound **15**, the absorption band in the visible-NIR region experienced hypsochromic shift, broadened with reduction in extinction coefficient compared to independent azaBODIPY and oxasmaragdyrin.

The steady state and time resolved fluorescence properties of compounds **6**-**15** were investigated and the data is included in table 1. The mono-functionalized tetraarylazaBODIPYs

6-**10** and mono-dipyrromethanyl azaBODIPY **11** showed one strong fluorescence band in the region of 690-710 nm with quantum yields in the range of 0.34-0.53. The singlet state lifetimes of compounds **6**-**11** measured by time-resolved fluorescence single photon counting method were fitted to the single exponential decay and measured singlet state lifetimes are in the range of 1.60-3.0 ns. The functionalized tetraarylazaBODIPY having hydroxyphenyl group at 1-position showed low quantum yield and singlet state lifetime owing to the presence of hydroxyl group. The dyad azaBODIPY-Pd (II) dipyrrin **13** showed very weak fluorescence with emission peak maxima at 670 nm (Figure 3b) with a quantum yield of 0.06 and singlet state lifetime of 1.74 ns (Figure 3b inset) due to presence of heavy Pd (II) ion, which quenches the fluorescence of azaBODIPY moiety.

The dyads azaBODIPY-BODIPY **12**, azaBODIPY-porphyrin **14** and azaBODIPY-oxasmaragdyrin **15** act as donor-acceptor systems and showed energy transfer from one unit to another. In dyad **12**, the BODIPY unit absorbs at higher energy and acts as donor whereas the azaBODIPY unit absorbs at lower energy and acts as energy acceptor. The dyad **12** on excitation at 500 nm, where BODIPY unit absorbs very strongly, the expected emission from BODIPY unit at 515 nm was completely quenched and a strong emission at 708 nm (Figure 3a) corresponding to azaBODIPY unit was observed with a quantum yield of 0.46. The time-resolved studies on compound **12**, upon excitation at 635 nm and emission collected at 708 nm showed single exponential decay with a lifetime of 2.88 ns (Figure 3a inset) due to azaBODIPY unit. These results support intramolecular energy transfer from BODIPY unit to azaBODIPY unit in dyad **12**.

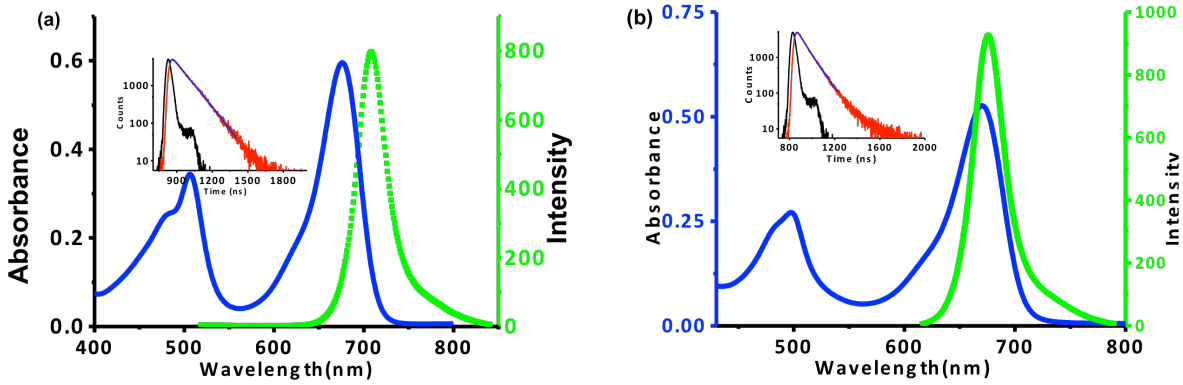
In azaBODIPY-porphyrin conjugate **14**, the porphyrin unit absorbs at higher energy and acts as donor whereas azaBODIPY unit acts as energy acceptor. The conjugate **14** upon

excitation at 415 nm where porphyrin unit absorbs strongly, the emission from porphyrin unit at 650 was almost quenched and a strong emission at 699 nm due to azaBODIPY unit was observed (Figure 3c). The quantum yield estimated was 0.47 due to azaBODIPY unit. The singlet state lifetime collected with the emission wavelength of azaBODIPY unit at 699 nm was fitted to single exponential decay (Figure 3c inset) and lifetime was found to be 2.19 ns. These observations also support an efficient energy transfer from porphyrin unit to azaBODIPY unit in conjugate **14**. In azaBODIPY-oxasmaragdyrin conjugate **15**, both azaBODIPY and oxasmaragdyrin moieties absorb and emit in the overlapping region. The conjugate **15** upon excitation at 440 nm showed weak emission band at 698 nm (Figure 3d) with a quantum yield of 0.06. The weak emission of conjugate was due to strong interaction between azaBODIPY and oxasmaragdyrin moieties which led to enhancement of non-radiative decay channels in dyad **15**. The singlet state decay of conjugate **15** collected with emission wavelength of 698 nm was fitted to single exponential (Figure 3d inset). This is in agreement with the quantum yield data of compound **15**. Thus, the preliminary photophysical studies on compounds **12**, **14** and **15** indicated the possibility of energy transfer at singlet state from energy donor to energy acceptor. Since dyad **12** showed very efficient energy transfer from BODIPY unit to azaBODIPY unit in $CHCl_3$, we have investigated absorption and fluorescence properties of dyad **12** in five different solvents such as toluene, CH_2Cl_2, $CHCl_3$, THF and CH_3CN as shown in Figure 4 and the relevant data is tabulated in Table 2. As clear from figure 4(a) and data in table 2, the dyad **12** showed similar absorption features in all solvents with slight changes in peak maxima and extinction coefficients. The steady state fluorescence spectra (Figure 4b) of dyad **12** in five different solvents were recorded at excitation wavelength of 490 nm where BODIPY unit exclusively absorbs strongly. The azaBODIPY-BODIPY dyad **12** on excitation at 490 nm in five

different solvents where BODIPY unit absorbs strongly, the emission was observed in the range of 702-712 nm, which corresponds to azaBODIPY unit indicating a possibility of energy transfer from BODIPY unit to azaBODIPY unit in dyad **12**. However, the preliminary data presented in table 2 indicates that the energy transfer from BODIPY unit to azaBODIPY unit in dyad **12** was less efficient in CH_3CN but more efficient in $CHCl_3$. Detailed photophysical investigation will be required to understand the energy transfer dynamics observed in these three dyads.

Table 1: Photophysical and Electrochemical Data of compounds **6-15.**

Compounds	λ_{abs}(nm) [logε(mol^{-1}dm^{3}cm^{-1})]	λ_{em} (nm)	Φ	τ (ns)	Electrochemical data	
					$E_{1/2ox}$(V)	$E_{1/2red}$ (V)
6	666 [4.85]	697	0.48	2.09	+1.35	-0.31, -1.07
7	668 [4.94]	700	0.34	1.64	+1.29	-0.36, -1.31
8	674 [4.80]	705	0.47	2.75	+1.42	-0.23, -0.91
9	678 [4.70]	710	0.53	2.95	+1.43	-0.20, -0.70
10	675 [4.82]	707	0.52	2.58	+1.40	-0.23, -0.88
11	668 [4.85]	687	0.46	2.26	+1.35	-0.36, -1.26
12	506 [4.50], 676 [4.80]	708	0.46	2.88	+0.16, + 1.40	-0.23, -0.57, -1.24
13	497 [4.43], 670 [4.72]	700	0.06	1.74	-0.12, + 1.39	-0.30, -1.15
14	421 [4.93], 670 [4.46]	699	0.47	2.19	-0.69, +1.39	-0.17, -1.30, -1.52 -1.77
15	448 [4.80], 666 [4.40]	698	0.06	2.11	+0.73, +1.37	-0.25, -0.41, -1.09, -1.6



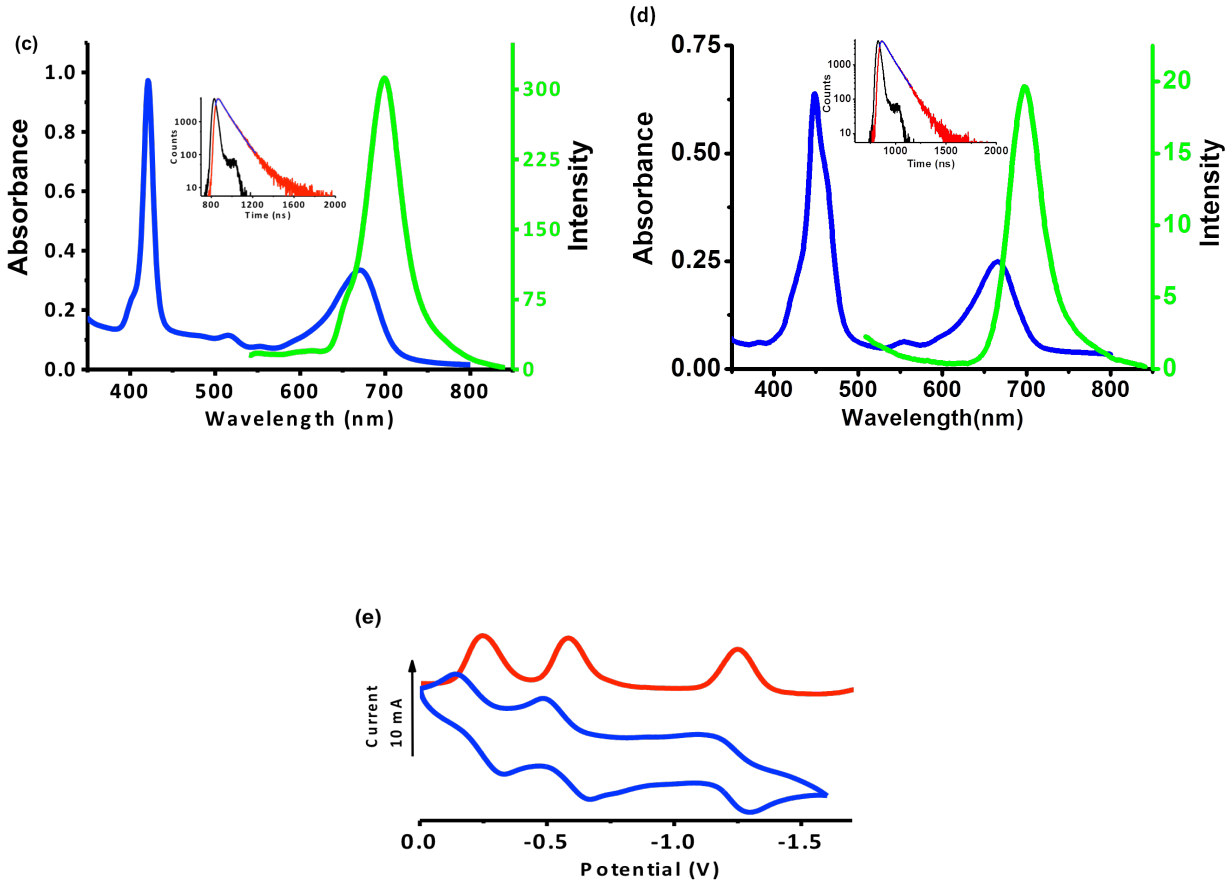


Figure 3: Overlay of absorption (blue line) and emission (green line); decay curve (inset) of compounds (a) Compound **12,** (b) Compound **13,** (c) Compound **14,** (d) compound **15** recorded in $CHCl_3$ (5×10^{-6} M); (e) the cyclic (blue line) and differential pulse voltammograms (red line) of compound **10** recorded in CH_2Cl_2 at a scan rate of 50 mV/s using tetrabutylammonium perchlorate as supporting electrolyte (f).

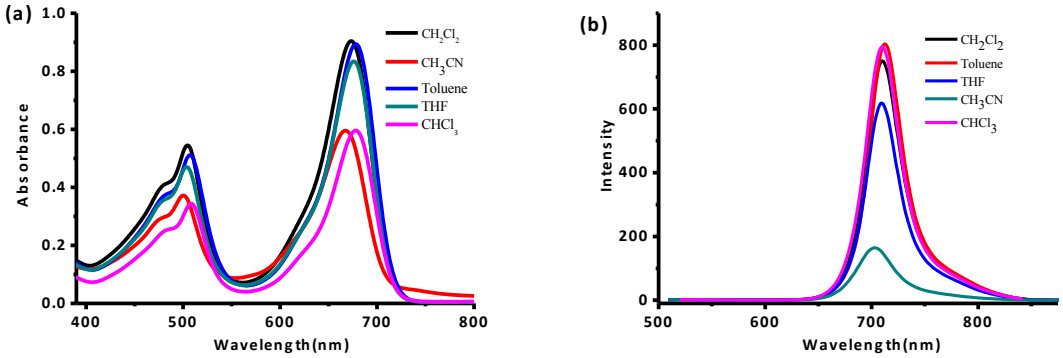


Figure 4: Comparison of (a) absorption spectra and (b) emission spectra of dyad **12** in five different solvents.

Table 2: Photophysical data of compound **12** in different solvents.

Solvents	λ_{abs}(nm) [logε(mol^{-1}dm^{3}cm^{-1})]	λ_{em}(nm)	Φ
Toluene	507 [4.70], 678 [4.95]	712	0.28
$CHCl_3$	506 [4.70], 676[4.95]	708	0.46
CH_2Cl_2	505 [4.73], 673[4.95]	710	0.25
THF	504 [4.67], 676 [4.91]	709	0.21
CH_3CN	500 [4.57], 667[4.77]	702	0.10

The electrochemical properties of compounds **6-15** were determined by cyclic voltammetry at a scan rate of 50 mV s^{-1} using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and the relevant data is included in Table 1. In general, azaBODIPYs are electron deficient and show one irreversible oxidation and two quasi-reversible reductions. Due to electron deficient nature of compounds **6-10**, the compounds are difficult to oxidize but easier to reduce. For example, the compound **6** showed irreversible oxidation at 1.35 V and two quasi-reversible reductions at -0.31 and -1.07 V, whereas the compound **9** having electron withdrawing nitrophenyl group shows irreversible oxidation at 1.43 V and quasi-reversible reductions at -0.20 and -0.70 V. Thus, due to presence of nitrophenyl group, the compound **9** is harder to oxidize but easier to reduce as compared to compound **6**. The compound azaBODIPY-BODIPY dyad **12** showed three quasi-reversible reductions at -0.23, -0.57 and -1.24 V. In this, the reductions at -0.23 and -1.24 V were due to azaBODIPY moiety whereas the reduction at -0.57 V was due to BODIPY moiety. Similarly, in azaBODIPY porphyrin dyad **14**, we observed two oxidations at + 0.69 and +1.39 V and four reductions at -0.17, -1.30, -1.52 and -1.77 V. In this case also, the oxidations were mainly due to porphyrin unit; the reductions at -0.17 and -1.30 were due to azaBODIPY moiety and the reductions at -1.52 and -1.77 V were due to porphyrin unit. The azaBODIPY-smaragdyrin dyad also showed oxidations and reductions corresponding to both the

constituted units. Thus, the dyads **12-15** showed redox behaviour of both the constituted moieties with slight shifts in their redox potentials indicating that the constituted units retain their individual characteristic features in dyads.

CONCLUSIONS:

The mono-functionalized tetraarylazaBODIPYs are highly desirable building blocks for the synthesis of different novel azaBODIPY based systems for various studies and applications. The mixed condensation approach of condensing two different nitrochalcones is the most straightforward method to afford mono-functionalized tetraarylazaBODIPYs. The condensation of two different nitrochalcones resulted in mixture of three azadipyrrins which on complexation with BF_2 unit afford desired mono-functionalized tetraarylazaBODIPYs. We have successfully synthesized five different mono-functionalized tetraarylazaBODIPYs in decent yields by adopting the mixed condensation approach. The use of mono-functionalized tetraarylazaBODIPYs was demonstrated by taking mono-dipyrromethanyl azaBODIPY as a key precursor and synthesized very novel four different azaBODIPY based systems such as azaBODIPY-BODIPY dyad, azaBODIPY-Pd(II) dipyrrin, azaBODIPY-porphyrin and azaBODIPY-oxasmaragdyrin conjugates in good yieds. The preliminary photophysical studies on conjugates revealed that azaBODIPY can act as good energy acceptor and there is a possibility of efficient intramolecular energy transfer within the dyads. Thus, the mono-functionalized azaBODIPYs open up possibilities to prepare a range fluorescent azaBODIPY based systems with multi-level applications.

MATERIALS AND METHODS:

General Experimental:

All the starting materials and solvents were procured from commercial sources and used without further purification. The NMR spectra were recorded in $CDCl_3$ at room temperature using a Bruker 400 MHz and 500 MHz instruments with tetramethylsilane (TMS) as an internal standard. The HR-Mass spectra were recorded with a Bruker maxis Impact and Q-Tof micro mass spectrometer using electron spray ionization method, TOF analyzer. Cyclic voltammetric and Differential Pulse Voltammetric (DPV) studies were carried out with an electrochemical system utilizing a three-electrode configuration consisting of a glassy carbon(working electrode), platinum wire (auxiliary) electrode and a saturated calomel (reference) electrode using TBAP as the supporting electrolyte. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Absorption and steady state fluorescence spectra were obtained by Varian instruments. For UV-Vis and fluorescence titrations, the stock solution for all compounds (5×10^{-6} M) was prepared by using spectroscopic grade $CHCl_3$ solvent. The fluorescence quantum yields (Φ) were estimated from the emission and absorption spectra by comparative method at the excitation wavelength of 648 nm using 3,5-dianisyl-1, 7-di(p-phenyl) azaBODIPY (Φ = 0.36 in chloroform)[12] as standard. The time resolved fluorescence decay measurements were carried out at magic angle using a picosecond diode laser based time correlated single photon counting (TCSPC) fluorescence spectrometer from IBH, UK. All the decays were fitted to single exponential. The good fit criteria were low chi-square (1.0) and random distributions of residuals.

General method for the synthesis of compounds 16(a-e):

Compound **16a (**3-(tolyl)-1-(p-tolyl)prop-2-en-1-one) was synthesized according to the reported literature procedure.[13] 4-methylacetophenone (1.00 g, 5.20 mmol) and 4-

methylbenzaldehyde (1.00 g, 5.33 mmol) were dissolved in 5 mL EtOH in a round bottom flask. 5 mL of an aqueous potassium hydroxide solution (875.5 mg, 15.60 mmol) was added dropwise which resulted in the formation of off white coloured solid. The reaction mixture was allowed to stir overnight. The product was filtered, washed with water and dried. The off white coloured solid was used for further synthesis without purification. Similarly, the compounds **16b-16e**[7, 14,15] were synthesized by the same procedure by reacting the corresponding aldehyde with 4-methyl acetophenone and the resulting product was used for next step without further purification.

General method for the synthesis of compounds 17(a-e):

Compounds **17 (a-e)** were synthesized according to the literature procedure[16] by the reaction of respective chalcones with nitromethane in presence of diethylamine.

To the methanolic solution of compound **17a** (2 g, 0.50 mmol) taken in a round bottomed flask, diethylamine (2 g, 0.50 mmol) was added followed by the addition of nitromethane (2 g, 0.50 mmol) under an inert atmosphere. The reaction mixture was refluxed overnight. After the completion of reaction (checked by TLC), the reaction mixture was neutralized with dilute hydrochloric acid and extracted with dichloromethane and water. The organic layers were collected and dried over anhydrous sodium sulphate. The solvent was evaporated under vacuum to afford the compound (3-(tolyl)-4-nitro-1-(p-tolyl)butan-1-one) **17a** as a pasty material which was used for further reaction without purification.

Compounds[7, 17] **17b-17e** were synthesized by following the above procedure and used without further purification.

Compound 17d (3-(4-(cyano)phenyl)-4-nitro-1-(p-tolyl)butan-1-one**):** viscous pale yellow liquid. Yield: 1 g (80%). ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.40 (s, 3H), 3.42-3.43 (m, 2H), 4.28 (p, 1H), 4.67-4.71 (dd, 1H), 4.82-4.86 (dd, 1H), 7.24 (d, ^3J = 8.0 Hz, 2H), 7.41 (d, ^3J = 8.0

Hz, 2H), 7.61(d, ^3J = 8.0 Hz, 2H), 7.78(d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.6, 38.8, 41.1, 128.1, 129.2, 129.4, 132.1, 138.2, 144.7, 196.0; HRMS Calcd for $C_{18}H_{16}N_2O_3Na$ 331.1053 $(M+Na)^+$, found 331.1056 $(M+Na)^+$.

General method for the synthesis of compounds 6 - 9:

The compounds **6 - 9** were prepared by the mixed condensation of compound **17a** with the compounds **17b**, **17c**, **17d** and **17e**.

Synthesis of compound 6 (4,4-Difluoro-1-(4-hydroxymethyl)benzene-3,5,7-tri-*p*-tolyl-4-bora-3a,4a,8-triaza-s-indancene):

In order to synthesize compound **6**, compounds **17a** and **17b** in butanol were taken in a round-bottomed flask equipped with a magnetic stirrer and reflux condenser. To this mixture, ammonium acetate was added and the reaction mixture was heated under reflux temperature for 12 h, which resulted in the formation of a mixture of dipyrromethenes. The reaction mixture was cooled and solvent was evaporated under vacuum. The blackish brown solid was precipitated by the addition of water to the reaction mixture. The solid was air-dried. To the solution of the above solid (1 g) in dichloromethane, triethylamine was added followed by the addition of $BF_3.OEt_2$. The colour of the solution changed from blue to greenish blue. The completion of the reaction was monitored using thin layer chromatography. The TLC showed three clear spots indicating the formation of three mixed condensation products. The reaction mixture was extracted with dichloromethane and water. The organic layers were collected and dried over anhydrous sodium sulphate. Solvent was evaporated under vacuum to obtain the crude product as brown coloured solid. Purification of the crude compound by column chromatography gave compound **6** as second moving band. The solvent was evaporated and brown crystalline solid was obtained. Yield: 187 mg (30%); mp: 228-235 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm):

2.41 (s, 6H), 2.44 (s, 3H), 4.78 (s, 2H), 7.00 (s, 1H), 7.01 (s, 1H), 7.26 - 7.29 (m, 6H), 7.4 (d, ^3J = 8.0 Hz, 3H), 7.94 -7.98 (m, 8H), 8.06 (d, ^3J = 8.1 Hz); ^{19}F NMR (470.59 MHz, $CDCl_3$, δ in ppm) -131.5 (q, ^3J (B, F) = 80.0 Hz, 2H); ^{11}B NMR (160.46 MHz, $CDCl_3$, δ in ppm) 1.21 (t, ^3J (B, F) = 32 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ in ppm): 21.4, 21.5, 21.6, 60.8, 118.5, 127.0, 128.8, 128.9, 129.2, 129.4, 129.5, 129.6, 131.9, 139.9, 141.3, 141.5, 142.0; HRMS calcd for $C_{36}H_{30}BF_2KN_3O$ 608.2088 $(M+K)^+$, found 608.2083 $(M+K)^+$.

Compounds **7-9** were prepared using the above procedure by the mixed condensation reaction of compound **17a** with the corresponding compounds **17b**, **17c**, **17d** and **17e**, respectively, followed by BF_2 complexation to obtain the desired products **7-10**.

Compound 7 (4,4-Difluoro-1-(4-hydroxy)benzene-3,5,7-tri-*p*-tolyl-4-bora-3a,4a,8-triaza-s-indancene): Colour: Dark brown crystalline solid; Yield: 60 mg (36%); 242-250 ^{0}C ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.41 (s, 6H), 2.42 (s, 2H), 6.91 (s, 1H), 6.97 (s, 1H), 7.26 -7.28 (m, 6H), 7.95 (d, ^3J = 8.1 Hz, 6H), 8.01 (d, ^3J = 8.3 Hz, 2H); ^{19}F NMR (470.59 MHz, $CDCl_3$, δ in ppm) -131.2 (q, ^3J (B, F) = 32.9 Hz); ^{11}B NMR (160.46 MHz, $CDCl_3$, δ in ppm) 1.23 (t, ^3J (B, F) = 32.0 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ in ppm): 21.4, 21.6, 115.6, 117.5, 118.1, 125.5, 129.0, 129.2, 129.3, 129.5, 129.8, 131.1, 139.5, 141.2, 141.3, 156.9; HRMS calcd for $C_{35}H_{29}BF_2N_3O$ 556.2372 $(M+H)^+$, found 556.2377 $(M+H)^+$.

Compound 8 **(**4,4-difluoro1-1-(1-yl)benzonitrile-3,5,7-tri-*p*-tolyl-4-bora-3a,4a,8-triaza-s-indancene)**:** Colour: Dark blue amorphous solid; Yield: 65 mg (35 %); 240-245 ^{0}C ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.41(s, 3H), 2.42 (s, 3H), 2.46 (s, 2H), 7.02 (s, 1H), 7.05 (s, 1H), 7.27 - 7.31 (m, 7H), 7.72 (d, ^3J = 8.4Hz, 2H), 7.92(d, ^3J = 8.0 Hz, 4H), 8.00 (d, ^3J = 8.4 Hz, 2H),

8.14 (d, ^{3}J = 8.4 Hz, 2 H); ^{19}F NMR (470.59 MHz, $CDCl_3$, δ in ppm) -131.6 (q, ^{3}J (B, F) = 32.9 Hz); ^{11}B NMR (160.46 MHz, $CDCl_3$, δ in ppm) 1.21 (t, ^{3}J (B, F) = 32.0 Hz); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ in ppm): 21.5, 21.6, 21.7, 22.3, 29.7, 111.8, 128.3, 128.7, 129.2, 129.3, 129.4, 129.5, 129.9, 132.1, 137.0, 139.3, 140.6, 141.3, 142.5, 144.4, 145.5,146.6, 157.1, 162.0; HRMS calcd for $C_{36}H_{28}BF_2N_4$ 565.2376 $(M+H)^+$, found 565.2375 $(M+H)^+$.

Compound 9 (4,4-Difluoro-1-(4-nitrophenyl)-3,5,7-tri-*p*-tolyl-4-bora-3a,4a,8-triaza-s-indancene): Colour: Dark brown amorphous solid; Yield: 55mg (32 %); 245-250 ^{0}C ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.42 (s, 2H), 2.43 (s, 2H), 2.47 (s, 2H), 7.0 (s, 2H), 7.28-7.32 (m, 7H), 7.93 (d, ^{3}J = 7.2 Hz, 4H), 8.01 (d, ^{3}J = 8.4 Hz, 2H), 8.22 (d, ^{3}J = 8.8 Hz, 2H), 8.30 (d, ^{3}J = 8.8 Hz, 2H); ^{19}F NMR (470.59 MHz, $CDCl_3$, δ in ppm) -131.7 (q, ^{3}J (B, F) = 28.2 Hz); ^{11}B NMR (160.46 MHz, $CDCl_3$, δ in ppm) 1.18 (t, ^{3}J (B, F) = 35.3 Hz); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ in ppm): 21.6, 21.7, 25.3, 77.2, 123.7, 128.2, 128.7, 129.1, 129.3, 129.4, 129.5, 129.6, 129.9, 139.0, 140.8, 141.3, 142.7, 147.4; HRMS calcd for $C_{35}H_{27}BF_2KN_4O_2$ 623.1833 $(M+K)^+$, found 623.1827 $(M+K)^+$.

Compound 10 (4,4-difluoro1-1-(1-yl)benzaldehyde-3,5,7-tri-*p*-tolyl-4-bora-3a,4a,8-triaza-s-indancen)**:** Colour: Dark brown crystalline solid**;** Yield 89 mg (89%); mp: 235-250 ^{0}C ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.42 (s, 3H), 2.43 (s, 3H), 2.45 (s, 3H), 7.04 (s, 1H), 7.07 (s, 1H), 7.29 (t, ^{3}J = 5 Hz, 6H), 7.96 (m, 9H), 8.22 (d, ^{3}J = 8.6, 2H), 10.08 (s, 1H); ^{19}F NMR (470.59 MHz, $CDCl_3$, δ in ppm): -131.6 (q, ^{3}J (B, F) = 32.9 Hz); ^{11}B NMR (160.46 MHz, $CDCl_3$, δ in ppm): 1.21 (t, ^{3}J (B, F) = 30.0 Hz); $^{13}C\{^{1}H\}$ NMR(100 MHz, $CDCl_3$, δ in ppm) 21.6, 21.7, 25.3, 123.7, 128.2, 128.7, 129.1, 129.3, 129.4, 129.5, 129.6, 129.9, 139.0, 140.8, 141.3, 142.7, 147.4; HRMS calcd for $C_{36}H_{28}BF_2KN_3O$ 606.1931 $(M+K)^+$, found 606.1938 $(M+K)^+$.

Synthesis of mono-dipyrromethanyl azaBODIPY 11:

To a solution of compound **10** (100 mg, 0.17 mmol) in dichloromethane (100 ml), pyrrole (1.7 mmol) was added, followed by the addition of catalytic amount of $BF_3.OEt_2$ (0.017 mmol). The reaction mixture was stirred at room temperature for 15 min. The completion of the reaction was checked by TLC, which indicates the disappearance of the spot corresponding to the reactant and formation of a new polar spot corresponding to the desired compound. The reaction was quenched with 0.1 M NaOH and extracted with dichloromethane and dried over anhydrous sodium sulphate. Evaporation of the solvent under vacuum afforded the crude product, which is purified by silica gel column chromatography (ethyl acetate/petroleum ether: 30/70%) to obtain the tritolyl monodipyrromethanyl azaBODIPY as deep blue coloured amorphous solid. Yield: 82 mg (73 %). mp: decomposes at ~235 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.41 (s, 9H), 5.10 (s, 1H), 6.0 (s, 2H), 6.19 (s, 2H), 6.75 (s, 2H), 6.97 (d, ^3J = 8.4 Hz, 2H), 7.23 - 7.32 (m, 8 H), 7.93 - 8.02 (m, 10 H); ^{19}F NMR (470.59 MHz, $CDCl_3$, δ in ppm) -131.5 (q, ^3J (B, F) = 28.0 Hz); ^{11}B NMR (160.46 MHz, $CDCl_3$, δ in ppm) 1.23 (t, ^3J (B, F) = 32.0 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ in ppm): 18.2, 29.7, 42.1, 108.1, 128.8, 129.4; HRMS calcd for $C_{44}H_{37}BF_2N_5$ 684.3112 $(M+H)^+$, found 684.3117 $(M+H)^+$.

Synthesis of azaBODIPY-BODIPY dyad 12 :

To a solution of compound **11** (50 mg, 0.07 mmol) in dichloromethane (100 mL), DDQ (24 mg, 0.10 mmol) was added with continuous stirring at room temperature. This mixture was stirred for around 15 min., followed by the successive addition of triethylamine (0.4 mL, 2.8 mmol) and $BF_3{\cdot}OEt_2$ (0.4 mL, 2.8 mmol). The reaction mixture was allowed to stir for further 30

min. The solvent was evaporated under vacuum and the crude product was purified by silica gel column chromatography using ethyl acetate/petroleum ether (40/60 %) to obtain compound **12** as greenish blue amorphous solid. Yield: 38 mg (71%). mp: >300 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.40 (s, 3H), 2.42 (s, 6H), 6.5 (s, 2H), 7.05 (s, 3 H), 7.08 (s, 1H), 7.28 - 7.32 (m, 6H), 7.67 (d, ^3J = 8.4 Hz, 2H), 7.96 - 8.01 (m, 8H), 8.22 (d, ^3J = 8.3, 2H); ^{19}F NMR (376.46 MHz, $CDCl_3$, δ in ppm): -131.5 (q, ^3J (B, F) = 32.9), -144.9 (q, ^3J (B, F) = 28.2); ^{11}B NMR (160.46 MHz, $CDCl_3$, δ in ppm) 1.26 (t, ^3J (B, F) = 32.0 Hz), 0.59 (t, ^3J (B, F) = 28.8 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ in ppm): 21.5, 21.6, 21.7, 118.6, 119.1, 128.5, 128.8, 129.1, 129.3, 129.5, 129.8, 130.8, 131.5, 134.1, 134.8, 135.3, 140.4, 140.8, 141.4, 142.2, 144.1, 144.8, 145.0, 146.3, 146.9; HRMS calcd for $C_{44}H_{33}B_2F_4KN_5$ 768.2504 $(M+K)^+$, found 768.2510 $(M+K)^+$.

Synthesis of azaBODIPY-Pd(II) dipyrrin dyad 13:

To a solution of compound **11** (30 mg, 1.50 mmol) in toluene taken in a round bottomed flask equipped with a magnetic stirrer and reflux condenser, triethylamine was added, followed by the addition of $Pd(acac)_2$. The reaction mixture was heated at reflux temperature under N_2 atmosphere. The progress of the reaction was monitored by thin layer chromatography. After 3 h, there was complete consumption of the reactant and the spot corresponding to the starting material completely disappeared and a new spot was formed. The solvent was evaporated under vacuum and the reaction mixture was extracted with dichloromethane and water. The organic layer was collected and passed through celite. Solvent was removed in a rotatory evaporator to obtain compound **13** as blue coloured amorphous solid. Yield: 18 mg (52 %), mp: >300 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.08 (s, 6H), 2.38 (s, 3H), 2.42 (s, 3H), 6.43 (s, 2H), 6.74 (s, 2H), 7.01 (s, 1H), 7.07 (s, 1H), 7.23-7.30 (m, 8H), 7.50 (d, ^3J = 8.0, 2H), 7.95-7.97 (d, ^3J = 8.1,

2H), 7.98 (d, ^3J = 8.1, 2H); ^{19}F NMR (470.54 MHz, $CDCl_3$, δ in ppm): -131.6 (q, ^3J (B, F) = 28.2); ^{11}B NMR (160.46 MHz, $CDCl_3$, δ in ppm) 1.26 (t, ^3J (B, F) = 30.5 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ in ppm): 21.5, 21.6, 22.3, 22.6, 26.4, 30.9, 31.5, 34.1, 116.9, 128.1, 129.2, 129.4, 130.8, 131.4, 133.3, 146.4, 187.2; HRMS $C_{49}H_{40}BF_2N_5NaO_2Pd$ $(M+Na)^+$ calcd for 908.2195, found 908.2193 $(M+Na)^+$.

Synthesis of azaBODIPY-porphyrin dyad 14:

Diacyl dipyrromethane was reduced to the corresponding dicarbinol **18** with $NaBH_4$. The dicarbinol so obtained was immediately condensed with compound **11 (**2.5 mmol**)** in dichloromethane using catalytic amount of TFA at room temperature, followed by oxidation with DDQ. After 2h, the solvent was evaporated and the crude compound was purified using silica gel column chromatography using ethyl acetate/petroleum ether (25/75) as eluent to obtain compound **14** as bright purple crystalline solid. Yield: 9 mg (14 %). mp: >300 ^{0}C ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): -2.73 (s, 2H), 2.21 (s, 3H), 2.45 (s, 3H;), 2.46 (s, 3H), 2.71 (s, 6H), 4.10 (s, 3H), 7.06 (bs, 2H), 7.37-7.26 (m, 12H), 7.56 (d, ^3J = 7.7 Hz, 4H), 8.03 (d, ^3J = 8.2 Hz, 2H), 8.07-8.15 (m, 8H), 8.34 (d, ^3J = 8.0, 2H), 8.49 (d, ^3J = 8.0, 2H), 8.87 (bs, 2H), 8.91 (d, ^3J = 4.9 Hz, 2H); 8.97 (d, ^3J = 6.49 Hz, 2H); ^{19}F NMR (470.54 MHz, $CDCl_3$, δ in ppm): -131.5 (q, ^3J (B, F) = 32.9), -144.9 (q, ^3J (B, F) = 28.2); ^{11}B NMR (160.46 MHz, $CDCl_3$, δ in ppm) 1.26 (t, ^3J (B, F) = 32.0 Hz), 0.59 (t, ^3J (B, F) = 28.8 Hz); HRMS calcd for $C_{76}H_{59}BF_2N_7O$ 1134.4849 $(M+ H)^+$, found 1134.4843 $(M+ H)^+$.

Synthesis of azaBODIPY-oxasmaragdyrin dyad 15:

Solution of compound **11** (50 mg, 0.073 mmol) in DCM was taken in a round-bottomed flask under an inert atmosphere. To this, oxatripyrrane **19** (29 mg, 0.073) was added followed by the addition of catalytic amount of trifluoroacetic acid. The reaction mixture was stirred at room temperature for 2 h. After two hours, DDQ was added and the reaction mixture was further stirred for another half an hour. The solvent was evaporated in a rotatory evaporator. The crude product was purified by silica gel column chromatography using ethyl acetate/petroleum ether (25/75) mixture as eluent to obtain compound **15** as greenish blue solid. Yield: 37 mg (28%). mp: >300 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.33 (s, 3H), 2.48 (s, 6H), 2.49 (s, 6H), 7.07 (s, 2H), 7.31 - 7.38 (m, 6H), 7.65 (d, ^{3}J = 7.4 Hz, 5H), 8.01 (d, ^{3}J = 8.00 Hz, 2H), 8.05 (d, ^{3}J = 8.0 Hz, 2H), 8.13 (t, ^{3}J = 16 Hz, 6H), 8.82 (s, 2H), 9.13 (s, 2 H), 9.47 (s, 2H), 9.54 (s, 2H); ^{19}F NMR (376.46 MHz, $CDCl_3$, δ in ppm): -131.4 (q, ^{3}J (B, F) = 32.9); ^{11}B NMR (160.46 MHz, $CDCl_3$, δ in ppm) 1.33 (t, ^{3}J (B, F) = 32.0 Hz); HRMS calcd for $C_{72}H_{55}BF_2N_7O$ 1082.4535 $(M+H)^+$, found 1082.4537 $(M+H)^+$.

ASSOCIATED CONTENT:

*Supporting Information:

The supporting information contains the characterization data (HRMS, ^{1}H, ^{11}B, ^{19}F, ^{13}C NMR spectra) and cyclic voltammograms of all new compounds.

ACKNOWLEDGEMENTS:

M. R. thanks the Science and Engineering Research Board (SERB), Government of India for financial support (Grant No. EMR/2015/002196). A. K. would like to acknowledge the SERB for NPDF fellowship (File Number: PDF/2017/000540).

References:

1. (a) Treibs, A.; Kreuzer, F. H. Difluorboryl-Komplexe von Di- und Tripyrrylmethenen. *Liebigs Ann. Chem*. **1968**, *718*, 208-223. (b) Loudet, A.; Burgess, K. BODIPY dyes and Their Derivatives: Syntheses and Spectroscopic Properties. *Chem. Rev*. **2007**, *107*, 4891-4932. (c) Boens, N.; Leen, V.; Dehaen, W. Fluorescent indicators based on BODIPY. *Chem. Soc. Rev*. **2012**, *41*, 1130-1172.
2. (a) Tasior, M.; O'Shea, D. F. BF_2-Chelated Tetraarylazadipyrromethenes as NIR Fluorochromes. *Bioconjugate Chem*. **2010**, *21*, 1130-1133. (b) Grossi, M.; Palma, A.; McDonnell, S. O.; Hall, M. J.; Rai, D. K.; Muldoon, J.; O'Shea, D. F. Mechanistic insight into the formation of tetraarylazadipyrromethenes. *J. Org. Chem*. **2012**, *77*, 9304-9312.
3. (a) Fu, G.-L.; Pan, H.; Zhao, Y.-H.; Zhao, C.-H. *Org.* Solid-state emissive triarylborane-based BODIPY dyes: Photophysical properties and fluorescent sensing for fluoride and cyanide ions. *Biomol. Chem*. **2011**, *9*, 8141-8146. (b) Fan, J.; Hu, M.; Zhan, P.; Peng, X. Energy transfer cassettes based on organic fluorophores: construction and applications in ratiometric sensing. *Chem. Soc. Rev.* **2013**, *42*, 29-43. (c) El-Khouly, M. E.; Fukuzumi, S.; D'Souza, F. Photosynthetic antenna-reaction center mimicry by using boron dipyrromethene sensitizers. *ChemPhysChem.* **2014**, *15*, 30-47.
4. (a) Watley, R. L.; Awuah, S. G.; Bio, M.; Cantu, R.; Gobeze, H. B.; Nesterov, V. N.; Das, S. K.; D'Souza, F.; You, Y. *Chem. - Asian J*. Dual Functioning Thieno-Pyrrole Fused BODIPY Dyes for NIR Optical Imaging and Photodynamic Therapy:Singlet Oxygen Generation without Heavy Halogen Atom Assistance. **2015**, *10*, 1335-1343. (b) Mahapatra, A. K.; Maji, R.; Maiti, K.; Adhikari, S. S.; Mukhopadhyay, C. D.; Mandal, D.

Ratiometric sensing of fluoride and acetate anions based on a BODIPY-azaindole platform and its application to living cell imaging. *Analyst* **2014**, *139*, 309-317.

5. (a) Kamkaew, A.; Lim, S. H.; Lee, H. B.; Kiew, L. W.; Chung, L. Y.; Burgess, K. BODIPY dyes in photodynamic therapy. *Chem. Soc. Rev.* **2013**, *42*, 77-88. (b) Awuah, S. G.; You, Y. Boron dipyrromethene (BODIPY)-based photosensitizers for photodynamic therapy. *RSC Adv.* **2012**, *2*, 11169-11183.
6. (a) Bandi, V.; Gobeze, H. B.; Nesterov, V. N.; Karr, P. A.; D'Souza, F. Phenothiazine-azaBODIPY-fullerene supramolecules: syntheses, structural characterization, and photochemical studies. *Phys. Chem. Chem. Phys*. **2014**, *16*, 25537-25547. (b) Bandi, V.; El-Khouly, M. E.; Ohkubo, K.; Nesterov, V. N.; Zandler, M. E.; Fukuzumi, S.; D'Souza, F. Excitation-Wavelength-Dependent, Ulttrafast Photoinduced Electron Transfer in Bisferrocene/BF_2-Chelated-Azadipyrromethene/Fullerene Tetrads. *Chem. - Eur. J*. **2013**, *19*, 7221-7230. (c) Hall, M.J.; Allen, L. T.; O'Shea, D. F. PET modulated fluorescent sensing from the BF_2 chelated azadipyrromethene platform. *Org. Biomol. Chem*. **2006**, *4*, 776-780. (d) Jiao, L.; Wu, Y.; Wang, S.; Hu, X.; Zhang, P.; Yu, C.; Cong, K.; Meng, Q.; Hao, E.; Vicente, M. G. H. Accessing Near-Infrared-Absorbing BF_2-Azadipyrromethenes via a Push-Pull Effect. *J. Org. Chem*. **2014**, *79*, 1830-1835. (e) Yuan, M.; Yin, X.; Zheng, H.; Ouyang, C.; Zuo, Z.; Liu, H.; Li, Y. Light Harvesting and Efficient Energy Transfer in Dendritic Systems: New Strategy for Functionalized Near-Infrared BF_2-Azadipyrromethenes. *Chem. - Asian J*. **2009**, *4*, 707-713.
7. Kumar, S.; Thorat, K. G.; Ravikanth, M. Synthesis and Properties of Covalently Linked AzaBODIPY-BODIPY Dyads and AzaBODIPY-$(BODIPY)_2$ Triads. *J. Org. Chem.* **2017**, *82*, 6558-6577.

8. Kumar, S.; Khan, T. K.; Ravikanth, M. Synthesis and properties of hexaarylated AzaBODIPYS. *Tetrahedron* **2015**, *71*, 7608-7613.

9. Koch, A.; Kumar, S.; Ravikanth, M. Use of Wittig reaction for the synthesis of conjugated Aza-BODIPYS and their spectral and electrochemical properties. *Tetrahedron* **2017**, *73*, 1459-1465.

10. Hall, M. J.; McDonnell, S. O.; Killoran, J.; O'Shea, D. F. A Modular Synthesis of Unsymmetrical Tetraarylazadipyrromethenes. *J. Org. Chem.* **2005**, *70*, 5571-5578.

11. Parisotto, S.; Lace, B.; Artuso, E.; Lombardi, C.; Deagostino, A.; Scudu, R.; Garino, C.; Medana, C.; Prandi, C. Heck functionalization of an asymmetric aza-BODIPY core: synthesis of far-red infrared probes for bio imaging applications. *Org. Biomol. Chem*. **2017**, *15*, 884-893.

12. Jokic, T.; Borisov, S. M.; Saf, R.; Nielsen, D. A.; Kuhl, M.; Klimant, I. Highly Photostable Near-Infrared Fluorescent pH Indicators and Sensors Based on BF_2-chelated Tetraarylazadipyrromethene Dyes. *Anal. Chem*. **2012**, *84*, 6723-6730.

13. (a) Chan, C.-K.; Tsai, Y.-L.; Chang, M.-Y. ($Bi(Otf)_3$ catalyzed disproportionation reaction of cinnamyl alcohols. *Tetrahedron* **2017**, *73*, 3368-3376. (b) Zhang, Y.; Yang, X.; Zhou, H.- C. Direct synthesis of functionalized PCN-333 via linker design for Fe^{2+} detection in aqueous media. *Dalton Trans.* **2018**, *47*, 11806-11811.

14. Bhat, I, K.; Kumar, A. Pyrazolines as Potent Antituberculosis and Cytotoxic Agents. *Asian J. Pharm. Clin. Res*. **2017**, *10*, 247-249.

15. Hajipor, A. R.; Khorsandi, Z. Application of Immobilised Proline on CNTs and Proline Ionic Liquid as Novel Organocatalysts in the Synthesis of 2-Amino-4H-pyran

Derivatives: A Comparative Study between their Catalytic Activities. *ChemistrySelect* **2017**, *2*, 8976-8982.

16. Du, D.-M.; Yang, W. Highly Enantioselective Michael Addition of Nitroalkanes to Chalcones Using Chiral Squaramides as Hydrogen Bonding Organocatalysts.*Org. Lett*. **2010**, *12*, 5451-5453.
17. Gut, A.; Lapok, L.; Jamroz, D.; Nowakowska, M. Synthesis of Thermally robust, Photostable Aza-Dipyrromethene Ligands Substituted with Nitro Groups. *Asian J. Org. Chem*. **2017**, *6*, 207-223.