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Aliphatic Amine Discrimination by Pentafluorophenyl Dibromo BODIPY**

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Abstract: Two new fluorescent BODIPY dyes have been designed and synthesized. They dyes differ in their *meso* substituents, which have different electronic properties. Their selective reactivity towards an Ar-S_N2 reaction has been explored as a potential basis for colorimetric and fluorescent discrimination of primary, secondary and tertiary aliphatic amines. This dual-mode, instantaneous recognition event is unprecedented.

Aliphatic amines constitute one of the most important and abundant classes of amines in nature.[1] Their importance can be felt by their widespread applications in textile, cosmetic, chemical, medicinal, agricultural, plastic, leather, metallurgical, pharmaceutical, and petroleum industries.[2] They also play crucial roles in synthetic chemistry, biology, and atmospheric sciences.[3] Apart from their vast diversity and use in day-to-day life including modern technology, they are usually associated with non-benignant, toxic, and carcinogenic properties, either in gaseous, aqueous, or non-aqueous media.[4] With these considerations along with characteristic properties specified to various degrees of aliphatic amines (primary, secondary, and tertiary), there should be a potential need for direct discrimination of these amines in a wide range of environments.

Over the past few decades, a number of methodologies have been proposed for amine analysis, including gas chromatography (GC), liquid chromatography (LC), mass spectrometry (MS), capillary electrophoresis (CE), potentiometry, and ion chromatography (IC).[5] However, these techniques involve tedious pre-concentration, which relies upon extraction and separation, prior to their analysis. Besides this disadvantage, current methodologies are expensive and require a high level of expertise. Furthermore, none of these techniques provide an in-situ amine discrimination and diagnosis with the naked eye, a quick and timely requirement in clinical settings and in the food industry.[6]

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[**] BODIPY = boron dipyrromethene (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene).

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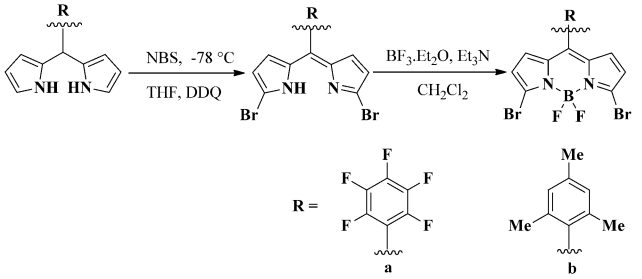
Molecular recognition provides an effective and promising approach fulfilling most of the above requirements. It affords fast and convenient read-out signals in the form of color and fluorescence.[7] However, owing to the range of sizes, conformations, and shapes of amines, besides their high polarity, it is really challenging to design a molecular scaffold providing aliphatic amine discrimination and analysis in both aqueous and organic media.[8] So far, very few efforts have been taken for the development of molecular systems for identification of aliphatic amines.[9] All these systems lack a clear-cut discrimination for various degrees of aliphatic amines. The binding events are valid only in organic media and mostly suffer from time-delayed responses. The recognitions display either a chromogenic or fluorogenic output for a given interaction. Moreover, there are scarce reports wherein any designed scaffold displays dual-mode responses in the form of fluorescence and color through the naked eye.[9] Our target was to achieve a molecular system which exhibits fluorescence along with a chromogenic response for amine discrimination. The BODIPY backbone was chosen because of its excellent fluorescence and color, and because it is structurally robust.

In our endeavor to develop the required molecular system providing instantaneous aliphatic amine discrimination through visual diagnosis, a typical Ar-S_N2 reaction of BODIPYs at the 3- and 5-positions considered.[10] To achieve selective control over the nucleophilic substitutions with various degrees of amines, we chose two new BODIPY dyes ($\mathbf{R_a}$ and $\mathbf{R_b}$), bearing electron-deficient and -rich moieties at *meso*-positions. The associated charge transfer (CT) and electron transfer properties of the system are expected to be strongly modulated through an ample variation.[11] This can serve as a probable basis for discrimination with fast and convenient signal transduction.

The synthesis of $\mathbf{R_a}$ and $\mathbf{R_b}$ is outlined in Scheme 1. 5-pentafluorophenyl-1,9-dibromodipyrromethene was obtained through the reported procedure[12a] and further dissolved in dry CH_2Cl_2 with subsequent addition of triethylamine and $BF_3.Et_2O$ at 0 °C. The reaction mixture was stirred at room temperature for 2 h. The same strategy was utilized for the synthesis of $\mathbf{R_b}$, with 5-mesityl-1,9-dibromodipyrromethene as starting material (see Scheme S1 and S2 in the Supporting Information).[12b,c] The identities of compounds $\mathbf{R_a}$ and $\mathbf{R_b}$ were confirmed by standard spectroscopic techniques in the form of NMR (Figure S10 in the Supporting Information), HR-LCMS (Figure S11 in the Supporting Information), and single-crystal XRD (Figure 1).



Scheme 1. Synthesis of BODIPYs ($\mathbf{R_a}$ and $\mathbf{R_b}$). NBS = *N*-bromosuccinimide, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

The absorption spectrum of $\mathbf{R_a}$ ($\varepsilon = 10\,300\,\mathrm{M^{-1}\,cm^{-1}}$, $\Phi = 0.37$) in CH_2Cl_2 shows a characteristic S_0 to S_1 transition at 539 nm and a weak absorption at 510 nm. On interaction with amines through Ar-S_N2 reaction at the 3-position, a strong modulation of ground-state electronic properties was observed. Upon addition of various amounts of methylamine and diethylamine, the absorption signal at 539 nm decreased with a concomitant increase in the intensity of the 510 nm band along with a slight blue shift. The given changes proceed through appearance of clear isosbestic points at 520 and 515 nm for primary and secondary amines (Figure 2).

The difference of 5 nm shift in the absorption signal between $\mathbf{R_a}$ with primary (1°) and secondary (2°) amines leads to their clear and visible discrimination with the appearances of respective yellow and pale yellow colors (Figure 4). The interaction of 1° amines is instantaneous, followed by 2° amines, while tertiary (3°) amines interact with a time delay of about an hour for the completion of the reaction. Spectral behavior finally resembles that with 2° amines and hence similar visual appearances are observed (Figure 4 and Figure S7 in the Supporting Information). The delay in the chemodosimetric reaction with 3° amines is attributed to the facile Ar-S_N2 reaction of 2° amines compared to 3°.

In the emission spectra, striking changes in intensities and wavelength shifts were observed upon addition of amines. $\mathbf{R_a}$ shows a characteristic emission at 554 nm upon excitation at 470 nm. Continuous addition of methylamine results in bifurcation of the 554 nm signal into peaks at 525 and 580 nm. The changes further proceed with a blue shift of the former and a red-shift of the later (Figure 3). These observations reflect the disappearance of the intrinsic BODIPY emission at 554 nm with predominance of newly existing strong charge transfer emission at 580 nm as a result of intramolecular charge transfer (ICT) from the amine nitrogen atom to the pentafluorophenyl ring at the *meso*-position. The above changes can be easily observed with the naked eye. In contrast, with diethylamine and triethylamine, quenching of 554 nm emission was observed as the reaction progressed (Figure 3). This quenching is attributed to effective photoinduced energy transfer (PET) from amine nitrogen towards the fluorophore.[13] The expected delay in the emission changes with 3° amines was observed, similar to that in absorption spectra (Figure 4 and Figure S7 in the Supporting Information). Hence instantaneous display of emission behavior and distinct variation in the output signals of $\mathbf{R_a}$ on addition of various degrees of aliphatic amines serves as another potential means of efficient and near-real time aliphatic amine discrimination.

The interaction of aliphatic amines was further probed through NMR (^{1}H, ^{11}B, and ^{19}F NMR) titration experiments. Addition of methyl amine to $\mathbf{R_a}$ in $CDCl_3$ results in the appearance of four distinct doublets in the ^{1}H NMR spectrum (Figure S8 in the Supporting Information), demonstrating the unsymmetrical nature of the resulting species. Continuing addition of amine result in clear distinction of doublets and no further changes in the ^{1}H NMR shifts. This result indicates the reaction completeness and the sole existence of 3-substituted product.

The mechanism of interaction was also supported by ^{19}F NMR titration of $\mathbf{R_a}$ with amines. Addition of methylamine results in up field and down field shifts of pentafluorophenyl ring signals (Figure S8 in the Supporting Information), an indication of charge-transfer modulations within the molecule as a result of amine binding through chemodosimetric Ar-S_N2 reaction.

As a result, we demonstrate that the resulting chemodosimetric behavior of $\mathbf{R_a}$ with the aliphatic amines is an outcome of the typical Ar-S_N2 reaction facilitated by an electron-deficient moiety (pentafluorophenyl) at the *meso*-position. On replacing the pentafluorophenyl moiety with a mesityl ring in $\mathbf{R_b}$

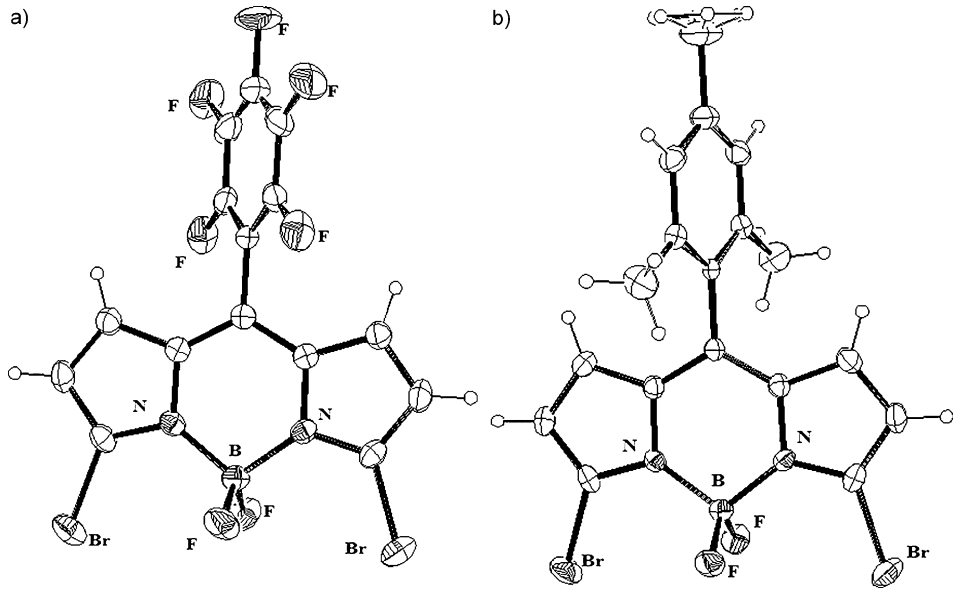


Figure 1. ORTEP representation of crystal structures of a) $\mathbf{R_a}$ and b) $\mathbf{R_b}$.

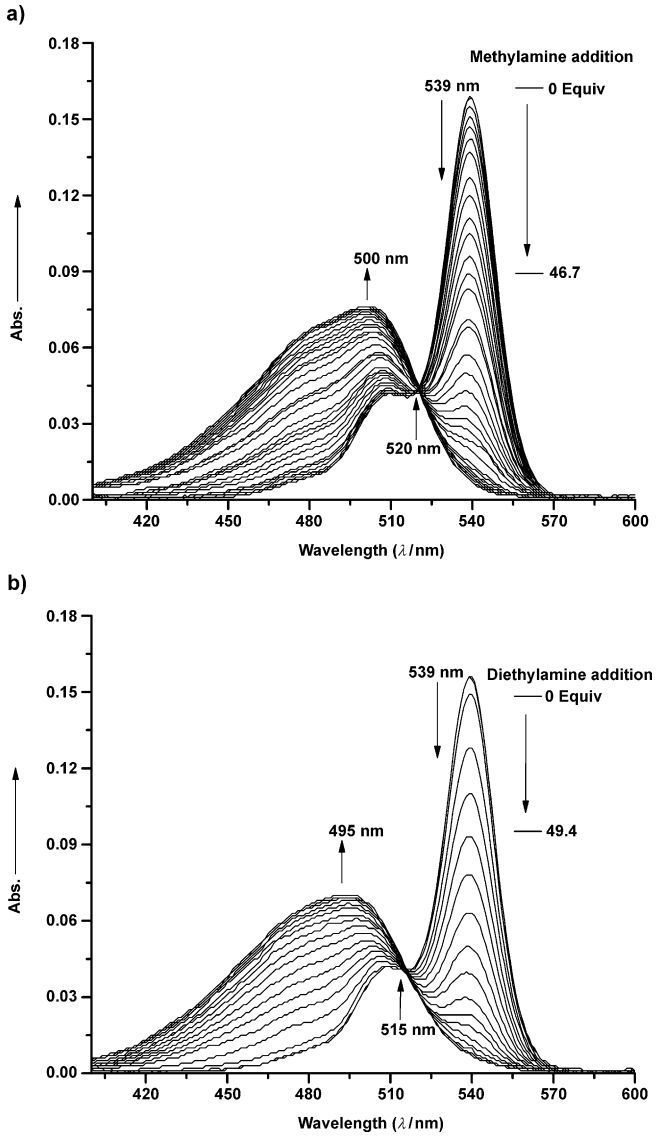


Figure 2. a) Absorption titration profile of $\mathbf{R_a}$ (1.6 μM) upon addition of various amounts of methyl amine in CH_2Cl_2, and b) with various amounts of diethylamine in CH_2Cl_2.

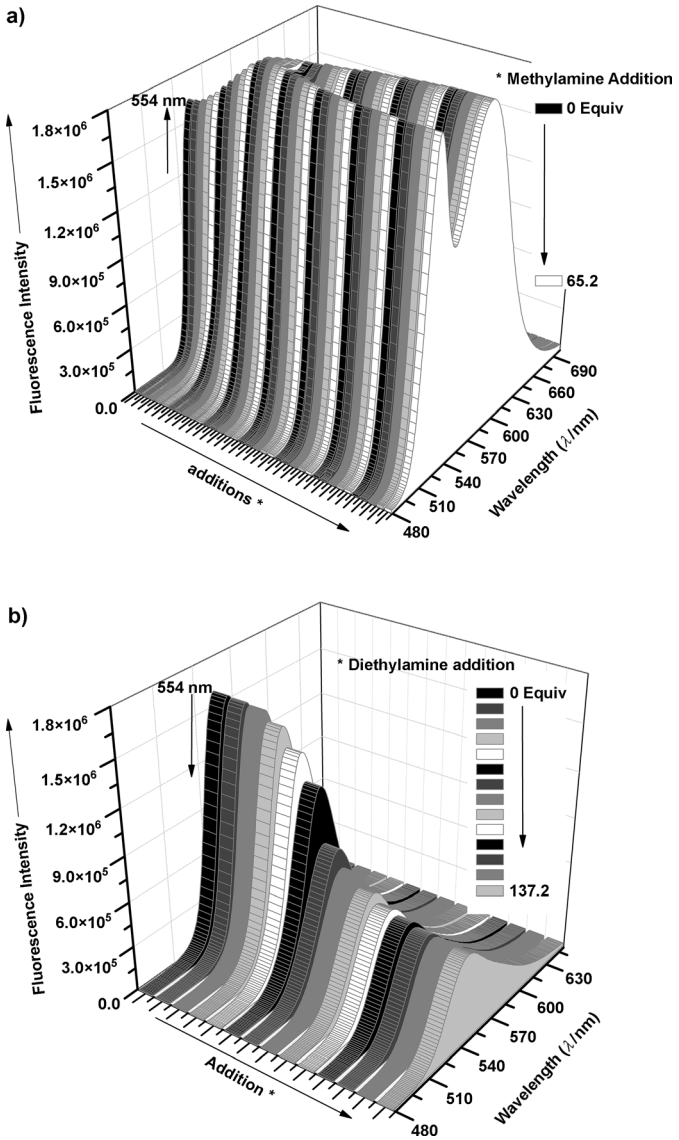


Figure 3. a) Emission titration profile of $\mathbf{R_a}$ (1.6 μM) upon addition of various equivalents of methylamine in CH_2Cl_2, and b) with diethylamine in CH_2Cl_2, upon excitations at 470 nm.

($\varepsilon = 13204\ M^{-1}cm^{-1}$, $\Phi = 0.30$), sluggishness in the Ar-S_N2 reaction was observed, and with a time-delayed response in both absorption and emission modes (Figures S3 and S4 in the Supporting Information). This finding further supports the role played by electron-deficient moieties at the *meso*-position in the BODIPY system towards nucleophilic substitutions at the 3- and 5-positions. The electronic effect of substituents on the amine nitrogen atom and hence variation in the electronic and charge-transfer processes act as the basis for a selective discrimination of various degrees of aliphatic amines.

A 1:1 binding mode of the given interactions was evaluated via ^{1}H NMR spectra of the products obtained through a chemical reaction between $\mathbf{R_a}$ and two equivalents of aliphatic amines (methylamine and diethylamine) in ambient conditions (Figure S11 in the Supporting Information). Repetition of similar results even with excess amine concentrations fully supported the 1:1 stoichiometry, which was also confirmed through single-crystal XRD (Figure 5). For practical applicability of the system, a library of aliphatic amines was tested, and similar trends were observed in various degrees of aliphatic amines (Table S2 in the Supporting Information). Surprisingly, the recognition behavior of $\mathbf{R_a}$ with amines was also observed in mixed CH_2Cl_2/aqueous media (Figure 4), which signals potential utility of the system in aqueous environments. Further, presence of $\mathbf{R_a}$ in a mixture of all three (1°, 2°, and 3°) amines revealed sole formation (>95%) of the 1° amine substituted product. The ratiometric response at the two concomitant absorption wavelengths can serve as an important means for calibrating and determining the respective amine concentrations in various media under consideration.[14]

Further to emphasize the selectivity of the dibromo BODIPY, we prepared a highly electron-deficient 3-fluoro-

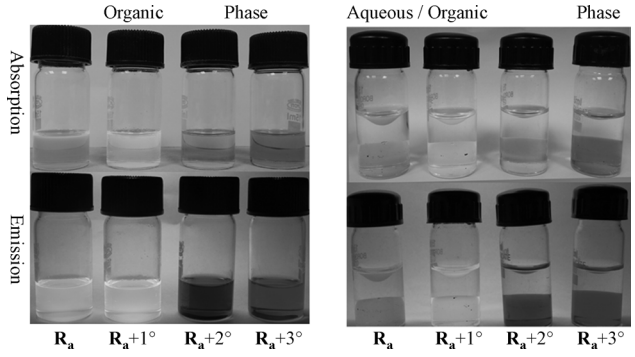


Figure 4. Visible absorption and emission changes of $\mathbf{R_a}$ in CH_2Cl_2 upon additions of various types of amines in organic and organic/aqueous media. Pictures were taken immediately after amine additions at ambient conditions. (See the Supporting Information for the figure in color.)

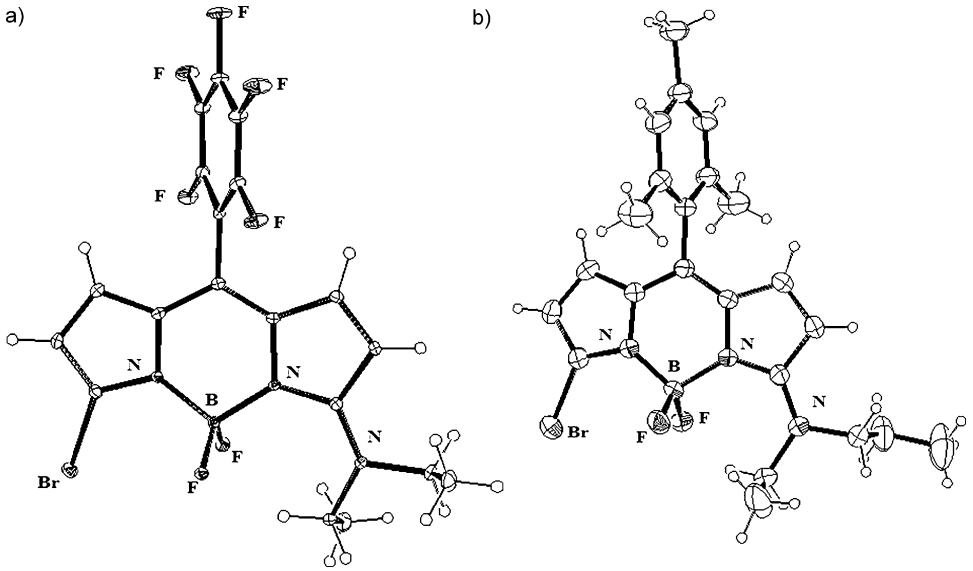


Figure 5. ORTEP representation of crystal structures of a) $\mathbf{R_a}$ with diethylamine, b) $\mathbf{R_b}$ with propylethylamine, confirming 1:1 stoichiometry.

5-bromo- pentafluorophenyl BODIPY derivative by the halogen exchange method. This is the first example to date of a BODIPY derivative having a fluorine atom at the α-pyrrolic position. This fluorine-substituted derivative was characterized by spectroscopic techniques (see the Supporting Information) and single-crystal XRD. All efforts to obtain difluoro-BODIPY failed due to the decomposition of the monofluoro-BODIPY on prolonged heating. Upon addition of various degrees of aliphatic amines to monofluorinated BODIPY, there was no chromogenic or fluorogenic output response, as shown in the Supporting Information. Thus, the discrimination of various degrees of amines is selective only for dibromo-BODIPY.

In conclusion, we have designed and synthesized two new BODIPY dyes with strong emission behavior visible to the naked eye. Pentafluorophenyl dibromo derivative $\mathbf{R_a}$ was explored and developed as a promising analytical tool, providing in situ and instantaneous discrimination of primary, secondary, and tertiary amines in organic and organic/aqueous media. The Ar-S_N2 reaction of aliphatic amines results in the selective modulation of charge-transfer properties of the molecule. This in turn offers an unambiguous discernment through dual-mode display in the form of color and fluorescence. Besides a facile Ar-S_N2 reaction at the 3- and 5-positions, the electron-deficient pentafluorophenyl ring along with substituents present on the amine nitrogen atom dictate excellent sensitivity and discrimination. Currently the suitability of the chemodosimeter for environmental and biological applications is being investigated and the results will be communicated in due course.

Experimental Section

General Information

Mass spectra were recorded on a Bruker HR-LCMS spectrometer. ^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectra were recorded using a Bruker instrument operating at 400 MHz in $CDCl_3$. UV/Vis spectra were recorded on Shimadzu spectrophotometry UV-1800. Fluorescence emission spectra were recorded on a Horiba Jovin Vyon Fluoro log 3–111 spectrophotometer.

Single-crystal data was collected on a Bruker APEX II diffractometer equipped with a graphite monochromator and $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. Data collection was performed using ϕ and ω scans. The structures was solved using direct method followed by full matrix least square refinements against F2 (all data HKLF 4 format) using SHELXTL. All calculations were carried out using SHELXL 97, PLATON 99, and WinGXsystemVer-1.6414. CCDC 995505 ($\mathbf{R_b}$), 995506 ($\mathbf{R_a}$ with diethylamine), 995507 ($\mathbf{R_b}$ with propylamine), 995513 ($\mathbf{R_a}$), and 1004955 (fluorine-substituted derivative) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General synthetic procedure for 1,9-dibromodipyrromethene

N-bromosuccinimide (2 equiv) in THF (5 mL) was added dropwise to dipyrromethane (100 mg, 1 equiv) in dry THF (5 mL) at −78 °C. Reaction progress was monitored by TLC. After reaction completion, excess bromine was quenched with aqueous $Na_2S_2O_3$. The organic phase was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. Brown oil was obtained after evaporation of the solvent under reduced pressure. The residue was dissolved in THF (10 mL), and DDQ (1.5 equiv) was added to oxidize the dipyrromethane. The reaction mixture was stirred for 10 min at room temperature. The residue was then immediately subjected to basic alumina column chromatography (hexane as elutant) to give the desired product.

5-Pentafluorophenyl-1,9-dibromodipyrromethene:

Dark red solid, 109 mg, 71 % yield, ^1H NMR (400 MHz; $CDCl_3$): $\delta =$ 6.37 ppm (s, 4H; β-pyrrole). ^{19}F NMR (376 MHz; $CDCl_3$): $\delta = -160.28$ (2F; *meta*), −151.15 (1F; *para*), −138.01 ppm (2F; *ortho*). MS (ESI-

HRMS, positive mode) found 468.8776, $C_{15}H_5N_2Br_2F_5$ requires 468.8792. UV/Vis (CH_2Cl_2): $\lambda_{max}=456$ nm.

5-Mesityl-1,9-dibromodipyrromethene

Orange solid, 127 mg, 80% yield, ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.07$ (s, 6H; *ortho*-Me), 2.34 (s, 3H; *para*-Me), 6.27 (d, $J=2$ Hz, 4H; β-pyrrole), 6.91 ppm (s, 2H; phenyl). MS (APCI-HR MS, positive mode) found 420.9737, $C_{18}H_{16}N_2Br_2$ requires 420.9733. UV/Vis (CH_2Cl_2): $\lambda_{max}=$ 445 nm.

General synthetic procedure for 3,5-dibromo BODIPY

1,9-dibromodipyrromethene (100 mg, 1 equiv) was dissolved in dry CH_2Cl_2 (20 mL) at lower temperature (ice bath), followed by addition of triethylamine (40 equiv) and dropwise addition of excess $BF_3{\cdot}Et_2O$ (40 equiv)). The reaction mixture was further stirred at room temperature and the progress of reaction was monitored by TLC. After reaction completion, organic phase was extracted with CH_2Cl_2 and washed with aqueous $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4, and solvent was evaporated under reduced pressure. The crude product was subjected to silica gel (100–200 mesh) column chromatography (CH_2Cl_2 and hexane as eluent) to get desired product.

*8-Pentafluorophenyl-3,5-dibromo BODIPY (**R_a**)*

Brown shiny crystals, 87 mg, 79% yield, ^{1}H NMR (400 MHz; $CDCl_3$): $\delta=$ 6.68 (d, $J=4.27$ Hz, 2H; β-pyrrole), 6.57 ppm (d, $J=4.35$ Hz, 2H; β-pyrrole). ^{19}F NMR (376 MHz; $CDCl_3$): $\delta=-158.74$ (2F; *meta*), -148.41 (1F; *para*), -146.92 (2F; Boron), -136.51 ppm (2F; *ortho*). ^{11}B NMR (128 MHz; $CDCl_3$): $\delta=0.62$ ppm (t, 1B). MS (APCI-HRMS, positive mode) found 515.8701. $C_{15}H_4BBr_2F_7N_2$ requires 515.8700. UV/Vis (CH_2Cl_2): $\lambda_{max}=539$ nm. $\varepsilon=10\,300\,M^{-1}cm^{-1}$. m.p. = 265.38 °C.

*8-Mesityl-3,5-dibromo BODIPY (**R_b**)*

Red solid, 100 mg, 90% yield, ^{1}H NMR (400 MHz; $CDCl_3$): $\delta=2.07$ (s, 6H; *ortho*-Me), 2.33 (s, 3H; *para*-Me), 6.44 (d, $J=4.15$, 2H; β-pyrrole), 6.53 (d, $J=4.40$, 2H; β-pyrrole), 6.92 ppm (s, 2H; phenyl). ^{13}C NMR (100 MHz; $CDCl_3$): $\delta=19.95$, 21.13, 122.81, 128.3, 130.32, 132.64, 135.85, 139.24, 143.30 ppm. ^{19}F NMR (376 MHz; $CDCl_3$): $\delta=-147.30$ ppm (q, 2F; BF). ^{11}B NMR (128 MHz; $CDCl_3$): $\delta=0.68$ ppm (t, 1B). MS (APCI-LR MS, negative mode) found 467.9473. $C_{18}H_{15}BBr_2F_2N_2$ requires 467.9641. UV/Vis (CH_2Cl_2): $\lambda_{max}=522$ nm. $\varepsilon=13\,204\,M^{-1}cm^{-1}$. m.p. = 218.57 °C.

8-Pentafluorophenyl-3-fluoro-5-bromo BODIPY

8-Pentafluorophenyl-3,5-dibromo BODIPY (200 mg, 0.427 mmol) was dissolved in (20 mL) dichloromethane. Excess equivalents of tetrabutyl ammonium fluoride were added to the reaction mixture and stirred overnight at room temperature. The reaction mixture was concentrated under reduced pressure and subjected to silica gel column to give 8-pentafluorophenyl-3-fluoro-5-bromo BODIPY. This F-BODIPY was recrystallized from pentane as a green solid (158 mg, 90% yield). ^{1}H NMR (400 MHz; [D_6]DMSO): $\delta=6.90$ (d, $J=5.26$, 1H; β-pyrrole), 6.01 (d, $J=3.37$, 1H; β-pyrrole), 5.94 (s, $J=5.30$, 1H; β-pyrrole), 5.75 ppm (d, $J=2.95$, 1H; β-pyrrole). ^{19}F NMR (376 MHz; [D_6]DMSO): $\delta=-139.51$–139.75 (q, 2F; BF), -139.85–139.94 (2F; *ortho*), -155.6–155.72(1F; *para*), -162.42–162.57 ppm (2F; *meta*). ^{11}B NMR (128 MHz; [D_6]DMSO): $\delta=0.79$ ppm (t, 1B). MS (ESI-LR MS, negative mode) found 450.9496. $C_{15}H_2BBrF_8N_2$ calcd. 450.9286.

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Keywords: amines · chemodosimetry · dyes/pigments · fluorescence · sensors

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