Inorganic Chemistry

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Synthesis, Spectral, Electrochemical, and Anion Binding Properties of 3,5-Bis(Dipyrromethanyl) Boron-Dipyrromethenes

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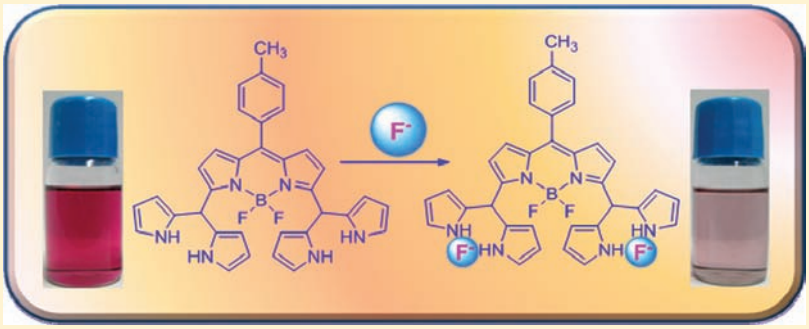
Supporting Information



ABSTRACT: Four new boron-dipyrromethenes (BODIPYs) containing dipyrromethanyl substituents at 3,5-positions, bis(3,5-dipyrromethanyl) BODIPYs **5**−**8**, were synthesized by treating their corresponding 3,5-diformyl BODIPYs **1**−**4** with excess pyrrole under mild acid catalyzed reaction conditions. The compounds **5**−**8** are stable and freely soluble in common organic solvents. One-dimensional, two-dimensional NMR, high resolution mass spectrometry (HRMS), absorption, fluorescence, and electrochemical techniques were used to characterize the compounds. The spectral and electrochemical studies indicated that dipyrromethanyl groups at 3,5-positions of BODIPY are less electron deficient compared to formyl groups at the same positions. The anion binding studies indicated that bis(3,5-dipyrromethanyl) BODIPY compounds containing four pyrrole NH groups showed preferential binding with F^- ion over other anions, as confirmed by using NMR, fluorescence, and electrochemical studies.

INTRODUCTION

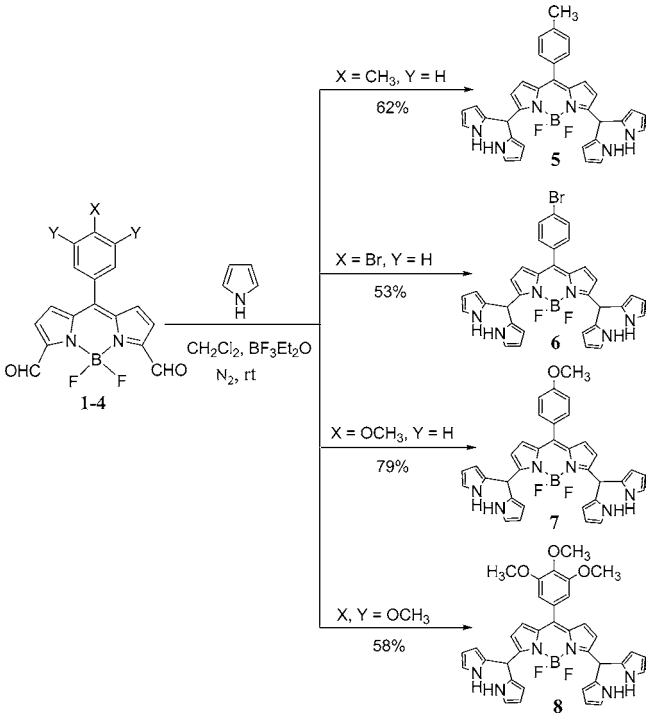
The synthetic chemistry of boron-dipyrromethenes (BODIPYs) has rapidly grown in recent years owing to their numerous applications in biological labeling and cell imaging, and also as artificial light harvesters, sensitizers for solar cells, fluorescent sensors, molecular photonic wires, and solid state dye lasers.[1] The remarkable properties of BODIPY fluorophores are their pronounced stability, high absorption coefficients, narrow emission profiles, and very good emission quantum yields which reach unity in the best cases. The main reasons for the rapid growth of synthetic chemistry of BODIPYs are their ease of synthesis and potential for derivatization. Several new types of BODIPY dyes have been synthesized recently by using functionalized BODIPYs as these dyes are amenable for functionalization at all positions.[2] For example, BODIPYs are subjected to halogenation[3] at 3,5- and 1,7-positions and, halogenated BODIPYs have been used as building blocks to synthesize several new types of BODIPY derivatives[4] including cascade type BODIPY arrays.[5] Similarly, the BODIPY systems containing active methyl groups at 3,5-positions have been used to synthesize π-extended conjugated BODIPY systems.[6] Recently, Ziessel et al. developed a route to introduce ethynyl functional groups in place of fluorides of BODIPY and used these for the synthesis of very interesting light harvesting systems.[7] We recently reported the facile synthesis of 3,5-diformyl BODIPYs under simple reaction conditions and demonstrated their use as pH-based optical sensors.[8] However, aldehyde functional groups on BODIPY core are very useful to synthesize several new types of BODIPYs, and herein we report the synthesis of four novel 3,5-bis(dipyrromethanyl) BODIPYs **5**−**8** by treating 3,5-diformyl BODIPYs **1**−**4** with excess pyrrole in the presence of mild acid. The 3,5-bis-(dipyrromethanyl) BODIPYs **5**−**8** containing four pyrrole NH protons are expected to bind anions which can be sensed by following changes in the spectral and electrochemical properties of BODIPY unit. Our studies with various anions indeed indicated that the dyes **5**−**8** can act as exclusive sensors for F^- ion.

RESULTS AND DISCUSSION

The required 3,5-diformyl BODIPYs **1**−**4** were prepared in a two-step, one-pot reaction starting with corresponding *meso*-aryl dipyrromethanes as reported earlier.[8] The diformyl compounds **1**−**4** were treated with 40 equiv of pyrrole in dichloromethane in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ at room temperature for 15 min (Scheme 1). Thin layer chromatography (TLC) analysis indicated the disappear-

Received: December 23, 2011
Published: March 20, 2012

Scheme 1. Synthesis of 3,5-Bis(dipyrromethanyl)-BODIPYs 5−8



ance of spots corresponding to 3,5-diformyl compounds **1−4** and by the appearance of new less polar spots corresponding to the required 3,5-bis(dipyrromethanyl) BODIPY **5−8**. Column chromatographic purification on silica afforded stable corresponding 3,5-bis(dipyrromethanyl) BODIPY **5−8** as red solid powder. The compounds **5−8** are soluble in all commonly used solvents and were characterized by mass, NMR, UV−vis, fluorescence, and electrochemical techniques. The composition of the compounds **5−8** were confirmed by high resolution mass spectrometry (HRMS) and elemental analysis. The compounds **5−8** were characterized in detail using one- and two-dimensional (1D and 2D) NMR techniques, and the comparison of ^{1}H, ^{19}F, and ^{11}B NMR spectra of **5** with corresponding diformyl BODIPY **1** and 3,5-unsubstituted *meso*-aryl BODIPY **9** is shown in Figure 1. A representative spectrum of ^{1}H−^{1}H COSY NMR for compound **5** is presented in Figure 2. We observed earlier[8] that the presence of two electron withdrawing formyl groups at the 3 and 5 positions of BODIPY core in compounds **1−4** alters the π-delocalization significantly which is reflected in the downfield shifts of type a and type b pyrrole protons of BODIPY core compared to unsubstituted BODIPY **9** (Figure 1a). In compounds **5−8**, the type a and type b pyrrole protons of BODIPY core appeared as doublets at ∼6.40 and ∼6.70 ppm respectively as confirmed by ^{1}H−^{1}H COSY NMR (Figure 2) because of symmetric environment like diformyl BODIPYs **1−4**. However, these protons shifted upfield compared to **9** as well as compared to their corresponding 3,5-diformyl BODIPYs **1−4** supporting the less electron-withdrawing nature of dipyrromethanyl groups in **5−8**. The 12 pyrrole protons and two meso CH protons of dipyrromethanyl units appeared as sets of two multiplets at ∼6.50 ppm and ∼6.80 ppm and four pyrrole NH protons appeared as broad singlet at ∼8.47 ppm. In ^{11}B NMR, compounds **5−8** showed a typical triplet like diformyl BODIPYs **1−4**. However, compared to diformyl BODIPYs **1−4**, the compounds **5−8** showed further downfield shifts (Figure 1b). Furthermore, the compounds **5−8** showed one quartet in ^{19}F NMR indicating that fluorines are under a chemically equivalent environment. However, in ^{19}F NMR, compounds **5−8** showed ∼10 ppm downfield shift compared to **9** but 5 ppm upfield shift compared to diformyl BODIPYs **1−4** (Figure 1c). Thus, the NMR studies clearly indicated that the presence of dipyrromethanyl groups at 3- and 5-positions alters the π-delocalization of BODIPY core but less significant compared to formyl groups at the same positions of the BODIPY core which we attributed to the less electron withdrawing nature of the dipyrromethanyl groups in compounds **5−8** compared to formyl groups in compounds **1−4**.

Spectral and Electrochemical Properties of Compounds 5−8. The compounds **5−8** were characterized further by absorption, fluorescence, and cyclic voltammetry techniques. The absorption properties of compounds **5−8** were studied in four different solvents of varying polarity, and the relevant data of compounds **5−8** along with 3,5-diformyl BODIPY **1** and 3,5-unsubstituted BODIPY **9** in $CHCl_3$ are presented in Table 1. The comparison of normalized absorption spectra of compounds **1**, **5**, and **9** recorded in $CHCl_3$ is presented in Figure 3a. In general, the BODIPYs such as **9** exhibit one strong $S_0 \rightarrow S_1$ transition at ∼500 nm with one vibronic component on the higher energy side and an ill defined band at ∼400 nm corresponding to a $S_0 \rightarrow S_2$ transition.[9] Compounds **5−8** showed similar absorption features like BODIPY **9**. However, the following differences and similarities were noted in absorption spectra of compounds **5−8** when compared to **1** and **9**; (1) $S_0 \rightarrow S_1$ transition in compounds **5−8** experienced bathochromic shift compared to **9** but showed a slight hypsochromic shift compared to **1**; (2) compounds **5−8** showed relatively broader absorption spectra with a bandwidth ∼900 cm^{-1} compared to **1** and **9**; (3) the extinction coefficients of compounds **5−8** are lower compared to **9** but higher as compared to **1**; (4) the absorption band in compounds **5−8** showed slight blue shift in polar solvents like CH_3OH compared to nonpolar solvents like toluene. This observation is in line with the general behavior of other BODIPYs like **9** and diformyl BODIPYs **1−4**.

The fluorescence properties of compounds **5−8** were studied in four different solvents of varying polarity using both steady state and time-resolved fluorescence techniques. The comparison of steady state fluorescence spectra of compounds **5**, **1**, and **9** is presented in Figure 3b and the relevant data are included in Table 1. The following observations were noted by close inspection of Figure 3b and data presented in Table 1: (1) the compounds **5−8** showed relatively broad and strong fluorescence band which is bathochromically shifted compared to **9** and **1**; (2) compounds **5−8** exhibited relatively larger Stokes shifts compared to BODIPYs **9** and **1**; (3) the quantum yields (Φ_f) of compounds **5−8** are higher than unsubstituted BODIPY **9** but significantly lower than their corresponding diformyl BODIPYs **1−4**. Furthermore, the quantum yields are dependent on the type of meso-substituent, and it is very low for BODIPYs containing an electron donating meso-aryl substituent that may be involved in photoinduced electron transfer with the BODIPY core; (4) the fluorescence band of compounds **5−8** were hypsochromically shifted and quantum yields were decreased with an increase in the polarity of the solvent; (5) compounds **5−8** showed single exponential decay (Supporting Information, Figure S21) and their singlet state

dx.doi.org/10.1021/ic202758r | Inorg. Chem. 2012, 51, 4285−4292

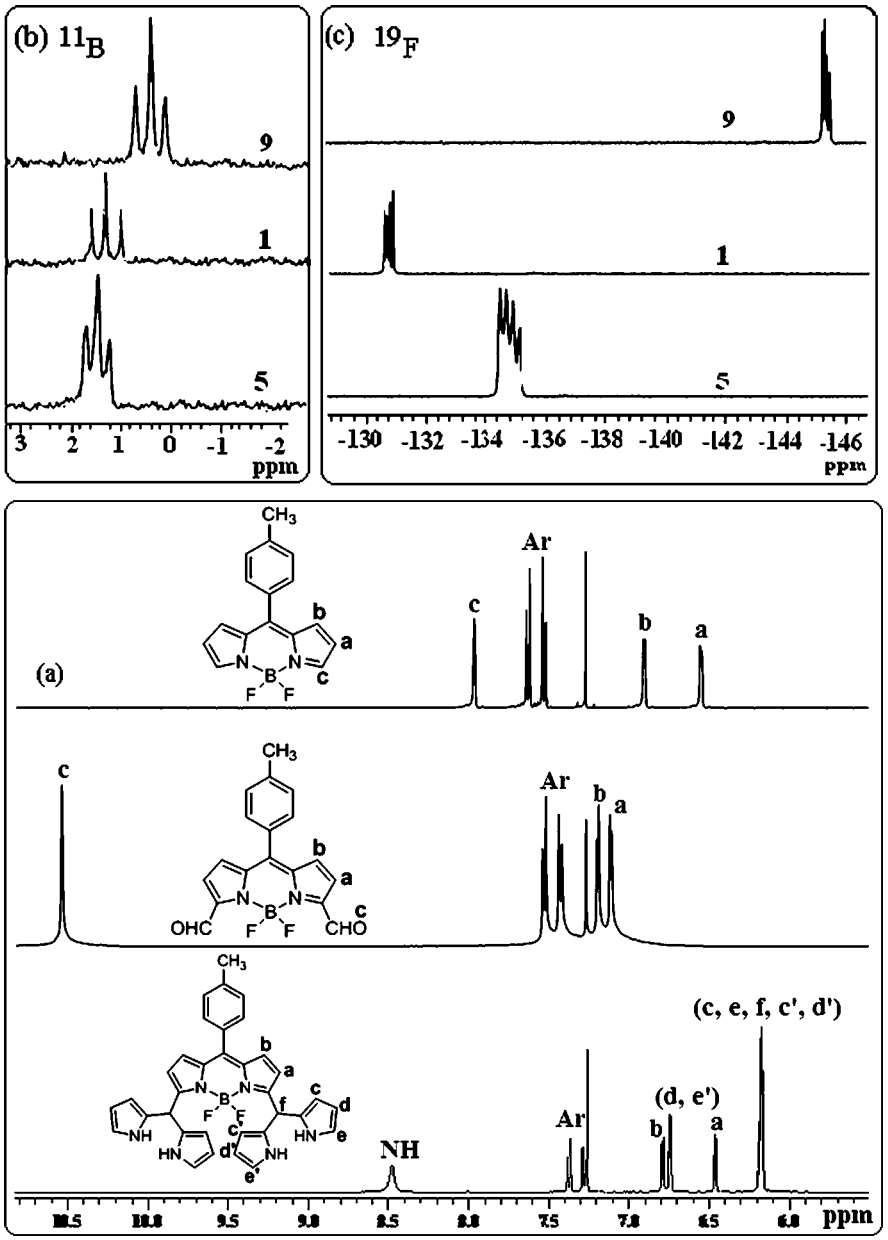


Figure 1. Comparison of (a) ^{1}H, (b) ^{11}B, and (c) ^{19}F NMR spectra of compounds **9**, **1**, and **5** in the selected region recorded in $CDCl_3$.

lifetimes (τ_f) were larger than **9** but lower than diformyl BODIPYs **1**−**4** and (6) the radiative K_r and nonradiative rates K_{nr} were in agreement with their quantum yields. Thus, absorption and fluorescence studies of **5**−**8** indicated that the presence of dipyrromethanyl groups at 3,5-positions of BODIPY alter the electronic properties compared to unsubstituted BODIPY, and the magnitude is comparatively less than their corresponding diformyl BODIPYs supporting their less electron withdrawing nature compared to formyl groups in BODIPY **1**−**4**.

The electrochemical properties of BODIPYs **5**−**8** were studied by cyclic voltammetry in CH_2Cl_2 using tetrabutylammonium perchlorate as the supporting electrolyte. A comparison of first reduction waves of compounds **1**, **5**, and **9** is shown in Figure 4, and the relevant data are included in the Table 1. The 3,5-unsubstituted BODIPYs like BODIPY **9** show one oxidation and two reductions.[9] Our earlier study[8] on 3,5-diformyl BODIPYs such as BODIPY **1** indicated that these compounds because of their electron deficient nature exhibit only two reversible reductions which are at much lower potentials compared to **9**. Compounds **5**−**8** also showed one reversible and one quasi-reversible reduction as the dipyrromethanyl groups are also electron deficient in nature but less effective as compared to formyl groups. Thus, the reduction potentials of compounds **5**−**8** shifted toward more negative compared to diformyl BODIPYs **1**−**4** indicating that compounds **5**−**8** were difficult to reduce compared to compounds **1**−**4**. However, the BODIPYs **5**−**8** are easier to reduce by ~200 mV compared to **9** supporting the electron withdrawing nature of dipyrromethanyl groups present at the 3,5-positions of BODIPYs **5**−**8**.

Anion Binding Studies. In recent years, anion sensing and recognition has grown into an area of great interest in supramolecular and biological chemistry.[10] Most synthetic anion chemosensors generally involve the covalent linking of an optical-signaling chromophoric fragment to a neutral anion

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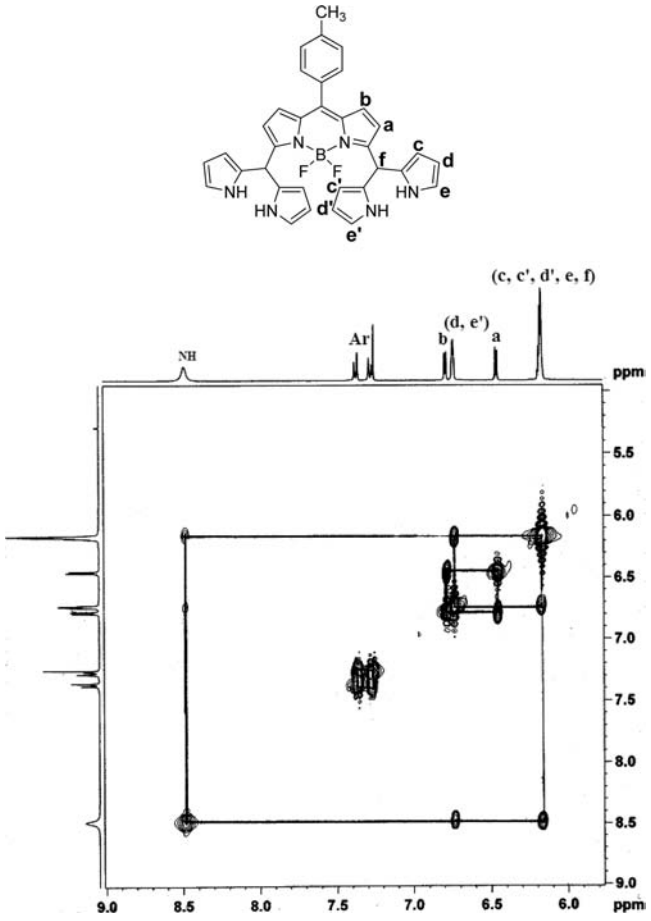

Figure 2. $^1H-^1H$ COSY spectrum of compound **5** in $CDCl_3$.

receptor containing urea, thiourea, amide, phenol, or pyrrole subunits, which can provide one or more hydrogen bond donor sites for selective binding and sensing of some anions, especially for F^-, AcO^-, and $H_2PO_4^-$.[11] Thus, the earlier studies showed that pyrroles are excellent hydrogen bond donor groups in synthetic anion receptor systems, and the pioneering work of Sessler,[12] Gale,[13] and others[14] established pyrrole as an effective anion receptor group. Since BODIPY compounds **5**–**8** contain four pyrrole groups and one fluorescent signaling unit, we thought that these systems can be used as effective anion sensors. We explored the anion binding properties of BODIPY **5** with various anions including F^-, Cl^-, Br^-, I^-, OH^-, AcO^-, ClO_4^-, $H_2PO_4^-$, and our studies clearly showed that **5** is highly

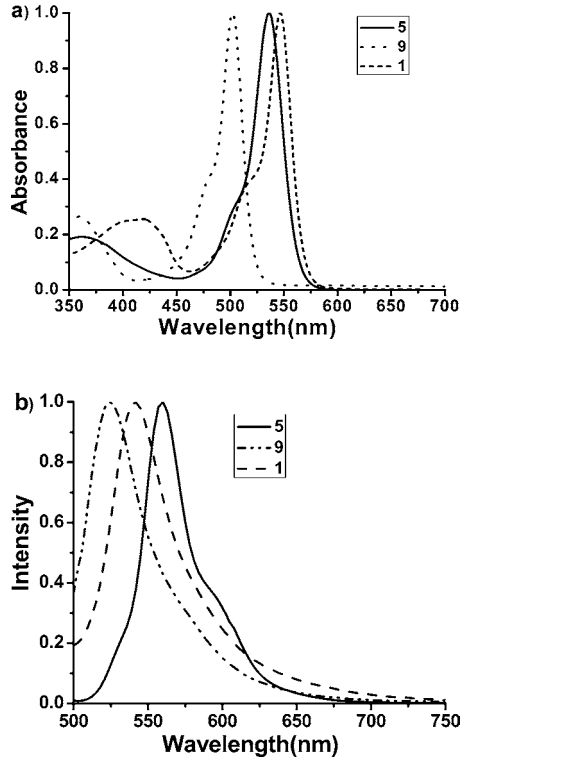

Figure 3. Comparison of normalized (a) absorption and (b) emission spectra of compound **5** along with **1** and **9** recorded in chloroform (excitation wavelength used was 488 nm).

selective fluoride sensor as confirmed by NMR, optical, and electrochemical studies.

The fluoride anion binding to **5** was first followed by ^1H NMR titration of **5** with increasing amounts of fluoride ion in $CDCl_3$. We noticed more numbers of signals and systematic shifts for NH and other dipyrromethanyl protons of **5** by the addition of increasing amounts of tetrabutylammonium fluoride to compound **5**. Hence we used $^1H-^1H$ COSY NMR to identify all signals which appeared upon the addition of F^- ion to compound **5**. The changes in the chemical shifts of NH protons on addition of F^- up to 2 equiv to compound **5** are shown in Figure 5a; the comparison of changes in the chemical shifts of dipyrromethanyl core protons, BODIPY core protons, and meso-aryl protons before and after addition of F^- to compound **5** is shown in Figure 5b and $^1H-^1H$ COSY NMR spectrum of **5** + F^- is shown in Figure 5c. As it is clear from Figure 5a, upon increasing addition of F^- ion to **5**, the NH

Table 1. Photophysical and Electrochemical Data of Compounds 5–8, along with 1 and 9

compound	solvent	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\nu_{st}$ (cm^{-1})	ε_0 (ε)	ϕ	τ (ns)	K_r (10^9 s^{-1})	K_{nr} (10^9 s^{-1})	$E_{red}(V)^a$ I	$E_{red}(V)^a$ II
9	$CHCl_3$	501	517	618	4.74	0.03	0.51	0.059	1.9	−0.800	−1.820
1	$CHCl_3$	546	556	329	4.09	0.31	5.9	0.053	0.117	−0.132	−1.040
2	$CHCl_3$	550	560	325	3.77	0.30	5.5	0.055	0.127	−0.067	−0.979
3	$CHCl_3$	544	554	332	4.25	0.09	1.4	0.064	0.650	−0.148	−1.055
4	$CHCl_3$	548	570	704	4.06					−0.107	
5	$CHCl_3$	537	562	828	416	0.12	1.6	0.070	0.550	−0.659	−1.661
6	$CHCl_3$	543	568	811	4.00	0.17	1.3	0.131	0.638	−0.672	−1.566
7	$CHCl_3$	536	563	895	4.24	0.07	1.4	0.050	0.664	−0.623	−1.665
8	$CHCl_3$	541	560	627	3.71					−0.650	−1.589

[a] ε (extinction coefficient), λ_{abs} (absorption maxima), λ_{em} (emission maxima), $\Delta\nu$ (Stokes shift), Φ (quantum yield), τ (lifetime), k_r (radiative decay), k_{nr} (nonradiative decay).

dx.doi.org/10.1021/ic202758r | Inorg. Chem. 2012, 51, 4285–4292

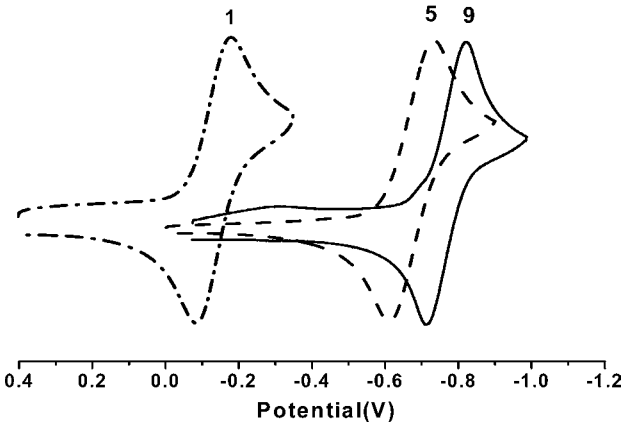

Figure 4. Comparison of reduction waves of cyclic voltammograms of compounds **1**, **5**, and **9** in dichloromethane containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV s^{-1} scan rate.

protons which appeared earlier as broad singlet at 8.47 ppm experienced a downfield shift and appeared as a doublet at ~12.35 ppm upon addition of 2 equiv of F^-. The continuous downfield shift of NH protons and the occurrence of a doublet with increasing F^- ion concentration indicated the strong coupling between NH proton and F^- because of NH···F^- hydrogen bond formation. Similarly, the 12 pyrrole protons of dipyrromethanyl group (c, c′, d, d′, e, e′) also experienced shifts on binding to F^- ion (Figure 5b). In ^1H NMR, as described above, the compound **5** exhibited two signals at 6.17 and 6.74 ppm corresponding to 10 and 4 protons of the dipyrromethanyl group. However, on binding with F^- ion, these protons appeared as four sets of signals which appeared at slightly higher field, and these signals were identified by using $^1H-^1H$ COSY NMR studies (Figure 5c). In COSY of **5** + F^-, the NH protons at 11.7 ppm showed a cross peak with signals at 6.05 and 6.74 ppm, which in turn showed cross peaks with each other and also with a signal at 6.13 ppm. Thus, we identified the signals at 6.05, 6.13, and 6.74 ppm as (e, d′), (c, c′), and (d, e′) types, respectively. The singlet at 6.22 ppm corresponding to two protons was identified as meso-protons of dipyrromethanyl group (f-type) which did not show any shift on addition of F^- ion. The two doublets that appeared at 6.45 ppm and 6.78 ppm corresponding to type a and type b pyrrole protons of BODIPY unit in compound **5** shifted by 0.3 ppm downfield and appeared as doublets at 6.71 and 7.05 ppm respectively in **5** + F^-. Thus, NMR studies clearly indicated the binding of fluoride ion to the pyrrole moieties of the dipyrromethanyl group of compound **5**. The Job's plot analysis using ^1H NMR confirmed the 1:2 stoichiometry for **5** and F^- interaction (Supporting Information, Figure S33).

The interaction of **5** with F^- ion was investigated by absorption spectroscopy. Upon addition of increasing amounts of F^- ion to compound **5**, a slight increase in the intensity of the absorption band with almost no shift in the peak maxima was observed indicating that absorption spectroscopy is not a very useful tool for studying **5** and F^- interaction. However, we observed significant changes in the fluorescence spectrum of compound **5** on binding with F^- ion. Figure 6 shows the fluorescence spectral changes of **5** in CH_2Cl_2 upon addition of increasing amounts of F^- ion and the spectra were recorded after 5 minutes. It is clear from Figure 6 that its intense fluorescence peak at 565 nm is nearly quenched upon addition of 30 equiv of F^- to compound **5**. Inset in Figure 6 shows the plot of the fluorescence intensity at 565 nm versus the molar equivalents of F^- ion used in the titration which also indicates that the fluorescence intensity reaches a plateau upon addition of 30 equiv of F^- ion. Furthermore, when excess amount of F^- ion was added, we did not observe any further changes in the fluorescence intensity and compound **5** is stable. The significant change in the fluorescence spectrum of compound **5** was noted upon addition of around 2 equiv of F^- ion, and the detection limit for F^- ion is between 0.020 and 0.035 mM under our experimental conditions. The Job plot analysis using fluorescence spectroscopy also supported 1:2 stoichiometry for **5** and F^- ions interaction (Supporting Information, Figure S33). From the Benesi–Hildebrand equation, the binding constant of 18000 M^{-1} was evaluated for receptor–anion complexation. The formation of a hydrogen bond between pyrrole NH and F^- assists in the photoinduced electron transfer (PET) resulting in quenching of the fluorescence in compound **5**. Furthermore, the addition of 30 equiv of F^- ion to compound **5** changes the color of the solution from pink to faded pink, whereas in the presence of other anions such as Cl^-, Br^-, I^-, OH^-, AcO^-, ClO_4^-, $H_2PO_4^-$, there is no change in the pink color of compound **5** (Supporting Information, Figure S35). Attempts have been made to extract the bound F^- ion from the receptor by washing with water. However, the fluorescence signal of the original compound was not recovered, indicating the F^- ion is strongly bound to compound **5**.

The specific binding of **5** with F^- ion was further probed by following changes in the first reduction of compound **5** upon addition of F^- ion using cyclic and square wave voltammetric techniques. Figure 7 shows the systematic changes in the reduction wave of compound **5** on increasing addition of fluoride ion. As it is clear from Figure 7, the increasing addition of F^- ion to **5** resulted in a shift of potential toward less negative by 150 mV indicating that F^- ions binding to dipyrromethanyl moieties of **5** make the boron-dipyrromethene unit of **5** more electron deficient, and hence it undergoes reduction at a lower potential. No change in the reduction of **5** was observed on addition of other anions. These results indicate that **5** can also be used as specific electrochemical sensor for fluoride ions.

■ CONCLUSIONS

We used our previously synthesized 3,5-bisformyl BODIPYs as key synthons to prepare novel 3,5-bis(dipyrromethanyl) BODIPYs in one step under simple reaction conditions. The compounds are stable and possess decent photophysical properties. The spectral and electrochemical properties of 3,5-bis(dipyrromethanyl) BODIPYs indicated that dipyrromethanyl groups are less electron deficient than formyl groups and alter the properties of BODIPYs moderately. The presence of four pyrrole NH groups however are very useful for binding of anions, and our studies showed that these systems exhibit specific selectivity for F^- ion over other anions as verified by NMR, fluorescence, and electrochemical properties. Furthermore, BODIPYs containing two dipyrromethanyl groups are interesting synthons for the synthesis of several novel compounds including macrocycles, and such synthetic efforts are presently underway in our laboratory.

■ EXPERIMENTAL SECTION

General Experimental. The chemicals such as $BF_3{\cdot}Et_2O$, 2,3-dichloro-5,6-dicyano-1,4- benzoquinone (DDQ) were used as

dx.doi.org/10.1021/ic202758r | Inorg. Chem. 2012, 51, 4285–4292

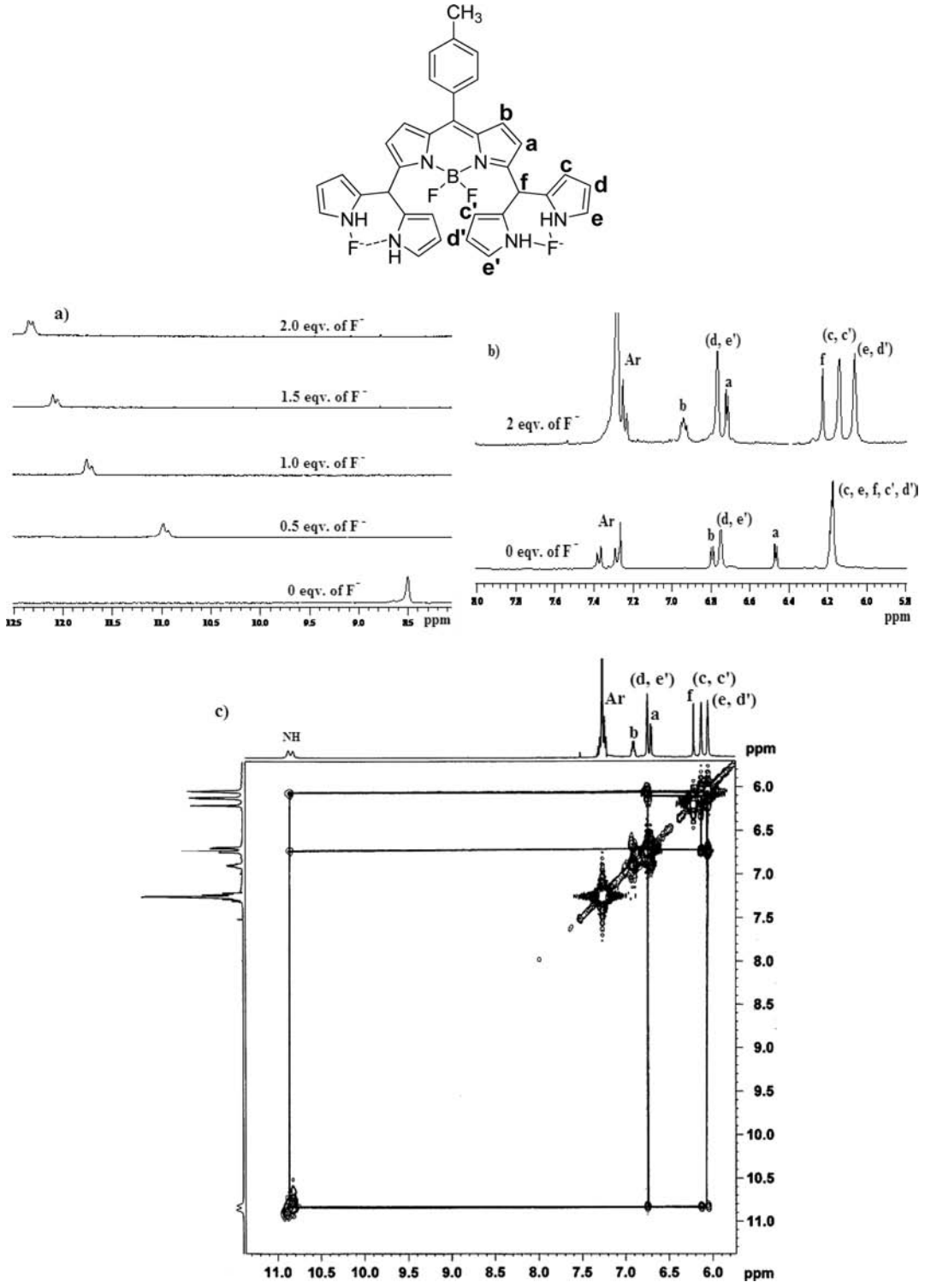

Figure 5. ^{1}H NMR spectra of **5** (1.3×10^{-2} M) in the presence of different concentrations of F^{-} ions. Concentrations of F^{-} ion was varied from 0 to 2.0 equiv. (a) The effect on NH protons; (b) the effect on pyrrole and aryl protons; and (c) ^{1}H−^{1}H COSY spectrum of compound **5** + F^{-} in $CDCl_3$.

obtained from Aldrich. All other chemicals used for the synthesis were reagent grade unless otherwise specified. Column chromatography was performed on silica (60−120 mesh). The ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker 400 MHz instrument using tetramethylsilane ($Si(CH_3)_4$) as internal standard. ^{1}H−^{1}H COSY experiments were performed on a Bruker 400 MHz instrument. 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 ThermoQuest microanalysis instrument, and the FTIR spectra were measured on Perkin−Elmer spectrometer using KBr pellets. The fluorescence quantum yields (Φ_f) were estimated from the emission and absorption spectra by a comparative method at the excitation wavelength of 488 nm using Rhodamine 6G (Φ_f = 0.88)[15] as standard. The time-resolved fluorescence decay measurements were carried out at a magic angle using a picosecond diode laser based time correlated single photon counting (TCSPC) fluorescence spectrometer from IBH, UK. All the

dx.doi.org/10.1021/ic202758r | Inorg. Chem. 2012, 51, 4285−4292

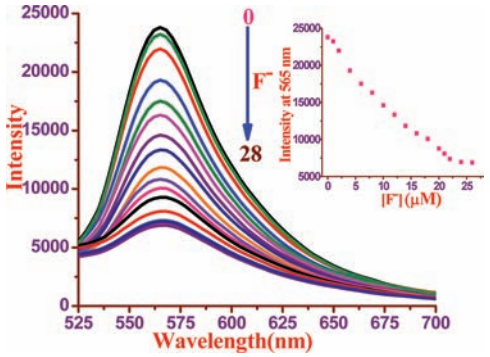

Figure 6. Quenching of fluorescence intensity of compound **5** (5 μM) during the titration with F^- (TBAF). The molar equivalents of TBAF used were 0, 1, 2, 4, 6, 8, 10, 12, 14, 16, 17, 18, 20, 22, 24, 26, and 28. The inset shows a linear-correlation plot between the intensity at 565 nm versus $[F^-]$ (μM).

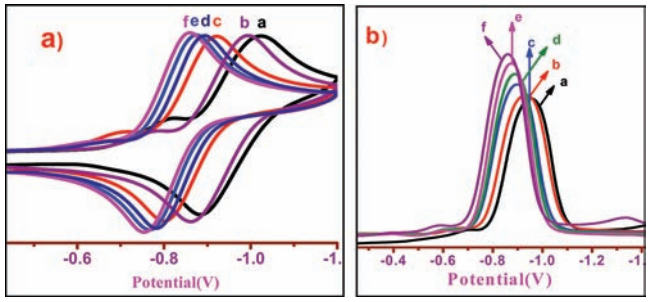

Figure 7. (a) Cyclic voltammograms and (b) square wave voltammograms of **5** (1.3×10^{-2} M) in the presence of different amounts of F^- ion. The F^- concentration is (a) 0, (b) 0.5, (c) 1.5, (d) 2.0, (e) 2.5, and (f) 3.0 mM, respectively.

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 (TBAP) as supporting electrolyte. Half wave potentials were measured using differential pulse voltammetry (DPV) and also calculated manually by taking the average of the cathodic and anodic peak potentials. The HR mass spectra were recorded with a Q-Tof micro mass spectrometer. For UV–vis and fluorescence titrations, the stock solution of compound **5** (5×10^{-6} M) was prepared by using spectroscopic grade $CHCl_3$. The association constant of the anion complex formed in solution has been estimated by using the standard Benesi–Hildebrand equation, viz.,

$$\frac{1}{I - I_0} = \frac{1}{I_1 - I_0} + \frac{1}{(I_1 - I_0)K_a[A^-]}$$

where I_0 is the intensity of the compound **5** before addition of anion, where I is the intensity in the presence of A^-, I_1 is intensity upon saturation with A^-, and K_a is the association constant of the complex formed. The Bu_4NF solution was prepared (1×10^{-2} M) in $CHCl_3$. The solution containing compound **5** was placed in a quartz cell (1 cm width), and Bu_4NF solution was added in an incremental fashion. Their corresponding UV–vis and fluorescence spectra were recorded at 298 K. In ^1H NMR titration, the spectra were measured on 400 MHz NMR spectrometer. A solution of **5** in $CDCl_3$ was prepared (5×10^{-3} M), and a 0.4-mL portion of this solution was transferred to a 5-mm NMR tube. A small aliquot of Bu_4NF in $CDCl_3$ was added in an incremental fashion, and their corresponding spectra were recorded.

General Procedure for 3,5-Bis(dipyrromethane)-BODIPYs (5–8). $BF_3{\cdot}Et_2O$ (0.175 mmol) was added to a solution of corresponding BODIPYs **1–4** (1.75 mmol) and pyrrole (70 mmol) in dichloromethane (100 mL) under N_2 atmosphere. The reaction was stirred at room temperature for 15 min. The reaction mixture was washed with 0.1 M NaOH solution and water thoroughly. The combined organic layers were dried over Na_2SO_4 and filtered. The pyrrole was evaporated under a vacuum to give dark red oil. The crude product was purified using silica gel column chromatography with petroleum ether/ethylacetate (80:20) and afforded pure 3,5-bis-(dipyrromethane)-BODIPYs **5–8** as a red solid.

3,5-Bis(dipyrromethanyl)-8-(Tolyl)- 4-bora-3a,4a-diaza-*s*-indacene (5). Yield: 88 mg, 62%. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.44 (s, 3H; $-CH_3$), 6.17–6.18 (m, 9H; py), 6.46 (d, ^3J (H, H) = 4.27 Hz, 2H; py), 6.74 (m, 5H; py), 6.79 (d, ^3J (H, H) = 4.27 Hz, 2H; py), 7.28 (d, ^3J (H, H) = 7.94 Hz, 2H; Ar), 7.38 (d, ^3J (H, H) = 8.25 Hz, 2H; Ar), 8.47 (br s, 4H; NH). ^{11}B NMR (128.3 MHz, $CDCl_3$, δ in ppm): 1.41 (t, ^1J (B–F) = 34 MHz, 1B). ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −135.4 (q, ^1J (F–B) = 35 MHz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.6, 29.9, 37.8, 107.2, 108.8, 117.9, 118.7, 129.3, 129.6, 130.5, 131.2, 159.9. HRMS. Calcd for $C_{34}H_{29}BF_2N_6$ $[(M + 1)^+]$: m/z 571.2593. Found: m/z 571.2586. IR (KBr, ν_{max}): 532.1, 726.4, 746.1, 769.3, 887.3, 956.6, 1027.7, 1126.3, 1174.8, 1250.5, 1312.6, 1347.7, 1434.2, 1511.1, 1546.8, 1578.6, 1603.3, 1713.5, 3423.7. Anal. Calcd for $C_{34}H_{29}BF_2N_6$: C, 71.59; H, 5.12; N, 14.73. Found: C, 71.50; H, 5.34; N, 14.65.

3,5-Bis(dipyrromethanyl)-8-(4-bromophenyl)- 4-bora-3a,4a-diaza-*s*-indacene (6). Yield: 150 mg, 53%. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.17–6.19 (m, 10H; py), 6.48 (d, ^3J (H, H) = 4.58 Hz, 2H; py), 6.74 (m, 6H; py), 7.35 (d, ^3J (H, H) = 8.55 Hz, 2H; Ar), 7.63 (d, ^3J (H, H) = 8.55 Hz, 2H; Ar), 8.48 (br s, 4H; NH). ^{11}B NMR (128.3 MHz, $CDCl_3$, δ in ppm): 1.36 (t, ^1J (B–F) = 34 MHz, 1B). ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −135.5 (q, ^1J (F–B) = 33.5 MHz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 37.9, 61.3, 63.8, 66.2, 107.3, 108.8, 117.9, 119.1, 125.1, 129.4, 130.8, 131.8, 132.7, 133.6, 143.1, 160.7. HRMS. Calcd for $C_{33}H_{26}BrBF_2N_6$ $[(M + 1)^+]$: m/z 635.1542. Found: m/z 635.1544. IR (KBr, ν_{max}): 573.6, 718.7, 777.2, 884.6, 973.3, 1008.4, 1060.7, 1120.4, 1263.3, 1305.5, 1339.1, 1432.6, 1485.9, 1547.2, 1570.4, 1637.6, 1718.5, 3357.4. Anal. Calcd for $C_{33}H_{26}BrBF_2N_6$: C, 62.39; H, 4.12; N, 13.23. Found: C, 62.12; H, 4.38; N, 13.12.

3,5-Bis(dipyrromethanyl)-8-(4-methoxyphenyl)- 4-bora-3a,4a-diaza-*s*-indacene (7). Yield: 88 mg, 79%. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.90 (s, 3H; -OCH_3), 6.18 (m, 9H; py), 6.48 (m, 2H; py), 6.75 (m, 5H; py), 6.82 (m, 2H; py), 7.01 (d, ^3J (H, H) = 6.42 Hz, 2H; Ar), 7.46 (d, ^3J (H, H) = 6.72 Hz, 2H; Ar), 8.47 (br s, 4H; NH). ^{11}B NMR (128.3 MHz, $CDCl_3$, δ in ppm): 1.39 (t, ^1J (B–F) = 33 MHz, 1B). ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −135.3 (q, ^1J (F–B) = 33 MHz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 37.8, 55.6, 107.2, 108.8, 114.1, 117.8, 118.6, 126.4, 129.7, 131.1, 132.2, 133.8, 144.9, 159.6, 161.7. HRMS. Calcd for $C_{34}H_{29}BF_2N_6O$ $[(M + 1)^+]$: m/z 587.2542. Found: m/z 587.2554. IR (KBr, ν_{max}): 536.0, 721.1, 740.5, 778.8, 886.4, 975.1, 1028.4, 1129.5, 1179.3, 1256.5, 1306.7, 1341.2, 1434.9, 1509.7, 1547.0, 1577.2, 1603.7, 1709.1, 3412.1. Anal. Calcd for $C_{34}H_{29}BF_2N_6O$: C, 69.63; H, 4.98; N, 14.33. Found: C, 69.72; H, 4.83; N, 14.15.

3,5-Bis(dipyrromethanyl)-8-(3,4,5-trimethoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (8). Yield: 88 mg, 58%. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.85 (s, 6H; -OCH_3), 3.93 (s, 3H; -OCH_3), 6.17–6.19 (m, 9H; py), 6.49 (d, ^3J (H, H) = 4.28 Hz, 2H; py), 6.75 (m, 7H; py+Ar), 6.87 (d, ^3J (H, H) = 4.27 Hz, 2H; py), 8.47 (br s, 4H; NH). ^{11}B NMR (128.3 MHz, $CDCl_3$, δ in ppm): 1.37 (t, ^1J (B–F) = 33 MHz, 1B). ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −135.3 (q, ^1J (F–B) = 33.5 MHz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 22.9, 29.9, 37.9, 56.5, 61.2, 107.3, 108.0, 108.9, 117.9, 118.8, 129.3, 129.6, 131.1, 133.7, 153.2, 160.3. HRMS. Calcd for $C_{36}H_{33}BF_2N_6O_3$ $[(M + 1)^+]$: m/z 647.2754. Found: m/z 647.2783. IR (KBr, ν_{max}): 534.1, 720.8, 740.1, 772.8, 879.4, 971.3, 1028.7, 1130.4, 1173.6, 1251.8, 1306.1, 1344.8, 1433.7, 1509.1, 1541.9, 1576.7, 1607.5,

dx.doi.org/10.1021/ic202758r | Inorg. Chem. 2012, 51, 4285–4292

1713.8, 3375.7. Anal. Calcd for $C_{36}H_{33}BF_2N_6O_3$: C, 66.88; H, 5.14; N, 13.00. Found: C, 66.75; H, 5.32; N, 13.13.

■ ASSOCIATED CONTENT

Supporting Information

Characterization data for all new compounds. Absorption, fluorescence, Job's plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.R. thanks Board of Research in Nuclear Sciences (BRNS) for financial support, and S.M. thanks IIT-Bombay for a fellowship.

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