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1, 7-Difluorophore Substituted AzaBODIPYs

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Abstract:

Four different 1,7-difluorophore substituted azaBODIPYs containing fluorophores such as naphthalene, anthracene and pyrene were synthesized over a sequence of steps involving Aldol condensation, Michael addition, dipyrromethene formation and BF_2-complexation. All these steps were optimized and the target 1,7-difluoro substituted azaBODIPYs along with other intermediate compounds were thoroughly characterized by HR-MS, 1D and 2D NMR spectroscopy. The absorption and electrochemical studies indicated a strong interaction between fluorophores and azaBODIPY moieties in compounds **1-4**. The fluorescence studies revealed that 1,7-difluoro substituted azaBODIPYs with fluorophores such as naphthalene and pyrene are fluorescent and invoked the possibility of singlet-singlet energy transfer from fluorophores to azaBODIPY moiety whereas 1,7-dianthracenyl substituted azaBODIPY was completely non-fluorescent due to efficient photo-induced electron transfer between anthracene and azaBODIPY moieties.

Keywords: Aza-BODIPYs, Photophysical properties, Fluorophores, Cyclic Voltammetry, Energy transfer.

Key topics: Fluorescent dyes, covalent conjugates.

Introduction

Donor-acceptor systems that show efficient light induced energy and electron transfer processes are important compounds to build solar light harvesting and opto-electronic devices.[1] Such systems are useful in achieving renewable energy sources for human consumption by using them to build light-to-electricity and light-to-fuel conversion devices.[1-6] Generally, porphyrins[7] and phthalocyanines[8] have been used in building these donor-acceptor systems because of their close resemblance to natural photosensitizer chlorophyll molecules. However, several other systems such as subphthalocyanines,[9] subporphyrins,[10] expanded porphyrins,[11] BF_2-chelated dipyrromethenes(BODIPYs) and aza-BODIPY dyes,[12,13,14] perylene diimides[15] etc. were also employed. Among these chromophores, azaBODIPYs, the structural analogues of BODIPYs, have gained much attention because of their attractive photophysical properties.[16] AzaBODIPYs absorb in the visible to NIR region with high extinction coefficients, emits above 700 nm with large fluorescence quantum yields. Thus, azaBODIPYs have been used in applications ranging from photosensitizers to photodynamic therapy systems.[17] The properties of azaBODIPYs can be fine tuned by introducing suitable substituents at 1,3,5,7-positions. D'Souza and co-workers[18] reported several azaBODIPY based systems in which the energy and electron donor systems were linked to azaBODIPY via spacer and demonstrated the efficient energy/electron transfer in these molecules. A perusal of literature revealed that the aza-BODIPYs in which energy/electron donor/acceptor groups connected directly to the aza-BODIPY core are very few. This may be because of the unstability of the intermediate compounds involved in the multi-step synthesis of substituted azaBODIPYs. Herein, we made an attempt to synthesize new 1,7-difluorophore substituted azaBODIPYs **1-3** in which the fluorophores such as naphthalene, anthracene and pyrene were directly connected to azaBODIPY

core at 1,7-positions. We also report the synthesis of 1,7-dinaphthalene appended azaBODIPY **4** in which the naphthalene groups were connected to azaBODIPY via benzyloxy spacer. We anticipated that the fluorophores in these conjugates acts as antenna and absorbs energy to transfer efficiently to azaBODIPY core. The photophysical studies revealed that there is a possibility of singlet-singlet energy transfer from fluorophores such as naphthalene and pyrene to azaBODIPY core and electron transfer between fluorophores such as anthracene to azaBODIPY core in directly connected 1,7-difluorophore substituted azaBODIPYs **1-3**.

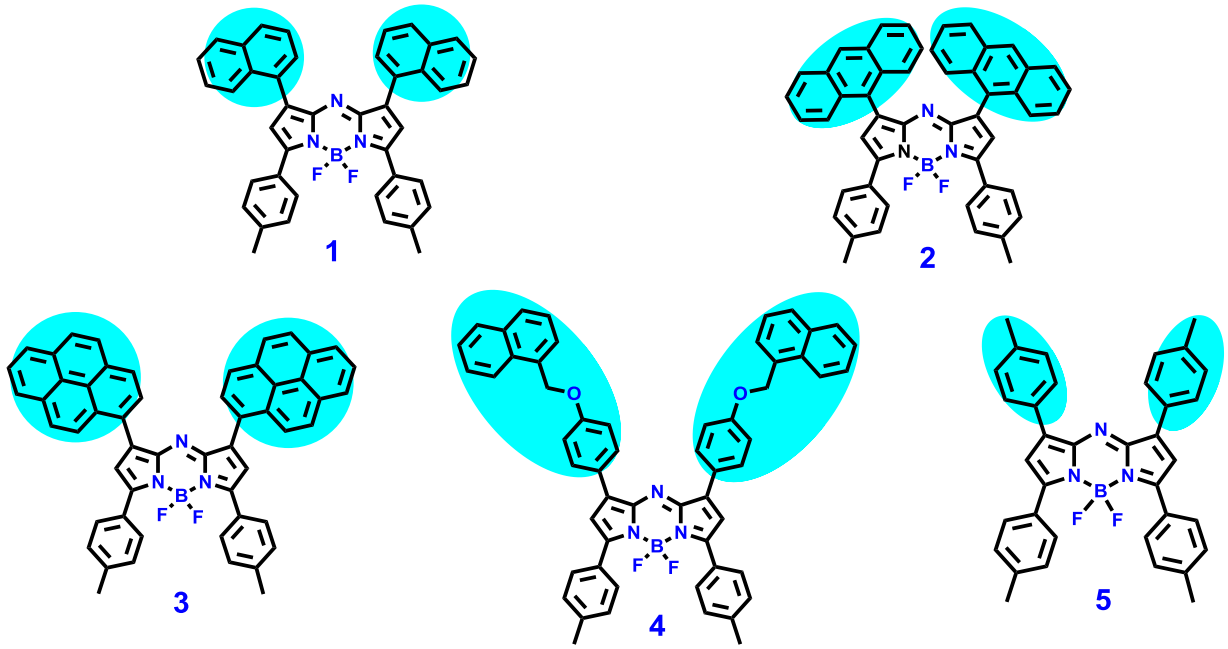
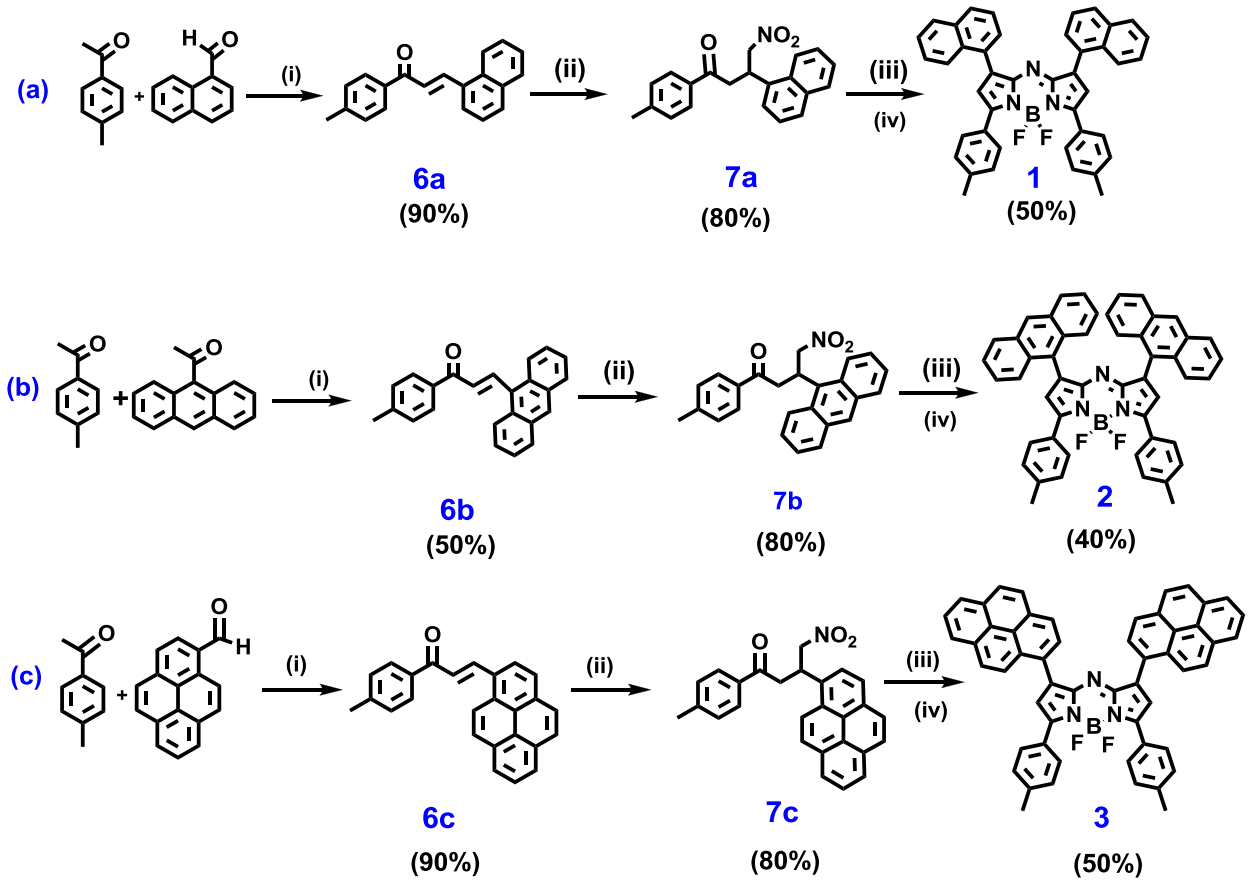


Figure 1. Structures of the newly synthesized 1, 7-difluorophore substituted azaBODIPYs **1-4** and reference compound **5**

Results and Discussion

The directly connected 1,7-difluorophore substituted aza-BODIPYs **1-3** were synthesized over a sequence of steps as shown in Scheme 1. The synthesis of 1,7-difluorophore substituted azaBODIPYs **1-3** involves the standard Aldol condensation, Michael addition,

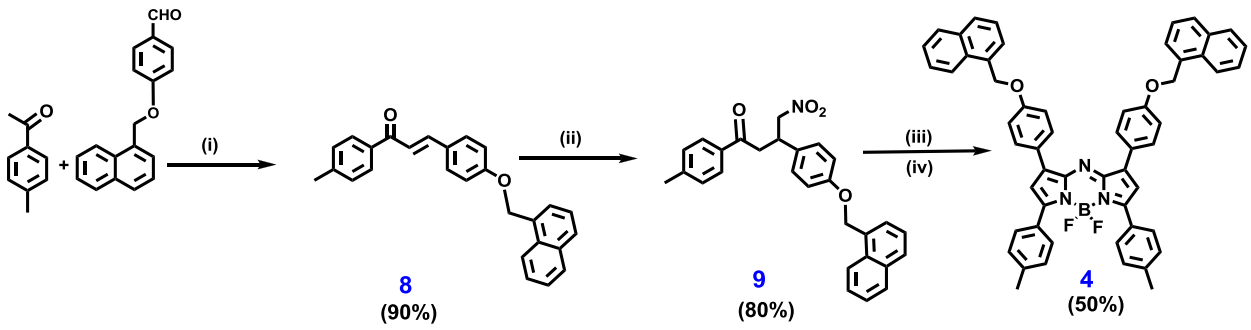
azadipyrromethene formation and BF_2 complexation. However, these steps are not straight-forward to prepare the directly connected 1,7-dinaphthyl- **1**, 1,7-dianthracenyl- **2** and 1,7-dipyrenyl- **3** substituted azaBODIPYs. Every synthetic step was done several times to optimize the conditions to afford pure intermediate compounds which were thoroughly characterized and used for preparing the target compounds, 1,7-difluorophore substituted azaBODIPYs.



Scheme I: (i) KOH, EtOH, rt, stir, 24 hr; (ii) Diethylamine, CH_3OH, reflux, 48 h; (iii) n-butanol, NH_4OAc, reflux, 24 h; (iv) CH_2Cl_2, triethylamine, $BF_3.OEt_2$.

In the first step, the appropriate aldehyde was reacted with 4-methylacetophenone under basic conditions to afford the aldol product **6a-6c** which was subjected to nitration under Michael addition conditions to obtain the corresponding nitro products **7a-7c**. The aldol products were

obtained only when we used 10 M solution of KOH instead of normal 2.5 M and stirred for overnight followed by work-up and column chromatographic purification. The solid aldol products **6a-6c** were obtained only after column chromatographic purification. The nitro products **7a-7c** were also required 15 equivalents of nitromethane and diethylamine and longer reaction times compared to the nitro product of the reference compound **5**. The appropriate nitro compound was then dimerized in *n*-butanol in the presence of NH_4OAc at reflux temperature to obtain the corresponding 1,7-difluorophore substituted azadipyrromethene, which was subsequently treated with $BF_3.OEt_2$ in the presence of triethylamine to afford the corresponding 1,7-difluorophore substituted azaBODIPYs **1-3**. Care needs to be taken in the purification of compounds **1-3** since the unidentified impurities and the target compounds have very less polarity differences. The compound **4** in which the naphthyl groups were connected to 1,7-phenyloxy groups of azaBODIPY was also prepared similarly in a sequence of steps as shown in Scheme II.



Scheme II: (i) KOH, EtOH, rt, stir, 24 hr; (ii) Diethylamine, CH_3OH, reflux, 48 h; (iii) n-butanol, NH_4OAc, reflux, 24 h; (iv) CH_2Cl_2 , triethylamine, $BF_3.OEt_2$.

All new 1,7-difluophore substituted azaBODIPYs **1-4** were freely soluble in common organic solvents and their identities were confirmed by HR-MS and detailed 1D and 2D NMR spectroscopy as discussed here for compound **1**. The ^1H NMR, ^1H-^1H COSY and NOESY NMR

spectra of compound **1** are shown in Figure 2. In ^{1}H NMR, the compound **1** showed three sets of doublets, four sets of multiplets and one singlet resonance for thirty protons corresponding to aryl, naphthyl and azaBODIPY core protons which were identified and assigned based on their position, integration and cross-peak correlations in 2D NMR spectra. The -CH_3 protons of 3,5-tolyl groups of compound **1** appeared as a singlet at 2.48 ppm showed NOE correlation with a multiplet appearing in the region of 7.29-7.36 ppm which we identified as type *a* protons of tolyl groups. The doublet resonance appeared at 8.06 ppm was due to type *b* protons of tolyl group based on their cross-peak correlation with type *a* protons. The type *b* protons showed NOE correlation with a singlet appeared at 7.12 ppm which we identified as type *c* protons of aza-BODIPY core. The NOE correlation between type *c* protons at 7.12 ppm with a multiplet resonance at 8.27 ppm helped in identifying the resonance at 8.27 ppm as type *d* protons of naphthyl groups. The resonances at 7.51 (type *e* and *f*), 7.85 (type *g*), 7.79 (type *h*) and 7.65 (type *j*) were similarly identified and assigned based on their cross-peak correlation in COSY and NOESY spectra. The NMR resonances of compounds **2-4** were similarly identified and assigned using 1D and 2D NMR spectroscopy. Thus, 1D and 2D NMR spectroscopy was used effectively to deduce the molecular structures of compounds **1**-**4**. The compounds **1-4** showed a triplet in the region of 1.50-1.62 ppm in ^{11}B NMR and a quartet at ~ -131 ppm in ^{19}F NMR.

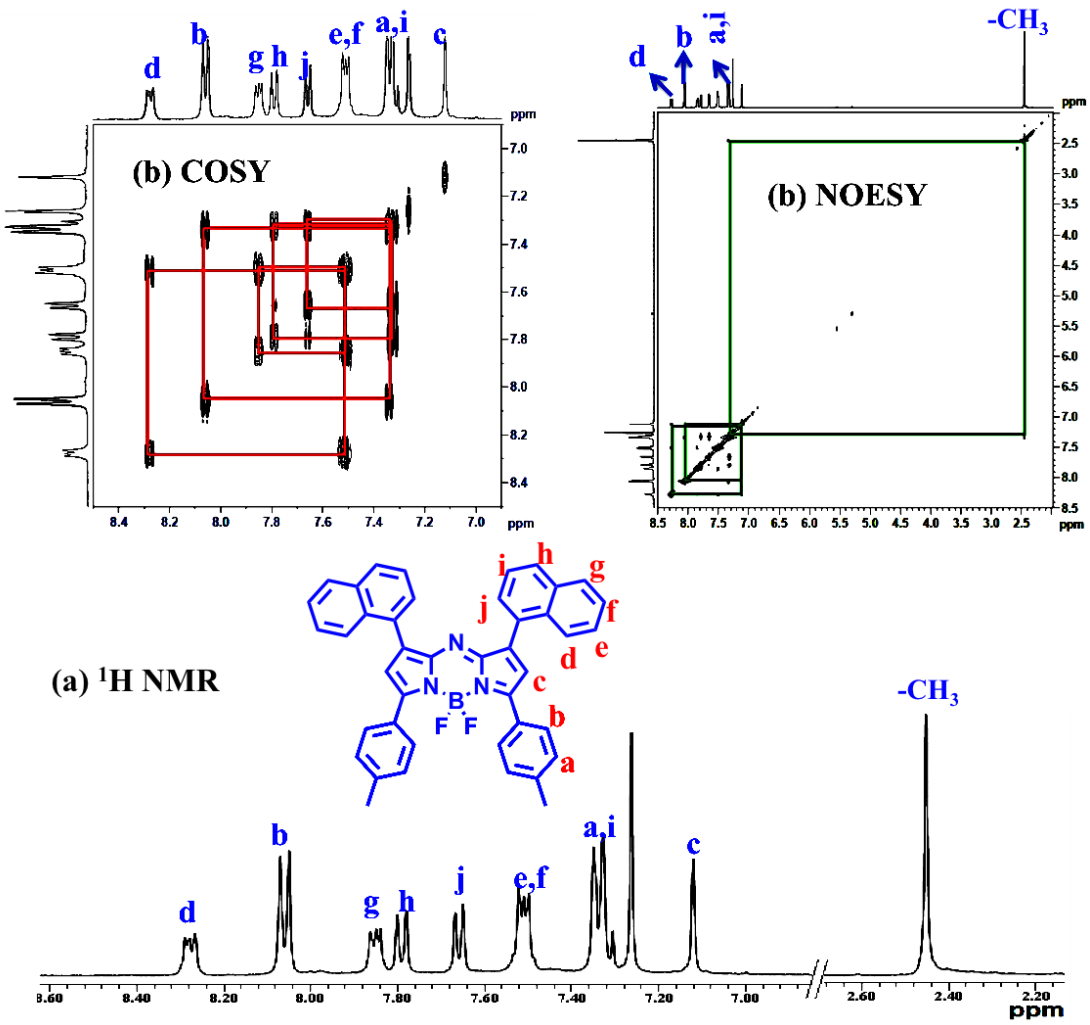


Figure 2. (a) ^{1}H NMR, (b) COSY and (c) NOESY spectra of 1,7–dinaphthyl aza-BODIPY **1** recorded in $CDCl_3$.

The absorption spectra of 1,7-difluorophore substituted azaBODIPYs **1-4** along with reference azaBODIPY, 1,3,5,7-tetratolyl azaBODIPY **5** were recorded in $CHCl_3$ and the relevant data are presented in Table 1. The comparison of absorption spectra of compounds **1-5** using the same concentration of ~1 X 10^{-5} M is presented in Figure 3(a). As clear from Figure 3(a), the compounds **1-4** showed similar absorption spectral features like the reference azaBODIPY **5** and exhibited one strong absorption band in the region of 630-700 nm

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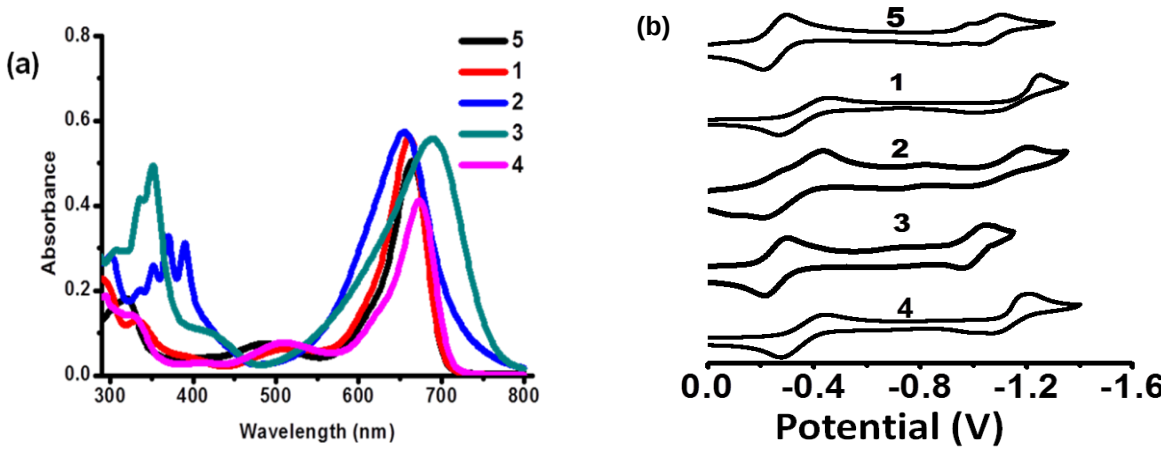
corresponding to the azaBODIPY moiety and less intense but sharp bands in 290-400 nm region corresponding to the fluorophores such as pyrene, anthracene and naphthalene. However, in compounds **1-4**, the absorption band experienced either bathochromic shift or hypsochromic shift depending on the kind of fluorophores present at the 1,7-positions. The absorption band is maximum broadened and red shifted in case of compound **3** whereas compound **2** showed hypsochromically shifted broadened absorption band compared to compound **5**. The extinction coefficients of compounds **1-4** were also varied compared to compound **5**. All these observations supports that the electronic properties of azaBODIPY core in compounds **1-4** were altered due to interaction between the fluorophores and azaBODIPY moieties and magnitude of alteration was dependent on the kind of fluorophore substituted at 1,7-positions.



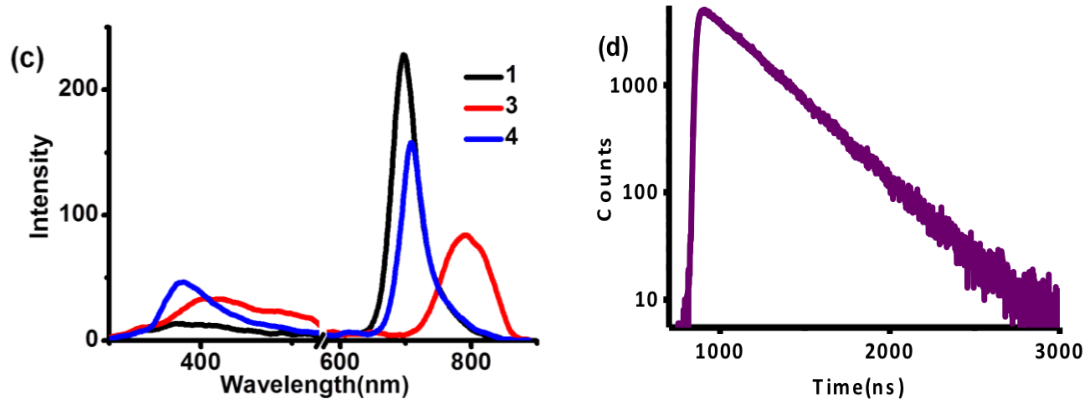


Figure 3. (a)Comparison of UV-Vis spectra of compounds **2** and **3** with compound **5** in chloroform (1 X 10^{-5} M conc.) (The inset shows the comparison of UV-Vis spectra of compounds **2, 3** and **5** in the region of 530-800 nm; (b) Comparison of reduction waves of compounds **1-5** at a scan rate of 50 mv/s using TBAP as supporting electrolyte; (c) Comparison of fluorescence spectra of compounds **1, 3** and **4** in chloroform (1 X 10^{-5} M conc.) (The inset shows the comparison of emission spectra of compounds **1, 3** and **4** in the region of 600-850 nm; (d) Fluorescence decay profile of compound **1** in chloroform.

The redox properties of compounds **1-4** along with reference compound **5** were studied by cyclic voltammetry at a scan rate of 50 mV/s using tetrabutylammonium perchlorate as a supporting electrolyte (0.1 M) in dichloromethane. The comparison of reduction waves of compounds **1-5** is shown Figure 3(b) and the relevant data are included in Table 1. Compounds **1-5** showed one ill-defined oxidation one quasi-reversible reduction and one irreversible reduction. The inspection of redox data presented in Table 1 shows that the reduction potentials of **1-4** were shifted more negatively by 40-100 mV compared to compound **5** which indicates that compounds **1-4** were relatively more difficult to reduce than compound **5**. This in turn suggests that the compounds **1-4** were relatively more electron rich than compound **5**. Furthermore, the Δ_{redox} which gives an estimate of HOMO-LUMO gap calculated from the difference of first oxidation potential and first reduction potential is altered depends on the kind of fluorophores substituted at 1,7-positions. The decreased HOMO-LUMO gap in compound **3**

compared to the reference compound **5** explains the large red shifts noted in absorption and emission bands whereas the hypsochromic shifts of absorption bands observed for compound **2** were in line with the increased HOMO-LUMO gap.

Table 1: Photophysical and electrochemical data of compounds **1-4** and **5** recorded in chloroform

	λ_{abs}(nm)	λ_{em}	Φ	$\tau_{azaBODIPY}$	Electrochemical data			Δ_{redox}
	($log(\varepsilon mol^{-1}dm^3\ cm^{-1})$)	(nm)		(ns)	$E_{1/2ox}$(V)	$E_{1/2red}$ (V)		(eV)
1	292(4.34), 664(4.74)	415, 693	0.023[a], 0.14[b]	2.03	1.33	-0.33	-1.17	1.66
2	249(5.13), 654(4.75)	-	-	-	1.47	-0.32	-1.13	1.79
3	243(4.90), 689(4.74)	405, 776	0.022[a], 0.25[b]	1.12	1.27	-0.27	-1.02	1.54
4	293(4.62), 673(4.72)	406, 701	0.024[a], 0.19[b]	1.86	1.27	-0.34	-1.15	1.61
5	654(4.70)	695	0.37[b]	2.00	1.36	-0.23	-1.06	1.59

log($\varepsilon mol^{-1}dm^3\ cm^{-1}$)-molar extinction coefficient, λ_{abs} (absorption maxima), λ_{em} (emission maxima), Φ (quantum yield), τ (lifetime).[a] at excitation wavelength 240 nm, [b] at excitation wavelength 630 nm and corresponding emission wavelengths

The fluorescence properties of compounds **1-5** were investigated in chloroform by both steady-state and time-resolved fluorescence techniques. The comparison of steady state fluorescence spectra of compounds **1**, **3** and **4** is shown in Figure 3(c) and the relevant data are included in Table 1. Since the compounds **1-4** contains fluorophores which absorb at high energy and can act as energy donors, there is a possibility of singlet-singlet energy transfer from fluorophore to azaBODIPY on selective excitation of fluorophore unit. Thus, we recorded the fluorescence spectra of compounds **1-4** on selective excitation of corresponding fluorophore as well as upon excitation of azaBODIPY unit. The reference azaBODIPY compound **5** upon excitation at 630 nm showed a strong emission band at 695 nm with a quantum yield of 0.37. The compounds **1**, **3** and **4** upon excitation at 630 nm showed a strong azaBODIPY emission in

the region of 670-800 nm with quantum yields varies from 0.14 to 0.25. The fluorescence peak maxima and the quantum yield were dependent on the type of fluorophore present at the 1,7-positions and as well as on the interaction between the fluorophore and azaBODIPY moieties in compounds **1, 3** and **4.** In case of compound **3**, we noticed much broader and significantly red shifted fluorescence band. This supports strong interaction between the pyrenes and azaBODIPY moieties in the excited state of compound **3** which needs further investigation. Interestingly, the azaBODIPY **2** containing anthracene substituents at the 1,7-positions did not show any fluorescence of azaBODIPY moiety indicating that the fluorescence of azaBODIPY moiety was completely quenched by anthracene substituents due to photoinduced electron between the fluorophores and azaBODIPY unit. The fluorescence spectra of compounds **1-4** were also recorded by selectively exciting donor fluorophore at 240 nm where the fluorophores such as naphthalene, anthracene and pyrene absorbs strongly. As clear from Figure 2c, upon excitation at 240 nm, the compounds **1, 3** and **4** showed weak emission from fluorophore moiety and strong emission from the azaBODIPY unit. This indicates that in compounds **1**, **3** and **4**, the fluorescence of fluorophore was significantly quenched and a strong emission corresponding to azaBODIPY unit was observed. The excitation spectra recorded for compounds **1**, **3** and **4** at the appropriate emission wavelength showed absorption features of both fluorophore and azaBODIPY units. All these observations support the possibility of singlet-singlet energy transfer from donor fluorophore to azaBODIPY unit in compounds **1**, **3** and **4**. The compound **2** upon selective excitation at 240 nm did not show any emission corresponding to both fluorophore and azaBODIPY moieties indicating a possibility of photo-induced electron transfer between anthracene and azaBODIPY. The singlet state lifetimes of compounds **1**, **3** and **4** in chloroform were measured using time-resolved photon counting (TCSPC) technique. Our

instrument has limitation which allowed to measure only the singlet state lifetime of azaBODIPY moiety and we could not measure the singlet state lifetimes of donor fluorophores such as naphthalene and pyrene in compounds **1**, **3** and **4**. The fluorescence decays of compounds **1**, **3** and **4** were fitted to single exponential and a representative fluorescence decay profile for compound **1** is shown in Figure 3d. The singlet state lifetimes of compounds **1**, **3** and **4** were in agreement with their fluorescence quantum yields. More studies are required to understand the excited state dynamics of 1,7-difluorophore substituted azaBODIPYs, specially compound **2**.

Conclusions:

In conclusion, we have prepared four different 1,7-difluorophore substituted azaBODIPYs over a sequence of steps. Since the fluorophores were bulkier and causing the steric constraints, the intermediate products were not stable enough to obtain the 1,7-difluorophore substituted azaBODIPYs readily. We optimized the reaction and purification conditions to afford the target 1,7-difluorophore substituted azaBODIPYs and their intermediate compounds. Absorption and electrochemical studies revealed that the fluorophores and azaBODIPY moieties were strongly coupled. The fluorescence studies supported a possibility of singlet-singlet energy transfer from fluorophores such as naphthalene and pyrene to azaBODIPY in 1,7-difluorophore substituted azaBODIPYs.

Experimental:

Materials and Methods

General Experimental: The chemicals such as $BF_3 \cdot OEt_2$ and 2,3-dichloro-5, 6-dicyano-1,4-benzoquinone (DDQ) were used as obtained from Aldrich. All other chemicals used for the

synthesis were reagent grade unless otherwise specified. Column chromatography was performed on silica gel. The ^{1}H, ^{11}B and ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker 400 and 500 MHz instruments. The frequencies for ^{13}C nucleus are 100.06 and 125.77 MHz, for ^{19}F nucleus are 376.49 and 470.56 MHz, and for ^{11}B nucleus are 128.37 and 160.46 MHz for 400 MHz and 500 MHz instruments respectively. Tetramethylsilane [$Si(CH_3)_4$] was used as an internal standard for ^{1}H and ^{13}C NMR, tetrafluorotoluene as an external standard for ^{19}F NMR and boric acid as an external standard for ^{11}B NMR. Absorption and steady state fluorescence spectra were obtained with Perkin-Elmer Lambda-35 and PC1 photon counting spectrofluorometer manufactured by ISS, USA instruments, respectively. The elemental analyses were performed on a Thermo Quest microanalysis instrument. The fluorescence quantum yields (Φ) were calculated from the emission and absorption spectra by comparative method at the excitation wavelength of 240 nm using Phenylalanine (Φ = 0.022 in water),[19] and at the excitation wavelength of 630 nm using 3,5-dianisyl -1,7-di(p-phenyl) azaBODIPY (Φ = 0.36 in chloroform)[20] 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. Cyclic voltammetric (CV) studies were carried out with BAS electrochemical system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The HR mass spectra were recorded with a Q-Tof micro mass

spectrometer. For UV-Vis and fluorescence titrations, the stock solution for all compounds (5×10^{-4} M) were prepared by using spectroscopic grade $CHCl_3$ solvent.

Synthesis of 3-(naphthyl)-1-(p-tolyl)prop-2-en-1-one (6a):

To a solution of 1-naphthaldehyde (1 g, 8.20 mmol) in absolute ethanol (40 mL), 4-methylacetophenone (1g, 8.3 mmol) was added. To this reaction mixture, aqueous solution of potassium hydroxide (40 ml, 2.5 M) was added dropwise at 0˚C and the solution was stirred at room temperature for a period of 24 h. The reaction mixture was allowed to cool in ice bath, during which the product precipitated. Filtration of the reaction mixture gave a pale white solid product**.** The crude product was purified by column chromatography petroleum ether/ethyl acetate (95:05) to obtain off-white coloured crystalline compound **6a**. Yield: 1.85 g (90%); ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.45 (s, 3H), 7.33 (d, ^3J (H, H) = 7.7 Hz, 2H), 7.51-7.64 (m, 5H), 7.88-7.93 (m, 3H), 7.99 (d, ^3J (H, H) = 8.1 Hz, 2H), 8.26 (d, ^3J (H, H) = 8.3 Hz, 1H), 8.64 (d, ^3J (H, H) = 15.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 21.8, 125.5, 125.6, 128.4, 129.0, 129.6, 129.8, 130.5, 131.3, 131.5, 135.5, 141.6, 144.2, 189.4; HRMS. Calcd for $C_{20}H_{17}O$ [$(M+H)^+$]: m/z 273.1274. Found: m/z 273.1265.

Synthesis of 3-(naphthyl)-4-nitro-1-(p-tolyl)butan-1-one (7a):

Samples of 3-(naphthyl)-1-(p-tolyl)prop-2-en-1-one **6a** (1 g, 3.96 mmol), nitromethane (1 mL, 19 mmol), and diethylamine (2 mL, 19 mmol) were dissolved in ethanol (50 mL) and refluxed for 28 h. The solution was cooled, acidified with hydrochloric acid (20 mL, 2.5 M) to precipitate the compound. The crude product was subjected to column chromatographic purification using petroleum ether/ethyl acetate (95:5) to yield white solid product **7a**. Yield: 1 g

(80 %); ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.40 (s, 3H), 3.39 (m, 2H; CH_2), 4.60-4.65 (dd, 1H), 4.86-4.91 (m, 2H), 5.14-5.20 (m, 1H), 7.25 (t, ^{3}J (H, H) = 3.5 Hz, 2H), 7.40-7.44 (m, 2H), 7.53 (t, ^{3}J (H, H) = 7.8 Hz, 1H), 7.58-7.62 (m, 1H), 7.79 (d, ^{3}J (H, H) = 8.1 Hz, 1H), 7.82 (d, ^{3}J (H, H) = 8.1 Hz, 1H), 7.89 (d, ^{3}J (H, H) = 9.5 Hz, 1H), ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 21.8, 41.4, 78.9, 122.5,125.4, 126.2, 127.0, 128.3, 128.5, 129.3, 129.5, 131.1, 134.0, 134.3, 1353, 144.7; HRMS. Calcd for $C_{18}H_{19}NO_4$ [$(M+Na)^+$]: m/z 356.1257, Found: m/z 356.1257.

Synthesis of azaBODIPY 1:

A solution of 3-(dinaphthyl)-4-nitro-1-(p-tolyl)butan-1-one **7a** (1 g, 3.2 mmol) and ammonium acetate (6.20 g, 80 mmol) in *n*-butanol (30 mL) was heated under reflux for 24 h. The product precipitated as blue-black solid. The reaction was allowed to cool to room temperature and solid was filtered to obtain the intermediate compound. To the dichoromethane solution of intermediate compound, triethylamine (100 eq.), was added followed by the addition of $BF_3.Et_2O$ (110 eq.) and stirring was continued for half an hour. The reaction mixture was washed with water and the organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (30:70), to afford pure aza-BODIPY **1** as brown solid. Yield: 0.94 g (50%); ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.45 (s, 6 H), 7.12 (s, 2H) 7.30 - 7.36 (m, 711 H), 7.44 - 7.55 (m, 5 H), 7.66 (dd, J = 7.17, 1.07 Hz, 3H), 7.79 (d, ^{3}J (H, H) J=8.24 Hz, 5H), 7.82-7.88 (m, 4H), 8.06 (d, ^{3}J (H, H) J = 8.24 Hz, 5H), 8.23-8.32 (m, 3H); ^{11}B NMR (160 MHz, $CDCl_3$, δ in ppm): 1.50 (t, ^{1}J (B-F) = 32 Hz, 1B); ^{19}F NMR (470 MHz, $CDCl_3$, δ in ppm): -131.8 (q, ^{1}J (F-B) = 23.5 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.8, 53.5, 123.1, 125.2, 125.9, 126.0, 126.5, 128.6, 128.9, 129.4, 129.7,

129.9, 130.0, 130.3, 131.8, 134.0, 141.8, 144.0, 146.7, 159.1; HRMS. Calcd for $C_{36}H_{30}BF_2N_3O_2$ $[(M+K)^+]$: m/z 664.2130; Found: m/z 664.2140.

Synthesis of 3-(anthracenyl)-1-(p-tolyl)prop-2-en-1-one (6b):

Samples of 9-anthranaldehyde (1 g, 8.20 mmol), 4-methylacetophenone (1 g, 8.3 mmol) were dissolved in absolute ethanol (40 mL). An aqueous solution of potassium hydroxide (40 ml, 10 M) was added dropwise at 0˚ C and the solution was stirred at room temperature for a period of 24 h. The reaction mixture was allowed to cool in ice bath, during which the product precipitated as sticky substance. The reaction mixture was then extracted with dichloromethane, and dried over sodium sulphate solution. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (95:5) afforded compound **6b** as orange crystalline solid. Yield: 1 g (50%); ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.46 (s, 3 H), 7.33 (d, ^3J (H, H) =8.01 Hz, 2 H), 7.41 - 7.64 (m, 8 H), 7.64 - 7.72 (m, 2 H), 7.99 - 8.08 (m, 6 H), 8.27 - 8.37 (m, 2 H), 8.46 (s, 1 H), 8.60 - 8.67 (m, 1 H), 8.80 (d, ^3J (H, H) =15.79 Hz, 1 H), 8.98 (d, ^3J (H, H) = 8.93 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 21.8, 125.5, 126.5, 128.4, 129.0, 129.6, 129.8, 130.5, 131.3, 131.5, 135.5, 141.6, 141.1, 189.4; HRMS. Calcd for $C_{24}H_{19}O$ $[(M+H)^+]$: m/z 323.1430; Found: m/z 323.1435.

Synthesis of 3-(anthracenyl)-4-nitro-1-(p-tolyl)butan-1-one (7b):

To a solution of 3-(anthracenyl)-1-(p-tolyl)prop-2-en-1-one **6b** (1 g, 3.96 mmol) in methanol, nitromethane (5 mL, 19 mmol), and diethylamine (10 mL, 19 mmol) was added and refluxed for 48 h. The solution was cooled, acidified with hydrochloric acid (20 mL, 2.5 M). The reaction mixture was then extracted with dichloromethane and purified by silica gel column

chromatography using petroleum ether/ethyl acetate (85:5) to yield white crystalline solid product **7b**. Yield**:** 1 g (80 %)**;** ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.38 (s, 3 H), 3.85 (dd, ^{3}J (H, H) = 4.77 Hz, 1 H), 3.98-4.09 (m, 1 H), 5.10 (dd, ^{3}J (H, H) = 6.97 Hz, 1 H), 5.28-5.40 (m, 1 H), 6.01-6.20 (m, 1 H), 7.20 (d, J = 8.07 Hz, 2 H), 7.44-7.54 (m, 2 H), 7.57-7.68 (m, 2 H), 7.80 (d, J = 8.07 Hz, 2 H), 7.97-8.17 (m, 3 H), 8.45 (s, 1 H), 8.69 (d, J = 9.17 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 21.6, 32.2, 42.4, 123.8, 124.0, 124.5, 125.3, 126.2, 127.1, 128.2, 128.7, 129.1, 129.2, 129.3, 130.5, 130.6, 131.6, 131.7, 131.9, 133.6, 144.4, 196.6; HRMS. Calcd for $C_{25}H_{21}KNO_3$ [$(M+K)^+$]: m/z 422.1153 Found: m/z 422.1168.

Synthesis of azaBODIPY 2.

A solution of 3-(anthracenyl)-4-nitro-1-(p-tolyl)butan-1-one **7b** (1 g, 3.2 mmol) and ammonium acetate (6.20 g, 80 mmol) in *n*-butanol (30 mL) was heated under reflux for 24 h. The product precipitated as blue-black solid. The reaction was allowed to cool to room temperature and solid was filtered to obtain the intermediate compound. To the dichoromethane solution of intermediate compound, triethylamine (100 eq.), was added followed by the addition of $BF_3.Et_2O$ (110 eq.) and stirring was continued for half an hour. The reaction mixture was washed with water and the organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The solvent was evaporated under reduced pressure and the crude product was purified using silica gel column chromatography with petroleum ether/ethyl acetate (30:70), to afford pure aza-BODIPY **2** as brown solid. Yield: 0.78 g (40%). ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.46 (s, 6 H), 7.01 (s, 2 H), 7.22 (dd, J = 8.62, 1.14 Hz, 4 H), 7.36 (d, ^{3}J (H, H) = 8.09 Hz, 4H), 7.76 (d, ^{3}J (H, H) = 8.39 Hz, 3 H), 7.83 (d, ^{3}J (H, H) = 8.70 Hz, 3 H), 8.12 (d, ^{3}J (H, H) = 8.24 Hz, 3 H), 8.19 (s, 1H); ^{11}B NMR (160 MHz, $CDCl_3$, δ in ppm): 1.62 (t, ^{1}J (B-F) = 32 Hz, 1B);

^{19}F NMR (470 MHz, $CDCl_3$, δ in ppm): -131.58 (q, ^1J (F-B) = 28 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.7, 22.7, 29.3, 31.9, 33.8, 114.0, 124.7, 125.5, 126.6, 127.9, 129.6, 130.8, 144.1, 147.2; HRMS. Calcd for $C_{50}H_{35}BF_2N_3$ [$(M+H)^+$]: m/z 726.2895. Found: m/z 726.2894.

Synthesis of 3-(pyrenyl)-1-(p-tolyl)prop-2-en-1-one (6c):

A sample of 4-methylacetophenone (1 g, 8.3 mmol) was added to a solution of 1-pyrene carboxaldehyde (1 g, 8.20 mmol) in absolute ethanol (40 mL). To this, an aqueous solution of potassium hydroxide (40 ml, 2.5 M) was added dropwise at 0˚ C and the solution was stirred at room temperature for a period of 24 h. The reaction mixture was allowed to cool in ice bath, during which the product precipitated. Filtration of the reaction mixture gave a pale yellow solid. The crude product was purified by using petroleum ether/ethyl acetate (95:5) to yield product **6c**. Yield: 1.85 g (90%); ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.46 (3H, s), 7.34 (2H, d, J = 7.9 Hz), 7.82 (1H, d, J = 15.3 Hz), 8.00-8.23 (9H, m), 8.41 (1H, d, J = 8.1 Hz), 8.55 (1H, d, J = 9.2 Hz), 8.96 (1H, d, J = 15.3 Hz); ^{13}C ($CDCl_3$, 125 MHz): 21.7, 63.9, 122.6, 123.0, 124.1, 124.2, 124.6, 125.0, 125.9, 126.0, 126.3, 126.5, 126.8, 127.0, 127.2, 127.3, 127.9, 128.6, 128.7, 128.9, 129.4, 130.3, 130.7, 130.8, 131.3, 132.8, 135.8, 141.0, 143.7, 193.1; HRMS. Calcd for $C_{26}H_{19}O$ [$(M+H)^+$]: m/z 347.1439. Found: m/z 347.1439.

Synthesis of 3-(pyrenyl)-4-nitro-1-(*p*-tolyl)butan-1-one (7c):

To a solution of 3-(pyrenyl)-1-(p-tolyl)prop-2-en-1-one **6c** (1 g, 3.96 mmol) in methanol, nitromethane (5 mL, 19 mmol), and diethylamine (10 mL , 19 mmol) was added and refluxed for 48 h. The solution was cooled, acidified with hydrochloric acid (20 mL, 2.5 M) to precipitate the compound. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (95:5) to yield white solid product **7c**. Yield**:** 1 g (80 %); ^{1}H NMR

(500 MHz, $CDCl_3$, δ in ppm): 2.38 (s, 3H), 3.36-3.37 (m, 2H), 4.95-5.08 (m, 2H), 5.42-5.50 (m, 1H), 7.22 (d, ^3J (H, H) = 8.0 Hz, 2H), 7.82 (d, ^3J (H, H) = 8.2 Hz, 2H), 7.92 (d, ^3J (H, H) = 8.0 Hz, 1H), 7.99-8.07 (m, 3H), 8.13-8.21(m, 4H), 8.48 (d, ^3J (H, H) = 9.4 Hz, 1H), ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 21.7, 41.9, 122.0, 123.4, 124.8, 125.2, 125.4, 125.6, 126.2, 127.3, 127.7, 128.2, 128.6, 128.7, 129.4, 130.8, 131.4, 132.7, 133.9, 144.6, 196.6; HRMS. Calcd for $C_{27}H_{21}KNO_3$ [$(M+K)^+$]: m/z 446.1153. Found: m/z 446.1152.

Synthesis of azaBODIPY 3:

A solution of 3-(pyrenyl)-4-nitro-1-(p-tolyl)butan-1-one **7c** (1g, 3.2 mmol) and ammonium acetate (6.20 g, 80 mmol) in *n*-butanol (30 mL) was heated under reflux for 24 h. The product precipitated as blue-black solid. The reaction was allowed to cool to room temperature and solid was filtered to obtain the intermediate compound. To the dichoromethane solution of intermediate compound, triethylamine (100 eq.), was added followed by the addition of $BF_3.Et_2O$ (110 eq.) and stirring was continued for half an hour. The reaction mixture was washed with water and the organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The solvent was evaporated under reduced pressure and the crude product was purified using silica gel column chromatography with petroleum ether/ethyl acetate (30:70), to afford pure aza-BODIPY **3** as brown solid. Yield: 0.94 g (50%); ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.50 (s, 6H), 7.40 (d, ^3J (H, H) = 7.78 Hz, 5H), 7.91 (t, ^3J (H, H) = 8.58 Hz, 5H), 8.02-8.07 (m, 4H), 8.11 (d, ^3J (H, H) = 8.93 Hz, 3H), 8.15 (d, ^3J (H, H) = 8.01 Hz, 3H), 8.19 (dd, ^3J (H, H) = 6.87 Hz, 8H), 8.27 (d, ^3J (H, H) = 7.78 Hz, 3H), 8.59 (d, ^3J (H, H) = 9.38 Hz, 4H); ^{11}B NMR (160 MHz, $CDCl_3$, δ in ppm): 1.59 (t, ^1J (B-F) = 32 Hz, 1B); ^{19}F NMR (470 MHz, $CDCl_3$, δ in ppm): -131.4 (q, ^1J (F-B) = 28 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.7, 29.9, 124.4,

125.2, 125.5, 126.1, 127.4, 127.8, 128.2, 129.6, 144.4; HRMS. Calcd for $C_{54}H_{35}BF_2N_3$ [$(M)^+$]: m/z 774.289. Found: m/z 774.289.

Synthesis of 3-(4-(naphthalen-1-ylmethoxy)phenyl)-1-(p-tolyl)prop-2-en-1-one (8):

To a solution of 4-(naphthalen-1-ylmethoxy)benzaldehyde (1 g, 8.20 mmol) in absolute ethanol (40 mL), 4-methylacetophenone (1 g, 8.3 mmol) was added. To this reaction mixture, aqueous solution of potassium hydroxide (40 ml, 2.5 M) was added dropwise at 0˚C and the solution was stirred at room temperature for a period of 24 h. The reaction mixture was allowed to cool in ice bath, during which the product precipitated. Filtration of the reaction mixture gave a pale white solid product. The crude product was purified by using petroleum ether/ethyl acetate (95:5) to obtain the product **8**. Yield: 1.85 g (90%); ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.43 (s, 3H), 5.54 (s, 2H), 7.09 (d, ^3J (H, H) = 8.7 Hz, 2H), 7.29 (d, ^3J (H, H) = 7.9 Hz, 2H), 7.45-7.64 (m, 7H), 7.78 (d, ^3J (H, H) = 15.6 Hz, 1H), 7.78-7.94 (m, 4H), 8.03 (d, ^3J (H, H) = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 21.8, 68.9, 115.5, 120.1, 123.7, 125.4, 126.1, 126.7, 126.8, 128.2, 128.7, 128.9, 129.4, 130.3, 131.6, 131.8, 133.9, 136.0, 143.5, 144.3, 160.9, 190.2; HRMS. Calcd for $C_{27}H_{23}O_2$ [$(M+H)^+$]: m/z 379.1693 Found: m/z 380.169.

Synthesis of 3-(4-(naphthalen-1-ylmethoxy)phenyl)-4-nitro-1-(p-tolyl)butan-1-one (9):

Samples of 3-(naphthyl)-1-(p-tolyl)prop-2-en-1-one **8** (1 g, 3.96 mmol), nitromethane (1 mL, 19 mmol), and diethylamine (2 mL, 19 mmol) were dissolved in ethanol (50 mL) and refluxed for 28 h. The solution was cooled, acidified with hydrochloric acid (20 mL, 2.5 M) to precipitate the compound. The crude product was subjected to column chromatographic purification using petroleum ether/ethyl acetate (95:5) to yield white solid product **9**. Yield: 1 g

(80 %); ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.39 (s, 3H), 3.71 (m, 2H), 5.05 (m, 2H), 5.47 (m, 1H), 7.24 (d, ^{3}J (H, H) = 8.1 Hz, 2H), 7.83 (d, ^{3}J (H, H) = 7.3 Hz, 2H), 7.93 (d, ^{3}J (H, H) = 8.2 Hz, 1H), 8.00-8.08 (m, 3H), 8.14-8.22 (m, 4H), 8.50 (d, ^{3}J (H, H) = 9.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 21.7, 41.8, 50.91, 121.9, 124.8, 125.1, 125.3, 125.5 126.2, 127.7, 128.2, 128.6, 128.7, 129.4, 130.7, 131.3, 132.6, 133.8, 144.5,196.5; LRMS Calcd for $C_{27}H_{23}O_2$ Found: m/z 438.1748.

Synthesis of azaBODIPY 4:

A solution of 3-(dinaphthyl)-4-nitro-1-(p-tolyl)butan-1-one **9** (1 g, 3.2 mmol) and ammonium acetate (6.20 g, 80 mmol) in *n*-butanol (30 mL) was heated under reflux for 24 h. The product precipitated as blue-black solid. The reaction was allowed to cool to room temperature and solid was filtered to obtain the intermediate compound. To the dichoromethane solution of intermediate compound, triethylamine (100 eq.) was added followed by the addition of $BF_3.Et_2O$ (110 eq.) and stirring was continued for half an hour. The reaction mixture was washed with water and the organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The solvent was evaporated under reduced pressure and the crude product was purified using silica gel column chromatography with petroleum ether/ethyl acetate (15:85), to afford pure aza-BODIPY **4** as brown solid. Yield: 0.94 g (50%); ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.40 (s, 6 H), 5.53 (s, 4 H), 6.92 (s, 2 H), 7.09 (d, ^{3}J (H, H)=8.70 Hz, 4 H), 7.23 - 7.30 (m, 4 H), 7.42 - 7.53 (m, 8 H), 7.59 (d, ^{3}J (H, H) =7.10 Hz, 2 H), 7.79 - 7.86 (m, 4 H), 7.93 (d, ^{3}J (H, H) = 8.24 Hz, 3 H), 7.99 - 8.11 (m, 5 H); ^{11}B NMR (160 MHz, $CDCl_3$, δ in ppm): 1.49 (t, ^{1}J (B-F) = 32 Hz, 1B); ^{19}F NMR (470 MHz, $CDCl_3$, δ in ppm): -131.48 (q, ^{1}J (F-B) = 23.08 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.8, 68.9, 76.9, 115.5, 120.1, 123.7, 125.4, 126.1, 126.7,

126.8, 128.2, 128.7, 128.9, 129.4, 130.4, 131.6, 131.8, 133.9, 136.0, 143.5, 144.3, 160.9, 190.2; HRMS. Calcd for $C_{27}H_{23}O_2$ [$(M+H)^+$]: m/z 838.3420, Found: m/z 838.3462.

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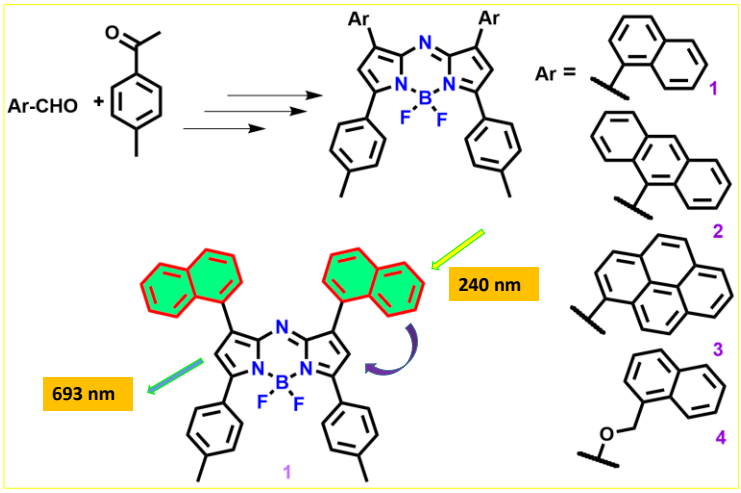
Table of Contents(Graphical Abstract):



AzaBODIPYs appended with different fluorophores such as naphthalene, anthracene and pyrene at 1,7-positions were synthesized over the sequence of steps and studied their photophysical and electrochemical properties.