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3,5-Diformylboron Dipyrromethenes as Fluorescent pH Sensors

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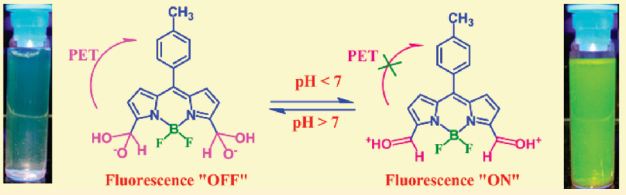
Supporting Information

ABSTRACT: A series of boron dipyrromethene (BODIPY) dyes containing two aldehyde functional groups at the 3 and 5 positions have been synthesized in low-to-decent yields in two steps. In the first step, the *meso*-aryl dipyrromethanes were treated with $POCl_3$ in *N*,*N*-dimethylformamide to afford 1,9-diformylated dipyrromethanes. In the second step, the diformylated dipyrromethanes were first in situ oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and then reacted with $BF_3 \cdot OEt_2$ to afford 3,5-diformylboron dipyrromethenes. The X-ray structural analysis indicated that the aldehyde groups are involved in intramolecular hydrogen bonding with fluoride atoms, which may be responsible for the stability of the diformylated BODIPY compounds. The presence of two formyl groups significantly alters the electronic properties, which is clearly evident in downfield shifts in the ^1H and ^{19}F NMR spectra, bathochromic shifts in the absorption and fluorescence spectra, better quantum yields, and increased lifetimes compared to 3,5-unsubstituted BODIPYs. Furthermore, 3,5-diformylboron dipyrromethenes are highly electron-deficient and undergo facile reductions compared to unsubstituted BODIPYs. These compounds exhibit pH-dependent on/off fluorescence and thus act as fluorescent pH sensors.



INTRODUCTION

Fluorescent chemosensors that are responsive to changes in the pH are widely used in analytical chemistry, physiology, and biosciences.[1] The fluorescence method offers several advantages over other methods for physiological pH measurements because of its high sensitivity. There are a wide range of fluorescent indicator dyes that can sense pH changes.[1] In recent years, a lot of work has been focused on the synthesis of 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene-based[2] (boron dipyrromethene or BODIPY[3]) fluorescent probes and their application[4] as selective and efficient sensors of ionic species. BODIPY dyes possess excellent qualities such as high photostability, high fluorescence quantum yields, narrow emission band widths, relatively high absorption coefficients, and excitation/emission wavelengths above 500 nm.[5] It is now well established that, by simple modifications on the BODIPY dye, it is possible to tune the absorption/emission peak maxima, which range from 500 to over 700 nm.[5] BODIPY-based fluorophores have been applied as pH sensors in organic solvents or aqueous/organic mixed media.[6−8] BODIPY dyes bearing phenolic,[6] (dialkylamino)phenyl,[7] and calix[4]arene[8] subunits at meso positions have been used as pH sensors, and these compounds showed deprotonation/protonation-dependent fluorescence off/on switching. A perusal of the literature reveals that aldehyde groups are generally not used for fluorescent pH sensors. This is because the aldehyde group present in the fluorophore is less sensitive toward pH variation, unlike hydroxy/amine/carboxylate groups. However, if an aldehyde group is placed appropriately in conjugation with the fluorophore, the fluorophore containing an aldehyde functional group can be used as a fluoresecent pH sensor. In this paper, we report a simple route for the synthesis of 3,5-diformylboron dipyrromethene dyes and demonstrate their use as fluorescent pH sensors. Because the electron-withdrawing aldehyde groups are placed directly in conjugation with electron-rich BODIPY, these compounds are sensitive toward the pH and act as fluorescent pH sensors. While we designed this project, Sathyamoorthi et al.[9a] and recently Ziessel et al.[9b] reported the synthesis of BODIPYs having a formyl group at the 3 position by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation of corresponding 3-methylboron dipyrromethenes (Scheme 1a). Furthermore, while our work was in progress, Jiao et al.[10] reported the synthesis of BODIPYs containing a formyl group at the 2 position by subjecting the appropriate BODIPYs to the modified Vilsmeier−Haack conditions (Scheme 1b).

However, their efforts to synthesize the diformylated BODIPYs under various reaction conditions remained unsuccessful, which they attributed to the instability of the diformylated BODIPYs.[10] Here we showed a different approach to synthesizing the first examples of 3,5-diformylboron dipyrromethenes, which are stable and isolated in 7−26% yield. Furthermore, we also showed the use of 3,5-diformylboron dipyrromethenes as fluorescent pH sensors, which exhibit fluorescence on and off states under acidic and basic pH regions, respectively.

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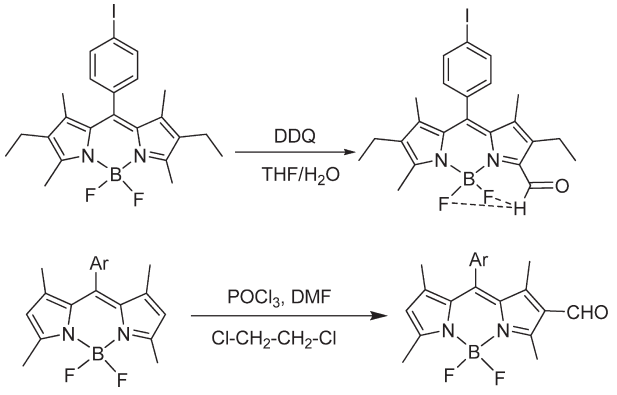
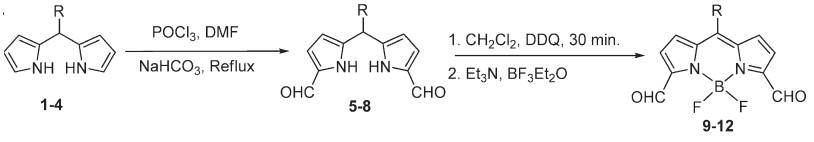
RESULTS AND DISCUSSION

The synthesis of 3,5-diformylboron dipyrromethenes **9**−**12**, starting from their corresponding unsubstituted dipyrromethanes (DPMs) **1**−**4**, is shown in Scheme 2. The required dipyrromethanes **1**−**4** were prepared according to Lindsey's procedure[11] by condensing the appropriate aldehyde with excess pyrrole in the presence of a catalytic amount of trifluoroacetic acid at room temperature. The DPMs were purified by flash silica gel column chromatography and afforded pure compounds **1**−**4** as white solids in 56−76% yield. The 1,9-diformyl dipyrromethanes[12] [DPM(CHO)$_2$] **5**−**8** were prepared in the next step by treating DPMs **1**−**4** with the Vilsmeier reagent in 1,2-dichloroethane at reflux temperature, followed by column chromatographic purification on silica, and afforded pure 1,9-diformyl dipyrromethanes **5**−**7** as white solids and 1,9-diformyl dipyrromethane **8** as a light-brown solid in 67−82% yield. Compounds **5**−**8** were characterized by various spectroscopic techniques, and the data for known compounds **5**−**7** are in agreement with those in the literature.[12] A signal at ∼10.7 ppm in ^{1}H NMR and a molecular-ion peak in mass spectra confirmed the identity of 1,9-diformyl dipyrromethanes **5**−**8**. The target 3,5-diformylboron dipyrromethenes **9**−**12** were prepared in two steps in a one-pot reaction. In the first step, the appropriate diformyl dipyrromethanes **5**−**8** were oxidized in dichloromethane with DDQ for 30 min, followed by treatment with triethylamine and $BF_3 \cdot OEt_2$ at room temperature for 10 min. Thin-layer chromatographic analysis showed a fluorescent yellow spot of the desired compound. The crude compounds were subjected to flash silica gel column chromatographic purification and afforded pure 3,5-diformylboron dipyrromethenes **9**−**12** as green solids in 7−26% yield. It is observed that $BF_3 \cdot OEt_2$ should be added immediately after the addition of triethylamine, and any time delay between the addition of these two reagents to the reaction mixture resulted in decomposition of the compound. The molecular-ion peaks in high-resolution mass spectra confirmed the identity of compounds **9**−**12**. ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectroscopies have been used to characterize compounds **9**−**12** in detail. In ^{1}H NMR, the absence of a signal at ∼7.94 ppm corresponding to 3,5 protons of BODIPY and the presence of a typical singlet at ∼10.5 ppm corresponding to an aldehyde proton support that formylation occurred at the 3 and 5 positions. The comparison of the ^{1}H, ^{19}F, and ^{11}B NMR spectra of 3,5-diformylboron dipyrromethene **9** with 3,5-unsubstituted BODIPY[13] **13** is presented in Figure 1, and relevant NMR data of compounds **9**−**12** along with compound **13** are presented in Table 1. As is clear from Figure 1 and the data in Table 1, the presence of two electron-withdrawing formyl groups at the 3 and 5 positions alters the π delocalization, which is reflected in the downfield shifts in ^{1}H, ^{19}F, and ^{11}B NMR. In ^{1}H NMR, the β-pyrrole protons H_a and H_b, which appear as two sets of signals at 6.55 and 6.90 ppm, respectively, in compound **13**,[13] experienced downfield shifts and appeared at 7.11 and 7.19 ppm, respectively, in compound **9**. Compounds **10**−**12** also exhibited similar downfield shifts of H_a and H_b, supporting alteration of the π delocalization upon the introduction of two formyl groups at the 3 and 5 positions. In ^{11}B NMR, compounds **9**−**12** showed a typical triplet like compound **13**. However, compounds **9**−**12** exhibited a 0.75 ppm downfield shift of the triplet and appeared at 1.26 ppm, unlike compound **13**, in which the triplet was observed at ∼0.5 ppm in ^{11}B NMR (Table 1). These kinds of significant downfield shifts observed in ^{11}B NMR were not very common for BODIPYs.[14] The downfield shifts observed in ^{1}H and ^{11}B NMR spectra for compound **9** compared to compound **13** indicate that the strong electron-withdrawing formyl groups make the BODIPY unit electron-deficient. The density functional theory (DFT) studies discussed later also indicated that the electron density is more toward formyl groups and the

Scheme 1. Synthesis of the Reported BODIPYs



Scheme 2. Synthesis of 3,5-Diformylboron Dipyrromethenes 9−12



Compound	R = CH_3	Br	OMe	OMe, MeO, OMe
DPM	**1**(76%)	**2**(62%)	**3**(73%)	**4**(56%)
DPM(CHO)$_2$	**5** (73%)	**6** (76%)	**7**(82%)	**8**(67%)
BODIPY(CHO)$_2$	**9** (14%)	**10**(9%)	**11**(26%)	**12**(7%)

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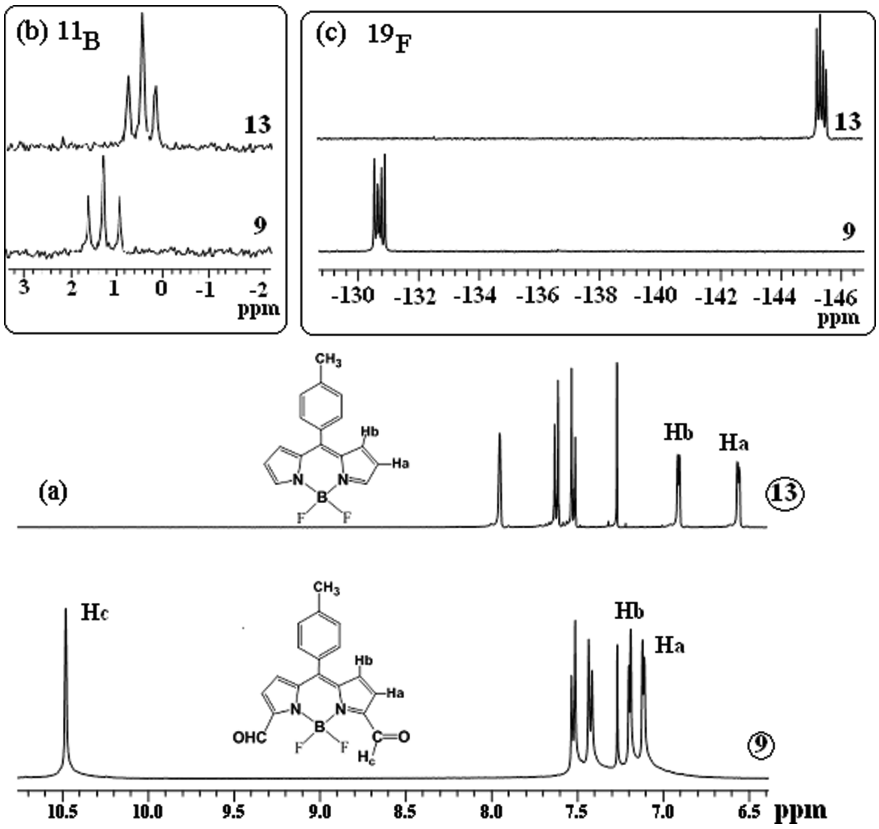

Figure 1. Comparison of (a) ^{1}H, (b) ^{11}B, and (c) ^{19}F NMR spectra of compounds **9** and **13** in selected regions recorded in $CDCl_3$.

Table 1. ^{1}H, ^{19}F, and ^{11}B NMR Data of Compounds 9−12 along with 13 Recorded in $CDCl_3$

	^{1}H NMR				
compound	H_a	H_b	H_c	^{19}F NMR	^{11}B NMR
13	6.55	6.90		−145.4	0.50
9	7.11	7.19	10.478	−130.8	1.26
10	7.07	7.20	10.476	−130.8	1.24
11	7.14	7.21	10.474	−130.7	1.28
12	6.84	7.18	10.480	−130.5	1.24

BODIPY ring remains electron-deficient in compound **9**. The most interesting observations were made in the ^{19}F NMR spectra of compounds **9**−**12**. In all reported BODIPYs such as **13**, the ^{19}F NMR spectrum corresponds to a single quartet because of coupling to ^{11}B ($I = {}^{3}/_{2}$ and J = 32 Hz) and resonances at approximately −147 ppm.[13]

However, in some recently reported BODIPY compounds,[15] the fluorines were found to be inequvalent and showed two sets of multiplets at ∼−140 ppm. In complexes **9**−**12**, we observed only one quartet in ^{19}F NMR, indicating that the fluorines are under a chemically equivalent environment. However, compounds **9**−**12** exhibited a ^{19}F NMR signal at ∼−131 ppm, a −15 ppm downfield shift compared to that of the other reported BODIPYs.[13] This unusual downfield shift was attributed to the presence of hydrogen bonding between fluoride ions and an aldehyde group. This observation is in line with the recently reported[16] 3,5-diamidoboron dipyrromethene dyes, in which the presence of internal hydrogen bonding between fluoride ions and amido protons resulted in a −16 ppm downfield shift of the signal in ^{19}F NMR. Furthermore, the ^{1}H NMR spectra recorded for compound **9** in five deuterated solvents of varying polarity such as benzene, chloroform, acetone, acetonitrile, and methanol clearly indicated that the aldehyde proton (H_c) is shifted upfield by 0.6 ppm in methanol compared to benzene (Figure S26 in the Supporting Information). Similar observations were made in ^{19}F NMR spectra recorded for **9** in deuterated chloroform and methanol (Figure S27 in the Supporting Information). In chloroform, the quartet signal in the ^{19}F NMR spectrum was observed downfield (−130 ppm) because of the presence of hydrogen bonding, while in methanol, the hydrogen bonding is absent, which is reflected in an upfield shift of the signal (−140 ppm). This supports the fact that the polar solvent breaks hydrogen bonding, whereas hydrogen bonding is stabilized in a nonpolar solvent. The 3,5-disubstituted BODIPYs[16,17] are the first class of compounds where intramolecular hydrogen bonding was established crystallographically. Because we inferred hydrogen bonding in compounds **9**−**12** from the ^{19}F and ^{1}H NMR study, we attempted to grow single crystals of compounds **9**−**12**. We successfully obtained single crystals for compound **11** by the slow evoporation of *n*-hexane/$CHCl_3$ (1:1) over a period of 1 week, which crystallized in a triclinic *P*1 unit cell. The crystal structure of compound **11** is shown in Figure 2. Compound **11** has a planar BODIPY framework, which is comprised of two pyrrole rings and a central six-membered boron ring like that reported in *meso*-(phenyl)boron dipyrromethene compound **14** (Table S1 in the Supporting Information). The dihedral angle between the *meso*-aryl ring and the BODIPY core

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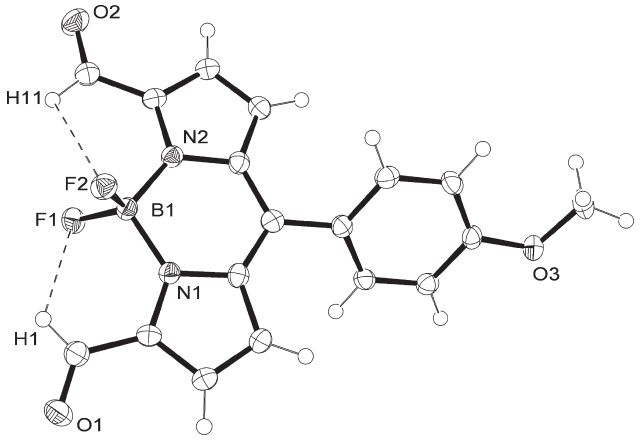

Figure 2. ORTEP diagram (50% probability) of compound **11**.

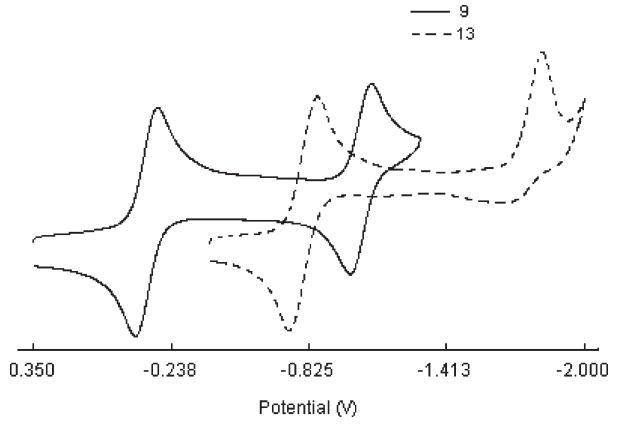

Figure 3. Comparison of the reduction waves of the cyclic voltammograms of compounds **9** and **13** in dichloromethane containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte recorded at a 50 mV s^{-1} scan rate.

is 48°, which is closer to that of **14** (~60°),[13] indicating the presence of free rotation of the *meso*-aryl group in compound **11**. The striking feature of compound **11** is the presence of intramolecular hydrogen bonding between the boron-bound fluoride groups and the aldehyde groups present at the 3 and 5 positions (Table S1 in the Supporting Information). Each fluoride in compound **11** is involved in hydrogen bonding with one of the aldehyde protons with C−H···F distances of 2.50 Å (C−H1···F1) and 2.91 Å (C−H11···F2). The presence of two formyl groups at the 3 and 5 positions also alters the bond lengths and angles slightly compared to those of **14** (Table S1 in the Supporting Information), which is attributed to the electron-withdrawing nature of the formyl groups.

Compounds **9**−**12** were further characterized by cyclic voltammetry, steady-state absorption and fluorescence, and time-resolved fluorescence techniques. The electrochemical properties of compounds **9**−**12** along with **13** were followed by cyclic voltammetry in CH_2Cl_2 using tetrabutylammonium perchlorate as the supporting electrolyte. A comparison of the reduction waves of compound **9** with those of compound **13** is shown in Figure 3. Compounds **9**−**11** showed no oxidation waves but two reversible reductions occurring at the boron dipyrromethene unit (Table S2 in the Supporting Information). The absence of oxidation in compounds **9**−**11** indicates the electron-deficient nature of the boron dipyrromethene unit. Compound **12** showed two oxidations at 0.81 and 1.32 V, which are due to the presence of an electron-rich 3,4,5-trimethoxyphenyl group at the meso position. The electron-deficient nature of the boron dipyrromethene unit in compounds **9**−**12** is clearly evident in the first and second reduction potentials, which were shifted by ~650 mV toward less negative compared to that of **13**, indicating that the 3,5-diformylboron dipyrromethenes **9**−**12** are very easy to reduce. This significant shift in the reduction potentials of compounds **9**−**12** compared to that of **13** supports the strong electron-withdrawing effect of the formyl groups present at the 3 and 5 positions in **9**−**12** (Table S2 in the Supporting Information). The absorption and fluorescence properties of compounds **9**−**12** were studied in different solvents of varying polarity (Table S3 in the Supporting Information), and the relevant data of compounds **9**−**12** along with compound **13** in $CHCl_3$ are presented in Table 2. The absorption spectra of compounds **9**−**12**, in general, showed a characteristic strong band corresponding to a $S_0 \rightarrow S_1$ transition in the 540−550 nm region with one vibronic component on the higher energy side. In addition, an ill-defined band at ~400 nm corresponding to a $S_0 \rightarrow S_2$ transition is also present. The absorption bands possess narrow spectral bandwidths in compounds **9**−**12**. These absorption features are in agreement with those of other BODIPY dyes such as **13**. Similarly, compounds **9**−**12** showed a single fluorescence band with a bandwidth comparable to that of unsubstituted BODIPY **13**. However, the data presented in Table 2 reveal the following differences and similarities between 3,5-diformylboron dipyrromethenes **9**−**12** and 3,5-unsubstituted BODIPY **13**: (1) Compounds **9**−**12** exhibited a 40−50 nm red shift in the $S_0 \rightarrow S_1$ absorption band (Figure 4a), and the molar absorption coeffiecients are 2−3 times lower compared to that of **13**. This is due to the presence of electron-withdrawing formyl groups in compounds **9**−**12**. (2) The absorption study of compounds **9**−**12** in different solvents (Table S3 in the Supporting Information) indicated that the absorption properties are greatly affected by the solvent polarity. The absorption band was blue-shifted and its intensity was reduced with an increase in the solvent polarity. Thus, compounds **9**−**12** shows strong absorption in less polar solvents like chloroform, which is shifted to blue with a very weak and broad absorption in polar solvents like methanol. This is due to the prevention of conjugation between formyl groups and the BODIPY core in polar solvents like methanol, but it is operational in nonpolar solvents like chloroform. Although BODIPY compounds such as **13**, which does not have formyl groups at the 3 and 5 positions, also exhibit slight hypsochromic shifts with an increase in the solvent polarity, the effects observed for compounds **9**−**12** were quite significant. (3) Compounds **9**−**12** showed typical emission features of BODIPY dyes, that is, narrow, slightly Stokes-shifted bands of mirror image shape. The smaller Stokes shift suggests that the difference between the ground and excited states is much less and these BODIPYs undergo less structural reorganization in the excited state, like any other reported BODIPY.[18] (4) Compounds **9**−**12** showed bathochromically shifted emission bands compared to that of 3,5-unsubstituted BODIPY **13** (Figure 4b). (5) Compounds **9** and **10** showed decent quantum yields compared to that of **13**; compound **11** showed a lower quantum yield, and compound **12** was completely nonfluorescent. The poor fluorescence behavior of compounds **11** and **12** is due to electron-rich *meso*-aryl groups that are involved in photoinduced electron transfer (PET) with the BODIPY core. (6) The fluorescence

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Table 2. Photophysical Data of Compounds 9−13 Recorded in $CHCl_3$[a]

compound	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\nu_{st}$ (cm^{-1})	log ε	Φ	τ (ns)	k_r ($\times 10^9$ s^{-1})	k_{nr} ($\times 10^9$ s^{-1})
13	501	517	618	4.74	0.03	0.51	0.059	1.90
9	546	556	329	4.09	0.31	5.9	0.053	0.117
10	550	560	325	3.77	0.30	5.5	0.055	0.127
11	544	554	332	4.25	0.09	1.4	0.064	0.650
12	548	570	704	4.06				

[a] log(ε/mol^{-1} dm^3 cm^{-1}) − molar extinction coefficient, λ_{abs} (absorption maxima), λ_{em} (emission maxima), $\Delta\nu$ (Stokes shift), Φ (quantum yield), τ (lifetime), k_r (radiative decay), and k_{nr} (nonradiative decay).

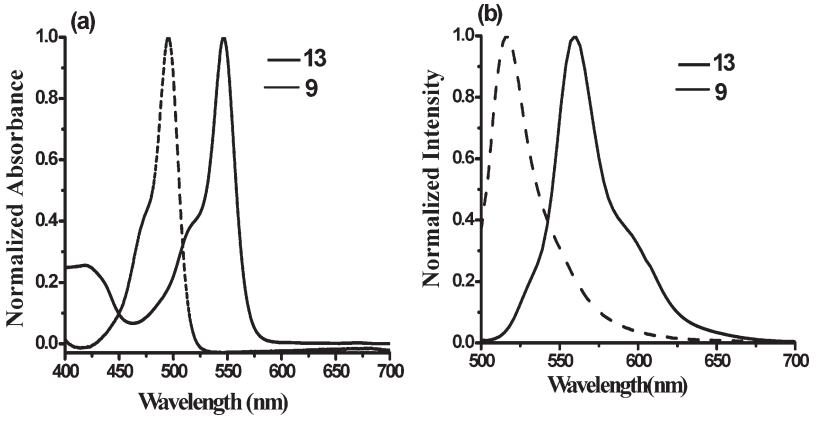

Figure 4. Comparison of normalized (a) absorption and (b) emission spectra of compounds **9** (—) and **13** (---) recorded in chloroform.

band of compounds **9**−**11** was hypsochromically shifted and quantum yields were decreased with an increase in the polarity of the solvent (Table S3 in the Supporting Information). These observations were in agreement with the general behavior of other BODIPYs. Thus, the steady-state absorption and fluorescence study revealed that compounds **9**−**12** exhibit altered properties compared to **13**, which is due to the presence of electron-withdrawing formyl groups at the 3 and 5 positions. The time-resolved fluorescence studies were carried out in order to understand their fluorescence properties in detail (Figure S28 in the Supporting Information). Compounds **9**−**11** showed single-exponential decay, and their singlet state lifetimes were larger than that of compound **13**. The fluorescence decay of compounds **9**−**11** studied in different solvents also showed generally single-exponential decay, and the lifetimes were parallel with their observed fluorescence quantum yields (Table S3 in the Supporting Information).

To understand the basis of having distinct properties of 3,5-diformylboron dipyrromethene at molecular and electronic levels, ab initio calculations were carried out on compounds **9** and **13** using the *Gaussian* program[19a] with DFT,[19b] the B3LYP[19c] method, and 6-31+G(d,p)[19d] as the basis set. The contours of the electronic distribution in highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states on these molecules suggested that there were very minute but essential differences between compounds **9** and **13** (Figure 5). Precisely, the HOMO states of the two molecules seem to be superimposable in the BODIPY nucleus, while close examination of the LUMO states of compounds **9** and **13** revealed that electrons were more delocalized toward the 3,5-diformyl groups in molecule **9**, making the BODIPY nucleus slightly electron-deficient. It was interesting to note that, although the 3,5-diformyl

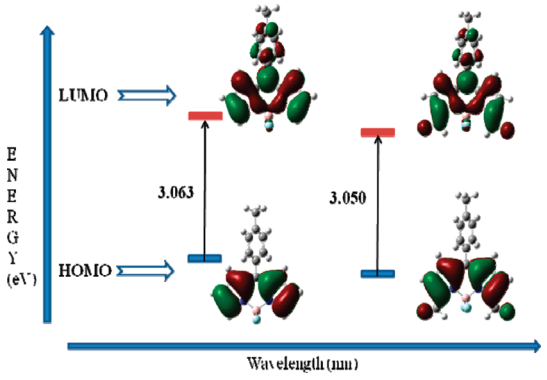

Figure 5. Energies and electron distribution patterns in the HOMO and LUMO states of molecules **13** (left) and **9** (right).

groups stabilize both states of BODIPY, the energy gap is just slightly less than that of molecule **13** (a difference of 0.013 eV was observed). Such an effect could have arisen through extension of π conjugation introduced in the system and the electron-withdrawing ability of the 3,5-diformyl groups. Although the HOMO−LUMO energies give a clear idea that 3,5-diformylboron dipyrromethenes are easily reducible, which is in agreement with our experimental results, the better indicators for the redox properties are electron affinity (EA) and ionization potential (IP) data. The EA is a fundamental property of atoms and molecules and is defined as the energy difference between an uncharged species and its negative ion.[20] For both molecules **9** and **13**, the negative ions were generated by defining the value of charge as −1 and multiplicity as 2. Similarly, the IP is defined as the amount of energy required for removing one electron from a

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Table 3. Data Generated from the Computational Study for Compounds 13 and 9

molecule	HOMO energy (eV)	LUMO energy (eV)	EA (eV)	IP (eV)
13	−6.1756	−3.1123	1.846	7.4465
9	−6.2733	−3.2225	2.881	8.6381

molecule and is generally computed as the energy difference between its cationic and neutral states.[21] The cations were generated by defining the value of charge as 1 and multiplicity as 2 for calculations. These ions were optimized with the above-mentioned protocol. The heats of formation were corrected for zero point for calculation of the EA and IP data. The computational data for the two molecules are given in Table 3. It is clear from the data that the EA for molecule **9** is higher than that for molecule **13**; i.e., molecule **9** is more reducible compared to **13**. The IPs of the two molecules indicate that molecule **9** is difficult to oxidize. Thus, the quantum-mechanics-based studies of these molecules were found to be in accordance with the experimental data.

It is well established in the literature that BODIPYs bearing hydroxyaryl[6]/diaminoaryl[7]/calix[4]arene[8] groups at the meso position can be used as deprotonation/protonation-dependent fluorescence off/on pH sensors. The phenolic, *N*,*N*-dialkylaniline, and calix[4]arene derivatives sense the alkaline, acidic, and near-neutral pH range, respectively. The low emission intensity of the phenolate or uncharged dialkylaniline forms has been attributed to charge transfer from phenolate or uncharged *N*,*N*-dialkylaniline donors to the excited-state BODIPY acceptor moiety. Interestingly, the fluorophore-bearing aldehyde group is generally not used as the fluorescent pH sensor. This is because of the electron-deficient nature of aldehyde, which prevents its involvement in charge transfer with the fluorophore. However, in BODIPY compounds **9**−**12**, the aldehyde groups at the 3 and 5 positions are relatively more electron-rich because these groups are directly involved in π conjugation of the BODIPY unit. Hence, we assumed that the aldehyde groups in BODIPY compounds **9**−**12** are as senstive as the phenolic/(dialkylamino)phenyl group toward the pH and can be used as fluorescent pH sensors. We carried out systematic pH-dependent absorption studies on compounds **9**−**12** and fluorescence studies on compounds **9**−**11** in an acetate buffer solution over a pH range of 4.0−9.0 (Table S4 in the Supporting Information), and the effect of the pH on the absorption and fluorescence of compound **9** is shown in Figure 6. The absorption spectra of compounds **9**−**12** as a function of the pH in an acetate buffer solution exhibited an increase of the respective absorption bands with increasing H^+ concentration without changes in the peak maxima, as shown in Figure 6a for compound **9**. Because the absorption studies are performed in a polar medium, the absorption bands of BODIPY are already hypsochromically shifted compared to a nonpolar medium like benzene; hence, no shifts in the absorption peak maxima are expected with changes of the pH in the buffer medium. The emission peak maxima of compounds **9**−**11** also remain unaltered in different pH solutions, but their intensities were significantly altered. For example, at pH 8, compound **9** was very weakly fluorescent. Furthermore, the fluorescence switching process was also found to be reversible. It was observed that compound **9** showed some emission at pH 7, but the emission intensity decreased as the pH of the alkaline medium was increased and compound **9** became completely nonfluorescent

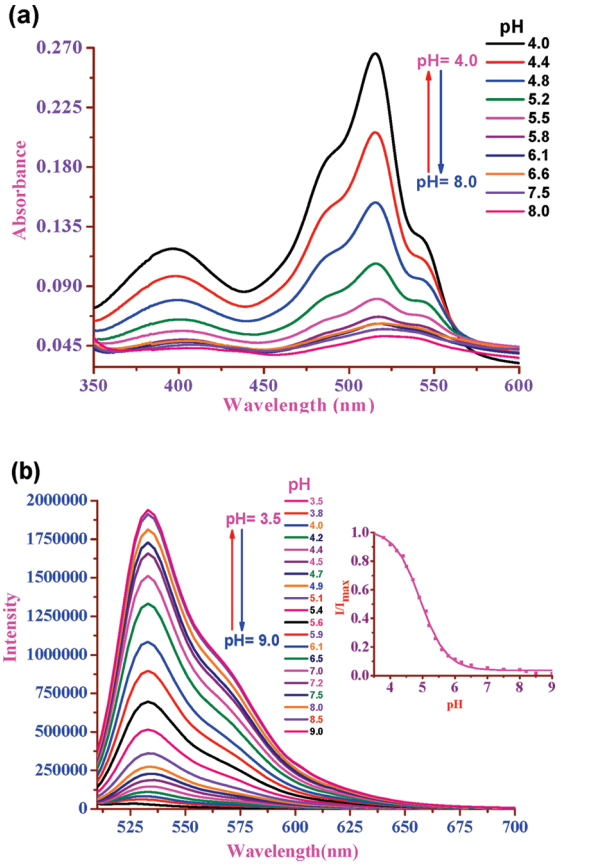

Figure 6. (a) Absorption spectra of compound **9** (5 μM) in an aqueous acetate buffer solution (0.1 M) as a function of the pH. (b) Fluorescence spectra of compound **9** (5 μM) in an acetate buffer solution (0.1 M) as a function of the pH. The excitation wavelength used was 488 nm. The inset shows the plot of I/I_{max} vs pH.

at pH 9. However, the decrease in the emission intensity is not very substantial as we move toward alkaline pH from pH 7, indicating that compound **9** is less fluorescent even at neutral pH. Upon a decrease from pH 7 to acidic pH (pH 4), the emission intensity was enhanced by 17 times and a maximum change was found within the pH range of 6.5−4.0 (pK_a = 6.39 at pH 4).[22] This is also clearly reflected in the sigmoidal response observed in the plot of I/I_{max} vs pH, where I_{max} is the maximum fluorescence intensity of compound **9** and I is the fluorescence intensity at a particular pH. Similar observations were made for compounds **10** and **11** (Table S4 in the Supporting Information). However, compound **12** was too weakly fluorescent to perform pH titration studies and compound **13**, which does not have formyl groups at the 3 and 5 positions, did not exhibit any changes in the fluorescence intensity upon variation of the pH. These significant changes in acidic and alkaline media represent two different "states", where the fluorescence is "switched off" (state I) in an alkaline solution and "switched on" (state II) in an acidic solution, as shown in Scheme 3. In an alkaline solution, the aldehyde group is electron-rich and engaged in PET quenching of the BODIPY excited state, and in an acidic medium, the PET quenching is prevented because of protonation of the aldehyde group. To confirm that 3,5-diformylboron dipyrromethenes exist in two different states, we recorded ^{1}H NMR spectra of compound **9** at basic and acidic media (Figure S29 in the Supporting Information). NMR spectra of compound **9**

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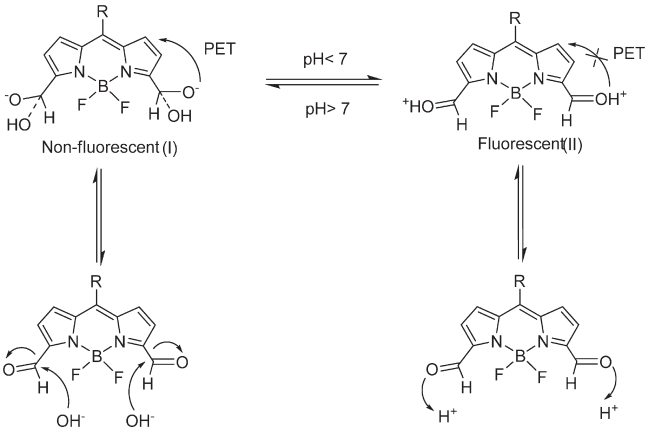
Scheme 3. Schematic Representation of the Fluorescence On/Off pH Sensor



in basic and acidic pH media are quite different from each other. In a basic medium, the aldehyde proton H_c appeared at 9.9 ppm, which experienced a substantial upfield shift in an acidic medium and appeared at 5.8 ppm, supporting the existence of compound **9** in two different states (Scheme 3). These changes are also clearly evident in the color of the solutions at different pH under a UV lamp. At acidic pH, the solution of **9** is bright fluorescent green, which faded at basic pH (Figure S47b in the Supporting Information). Thus, the pH-controlled fluorescence titration studies indicate that 3,5-diformylboron dipyrromethenes can be used as pH fluorescent sensors.

CONCLUSIONS

We synthesized stable 3,5-diformylboron dipyrromethenes in two steps starting from *meso*-aryl dipyrromethanes under simple reaction conditions. The X-ray structural analysis indicated that the two aldehyde groups are involved in intramolecular hydrogen bonding with the fluoride atoms and stabilization of the compounds. The formyl groups on the BODIPY framework alter the electronic properties of the BODIPY unit siginificantly, which is reflected in various spectroscopic and electrochemical properties. The electrochemical studies as well as quantum-mechanical studies at the DFT level indicated that the BODIPY unit in diformylboron dipyrromethenes is highly electron-deficient and readily undergoes facile reduction. The synthesized 3,5-diformylboron dipyrromethenes were used as fluorescent pH sensors, which is uncommon for aldehyde-containing fluorophores. Presently, we are using these 3,5-diformylboron dipyrromethenes to synthesize further eloborated structures such as 3,5-bis-(dipyrromethane)boron dipyrromethenes (Scheme S1 in the Supporting Information) for various studies.

EXPERIMENTAL SECTION

General Experimental Details. The 1,9-diformyl dipyrromethanes[12] **5**−**7** and BODIPY[13] **13** were synthesized by following the literature procedures. BF_3 Et_2O and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were used as obtained. All other chemicals used for the synthesis were reagent-grade unless otherwise specified. Column chromatography was performed on silica (60−120 mesh). The ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded in $CDCl_3$ using a Varian VXR 400 spectrometer operating at the appropriate frequencies using tetramethylsilnae [$Si(CH_3)_4$] as the internal reference. Absorption and steady-state fluorescence spectra were obtained with Perkin-Elmer Lambda-35 and PC1 photon-counting spectrofluorometers manufactured by ISS and USA Instruments, respectively. The fluorescence quantum yields (Φ_f) were estimated from the emission and absorption spectra by comparative method at the excitation wavelength of 488 nm using Rhodamine 6G (Φ_f = 0.76)[17a] 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 fluorescence spectrometer from IBH, U.K. All of the decays were fitted to a single exponential. The good fit criteria were low χ^2 (1.0) and random distributions of residuals. Cyclic voltammetric studies were carried out with a BAS electrochemical system utilizing a three-electrode configuration consisting of glassy carbon (working), platinum wire (auxiliary), and saturated calomel (reference) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Half-wave potentials were measured using differential-pulse voltammetry and also calculated manually by taking the average of the cathodic and anodic peak potentials. The HRMS spectra were recorded with a Q-Tof micro mass spectrometer. A single crystal of compound **11** (CCDC 768735) was obtained from the slow evaporation of a *n*-hexane/$CHCl_3$ solution. The intensity data collection for compound **11** has been carried out on a Nonius MACH3 four-circle diffractometer at 293 K. The structure solution for compound **11** was obtained using direct methods (*SHELXS-97*)[23] and refined using full-matrix least-squares methods on F^2 using *SHELXL- 97*.[24] For pH studies, the absorption and fluorescence titrations were performed in an acetate buffer solution (0.1 M) containing a minimum amount of methanol [1:99 (v/v) CH_3OH/buffer] at a probe concentration of 5 μM. A few microliters of 0.1 and 0.01 M solutions of HCl and/or NaOH were used to adjust the pH of the solutions.

Computational Details. The computational studies were performed with *Gaussian 03*[19a] installed on a Windows operating system. The structures were energy-optimized using quantum mechanics with DFT[19b] and B3LYP[19c] gradient-corrected correlation functional methods in conjugation with a standard 6-31G (p,d) basis set[19d] and parameters. For the optimized structures, population analysis studies were done. The redox properties of compounds **9** and **13** and EA and IP data were also calculated.[20,21] Simulations of the addition and removal of electrons from BODIPY systems (compounds **9** and **13**) were affected by simply setting the charges and multiplicities as (−1, 2) and (1, 2). With these charges and multiplicities and the 3D coordinates of neutrally optimized BODIPY systems, geometry optimizations were carried out for the respective anions and cations. From the heats of formation obtained, the total energies (TEs) were calculated by zero-point and basis-set corrections. The EA and IP data were calculated using the following formulas:

$$\mathrm{EA} = \mathrm{TE(neutral)} - \mathrm{TE(anion)}$$

$$\mathrm{IP} = \mathrm{TE(cation)} - \mathrm{TE(neutral)}$$

1,9-Diformyl-*meso*-(3,4,5-trimethoxyphenyl) Dipyrromethane. Dimethylformamide (5.1 mmol) was added to a 100 mL three-neck, round-bottomed flask, cooled to 5−10 °C, and flushed with nitrogen for 5 min. $POCl_3$ (4.23 mmol) was added dropwise over 15 min with stirring. Dry dichloroethane (10 mL) was then added, and the mixture was stirred at room temperature for 15 min. The mixture was cooled to 0 °C, *meso*-(3,4,5-trimethoxyphenyl)dipyrromethane (**4**; 4.23 mmol) in dry dichloroethane (20 mL) was added dropwise over 1 h, and the solution turned to deep-purple. The solution was warmed to 50 °C for 15 min and then allowed to cool to room temperature. A saturated sodium carbonate solution (50 mL) was added, and the reaction was stirred vigorously at room temperature for 2 h. The mixture was extracted

with ethyl acetate (3 × 100 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and evaporated. The crude compound was subjected to silica gel column chromatography and eluted with petroleum ether/ethyl acetate (70:30), which afforded pure 1,9-diformyl-*meso*-(3,4,5-trimethoxyphenyl) dipyrromethane (**8**) as a light-brown solid in 67% yield (0.8 g). Mp: 168−169 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.76 (s, 9H; $-OCH_3$), 5.45 (s, 1H; −CH), 6.07−6.09 (m, 2H; py), 6.63 (s, 2H; Ar), 6.85−6.87 (m, 2H; py), 9.12 (s, 2H; −NH), 10.86 (br s, 2H; −CHO). HRMS. Calcd for $C_{20}H_{20}N_2O_5$ $[(M + 1)^+]$: m/z 369.1450. Found: m/z 369.1436.

General Procedure for 3,5-Diformylboron Dipyrromethenes (9−12). 1,9-Diformyl dipyrromethanes **5**−**8** (1.7 mmol) were dissolved in dichloromethane (200 mL) and oxidized with DDQ (2.04 mmol) at room temperature. The reaction mixture was allowed to stir at room temperature for 30 min. Triethylamine (68 mmol), followed by $BF_3.Et_2O$ (85 mmol), was added to the reaction mixture successively without any time delay, and stirring was continued at room temperature for an additional 30 min. The reaction mixture was evaporated, and the crude product was purified using silica gel column chromatography with petroleum ether/ethyl acetate (75:25), which afforded pure 3,5-diformylboron dipyrromethenes **9**−**12** as blue-greenish solids.

3,5-Diformyl-8-tolyl-4-bora-3a,4a-diaza-*s*-indacene (9). Yield: 80 mg, 14%. Mp: 242−243 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.52 (s, 3H; $-CH_3$), 7.12 (d, ^3J(H,H) = 4.27 Hz, 2H; py), 7.20 (d, ^3J(H,H) = 4.27 Hz, 2H; py), 7.43 (d, ^3J(H,H) = 7.94 Hz, 2H; Ar), 7.53 (d, ^3J(H,H) = 7.94 Hz, 2H; Ar), 10.48 (br s, 2H; −CHO). ^{11}B NMR (100 MHz, $CDCl_3$, δ in ppm): 1.26 (t, ^1J(B−F), 1B). ^{19}F NMR (300 MHz, $CDCl_3$, δ in ppm): −130.8 (q, ^1J(F−B), 2F). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.8, 120.2, 129.9, 130.6, 131.4, 132.9, 137.9, 143.8, 151.0, 153.8, 184.4. HRMS. Calcd for $C_{18}H_{13}BF_2N_2O_2$ $[(M - F)^+]$: m/z 319.1054. Found: m/z 319.1042. IR (KBr, ν_{max}): 760.0, 997.2, 1135.1, 1186.8, 1232.5, 1268.7, 1342.4, 1387.6, 1477.7, 1542.4, 1567.7, 1672.9, 2924.6.

3,5-Diformyl-8-(4-bromophenyl)-4-bora-3a,4a-diaza-*s*-indacene (10). Yield: 40 mg, 9%. Mp: 238−239 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.06 (d, ^3J(H,H) = 4.75 Hz, 2H; py), 7.20 (d, ^3J(H,H) = 4.36 Hz, 2H; py), 7.49 (d, ^3J(H,H) = 6.74 Hz, 2H; Ar), 7.74 (d, ^3J(H,H) = 6.74 Hz, 2H; Ar), 10.48 (br s, 2H; −CHO). ^{11}B NMR (100 MHz, $CDCl_3$, δ in ppm): 1.24 (t, ^1J(B−F), 1B). ^{19}F NMR (300 MHz, $CDCl_3$, δ in ppm): −130.8 (q, ^1J(F−B), 2F). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 120.6, 127.7, 131.9, 132.3, 132.6, 132.7, 137.7, 151.6, 184.2. HRMS. Calcd for $C_{17}H_{10}BF_2N_2O_2Br$ $[(M - F)^+]$: m/z 382.9988. Found: m/z 382.9991. IR (KBr, ν_{max}): 602.3, 782.2, 1043.5, 1132.3, 1228.4, 1261.7, 1339.7, 1382.3, 1472.6, 1545.3, 1562.6, 1669.9, 2924.3.

3,5-Diformyl-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (11). Yield: 150 mg, 26%. Mp: 236−237 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.96 (s, 3H; $-OCH_3$), 7.12−7.14 (m, 4H; py + Ar), 7.21 (d, ^3J(H,H) = 4.36 Hz, 2H; py), 7.61−7.63 (d, ^3J(H,H) = 7.13 Hz, 2H; Ar), 10.47 (br s, 2H; −CHO). ^{11}B NMR (100 MHz, $CDCl_3$, δ in ppm): 1.28 (t, ^1J(B−F), 1B). ^{19}F NMR (300 MHz, $CDCl_3$, δ in ppm): −130.7 (q, ^1J(F−B), 2F). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 55.9, 114.9, 120.1, 126.0, 132.6, 133.7, 137.7, 150.6, 153.3, 163.9, 184.4. HRMS. Calcd for $C_{18}H_{13}BF_2N_2O_3$ $[(M - F)^+]$: m/z 335.1003. Found: m/z 335.0992. IR (KBr, ν_{max}): 629.3, 752.0, 815.9, 1176.5, 1232.9, 1265.6, 1339.1, 1385.1, 1466.0, 1537.9, 1571.1, 1671.0, 2923.5.

3,5-Diformyl-8-(3,4,5-trimethoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (12). Yield: 40 mg, 7%. Mp: 250−251 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.93 (s, 6H; *m*-OCH_3), 4.00 (s, 3H, *p*-OCH_3), 6.84 (s, 2H; Ar), 7.18 (d, ^3J(H,H) = 4.58, 2H; py), 7.21 (d, ^3J(H,H) = 4.28, 2H; py), 10.48 (br s, 2H; −CHO). ^{11}B NMR (100 MHz, $CDCl_3$, δ in ppm): 1.24 (t, ^1J(B−F), 1B). ^{19}F NMR (300 MHz, $CDCl_3$, δ in ppm): −130.5 (q, ^1J(F−B), 2F). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 56.7, 61.4, 109.1, 120.3, 128.5, 132.8, 137.8, 142.2, 151.1, 153.1, 153.6, 184.3. HRMS. Calcd for $C_{20}H_{17}BF_2N_2O_5$ $[(M - F)^+]$: m/z 395.1215. Found: m/z 395.1197. IR (KBr, ν_{max}): 633.1, 765.0, 1074.2, 1175.1, 1232.2, 1269.7, 1335.8, 1379.5, 1464.9, 1539.2, 1570.3, 1675.4, 2922.7.

■ ASSOCIATED CONTENT

Supporting Information. Spectral data of all compounds, fluorescence data, tables of crystal and absorption data, and X-ray crystallographic data for compound **11** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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