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ARTICLE TYPE

Triarylborane-Dipyrromethane Conjugates Bearing Dual Receptor Sites: Synthesis and Evaluation of Anion Binding Site Preference

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Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Synthesis and optical properties of four new triarylborane–dipyrromethane (TAB-DPM) conjugates (**3a-d**) containing dual binding sites (hydrogen bond donor and Lewis acid) have been reported. The new compounds exhibit selective fluorogenic response towards F^- ion. The NMR titrations show that the anions bind to TAB-DPM conjugates via the Lewis acidic triarylborane centre in preference to hydrogen bond donor (dipyrromethane) units.

Introduction

Fluoride ion is well known for its advantageous (e.g. dental care, anesthetics, osteoporosis and psychiatric drugs)[1-4] and injurious (water contamination[5] and chemical warfare agent[6]) role in both health care and environment. Synthesis of selective sensors for fluoride detection has become an important area of current research. In the past three decades, numerous hydrogen bond donor based fluoride sensors such as oligopyrrole[7], amide[8], indolocarbazole[9], guanidium cation[10], imidazolium cation[11] and urea/thiourea[12] have been reported. Anion receptors such as organostannanes[13], organosilanes[14] and organostibanes[15] have also received considerable attention owing to their high selectivity towards fluoride ion. Recently pnictonium[16] ions have been employed for the detection of fluoride ion in aqueous medium.

Owing to their inherent Lewis acidity, triarylboranes[17] have received much attention in recent decades. Several boron containing Donor-Acceptor (D-A) dyads[18], boron containing polyaryls[19], boryl appended metallocenes[20] and conjugated[21]/non-conjugated[22] boron containing polymers have been investigated for fluoride ion binding studies. Gabbai et al elegantly demonstrated the utility of ammonium[23]/phosphonium[24] ion decorated triarylboranes for the detection of fluoride/cyanide. Though several H-bond donor based and Lewis acid based fluoride sensors are known in the literature, the dual Lewis acid/hydrogen-bond donor receptors have not been reported[25].

Recently we became interested in developing colorimetric sensor for fluoride and cyanide ions.[26] As a part of the ongoing program we have synthesized triarylborane–dipyrromethane (TAB-DPM) conjugates which can act as dual receptor (containing Lewis acidic boron and H-bonding N-H binding sites) for fluoride detection and studied their optical properties. The results of these studies are reported in this paper.

Results and Discussion

Synthesis and Spectral Characterisation

The protocol employed for the synthesis of compounds **3a**, **3b**, **3c** and **3d** is shown in Scheme 1. Reaction of substituted aryl bromides (2-bromo-4-(diethoxymethyl)benzene for **2a**, 1-bromo(4-(diethoxymethyl)benzene for **2b**, 2-bromo-4-(1,1-diethoxyethyl)benzene for **2c** and 1-bromo-4-(1,1-diethoxyethyl)benzene for **2d** with n-BuLi and $BMes_2F$ followed by acidification gave the key precursors **2a**, **2b**, **2c** and **2d**. The Lewis acid catalyzed condensation reaction of pyrrole with corresponding boryl functionalized benzaldehyde/acetophenone (**2a-d**) afforded the target compounds **3a**, **3b**, **3c** and **3d**.

Compounds **3a**, **3b**, **3c** and **3d** are colourless solids and soluble in common organic solvents. All the compounds were characterized by NMR (^1H, ^{13}C, ^{11}B) and high resolution mass spectrometry (HRMS). The C-H and N-H proton signals of pyrrole moiety for **3c** and **3d** are upfield shifted compared to the corresponding resonances for **3a** and **3b**. The ^{11}B NMR shifts also follow the same trend. This may be due to the positive inductive effect of the methyl group at the meso-carbon of **3c** and **3d.** The structure of **3c** was confirmed by single crystal X-ray diffraction studies.

Single Crystal X-ray Diffraction Studies

The molecular structure of **3c** is shown in Figure 1. The asymmetric unit cell of **3c** contains two crystallographically distinct molecules. The geometrical parameters of both the molecules are almost the same. The boron centre in BAr_3 unit adopts trigonal planar geometry with the sum of C-B-C angles being 360° which is in-line with the reported values for related triarylboranes[27]. The dihedral angle between the B-C(ipso)$_3$ plane and spacer -C_6H_4 is 72.5°. In the solid state the intermolecular N-H---π (centre of pyrrole unit) interaction between the

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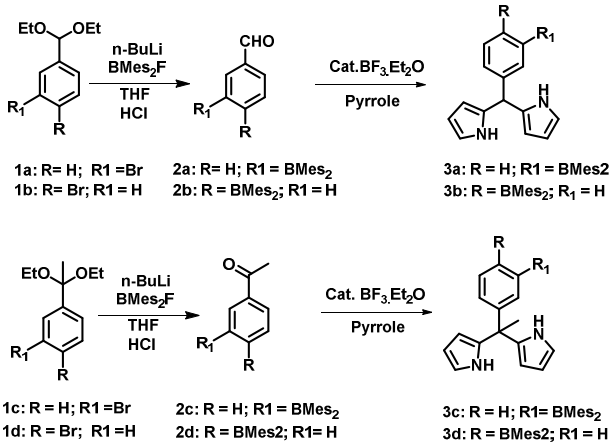
neighboring molecules generates an interesting 3D supramolecular structure. The Me groups on -$BMes_2$ unit effectively protrude into the hydrophobic voids present in the 3D structure. (The relevant data and figure are given in ESI).



Scheme 1: Synthesis of 3a – 3d

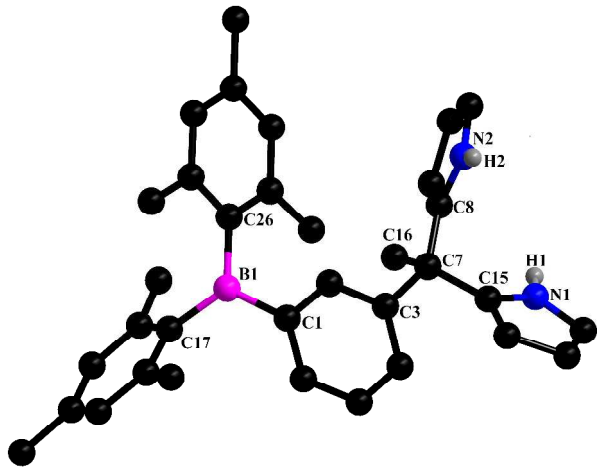


Figure 1: Molecular structure of **3c**

Table 1: Bond angles and bond lengths of **3c** obtained from single crystal X-ray diffraction studies

Bond length (Å)		Bond angle (º)	
B1-C1	1.560(4)	C1-B1-C26	115.3(2)
B1-C26	1.574(5)	C1-B1-C17	122.3(2)
B1-C17	1.574(4)	C17-B1-C26	122.2(2)
C3-C7	1.538(4)	C15-C7-C3	108.1(2)
C15-C7	1.518(4)	C8-C7-C16	108.0(2)
C8-C7	1.510(3)	C8-C7-C3	111.7(2)
C16-C7	1.538(4)	C16-C7-C15	109.5(3)

Optical Properties

UV-visible and fluorescence spectra of compounds **3a-d** are shown in Figure 2. The absorption spectra show two major bands corresponding to the dominant π-p_π (B) transition (~318 nm) and $\pi \rightarrow \pi^*$ transition (~260 nm) respectively. Upon excitation at ~315 nm, dichloromethane solutions of **3a-d** show single broad emission band with maxima at 470 nm with stokes shift of ~152 nm. The fluorescence quantum yields of **3a-d** are in the range, 0.30-0.41. The fluorescence emission maxima of **3b** (498 nm) is ~20 nm red shifted compared to that of **3a** (469 nm), **3c** (464 nm) and **3d** (470 nm). This is remarkable considering their structural similarities. Fluorescence studies were carried out in solvents with different polarities (Figure S15- Figure S18). The absorption and emission profile of **3b** is sensitive to solvent polarity while the other compounds do not show any changes in their optical properties.

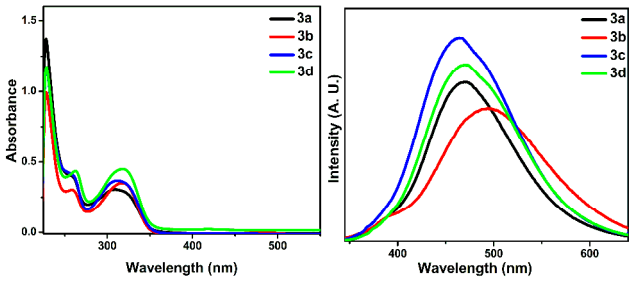


Figure 2: Comparison of absorption (left) and emission (right) spectra of dichloromethane solutions of **3a-d** (1×10^{-5}M), λ_{ex} = 315 nm.

Table 2: Photophysical Properties of triarylborane–dipyrromethane (TAB-DPM) conjugates (**3a-d**)

Compound	λ_{abs}(nm) (ε/M^{-1} cm^{-1})	λ_{em} (nm)	Q_F
3a	310 (3.1×10^4) 260 (3.9×10^4)	469	0.38
3b	318 (3.5×10^4) 258 (3.0×10^4)	498	0.30
3c	312 (3.7×10^4) 260 (4.1×10^4)	464	0.41
3d	318 (4.5×10^4) 262 (4.4×10^4)	470	0.39

[a]Quinine sulfate was used as the reference dye (Φ = 0.58 in 0.1 M H_2SO_4) for the measurement of Φ_F

The Lippert–Mataga plot[4b] was derived for all the four compounds using the relationship between solvent polarity parameter Δf and Stoke shift $\Delta \nu$ (eq-1). The excited state dipole moments are higher than the ground state dipole moments. The larger value for the change in dipole moment ($\Delta\mu$) for **3b** clearly indicates that CT characteristics are stronger for **3b** compared to **3a, 3c** and **3d**. TD-DFT optimization results showed significant reorganisation of the pyrrole units with respect to $BMes_2$ unit. Hence, the large Stokes shift observed for **3a-d** are due to significant geometric rearrangements in their excited states. The distinct behavior of **3b** (larger Stokes shift compared to **3a**, **3c** and **3d**) is possibly due to the combination of both CT and excited state structural reorganizations.

$$(\nu_a - \nu_f) = [2\Delta\mu^2 / hca_o^3]\,\Delta f + A \quad \text{----- eq 1}$$

$\Delta\mu$ is the electric dipole moment change upon an electronic transition ($\Delta\mu$) μg - μe, where μg and μe are the dipole moments in the ground and excited states, respectively and, h, c, a_O, and A are the Planck's constant, the speed of light, the Onsager radius of **3a-d** (since we don't have crystal structure for **3a**, **3b** and **3d**, a value is assumed as ~8.16 Å based on crystal structure of **3c**), and

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a constant, respectively.

$$\Delta f = [Ds - 1/2Ds + 1] - [n^2 - 1/2n^2 + 1]$$

where *D*s and *n* are the dielectric constant and refractive index of the solvent, respectively.

Table 3: Excited state and ground state dipole moments of **3a-d**

Compounds	(μ_g) (D)[a]	(μ_e) (D)	μ_e- μ_g (D)
3a	1.2	~7.1	~5.8
3b	1.8	~8.9	~7.1
3c	1.7	~7.5	~5.8
3d	1.7	~7.9	~6.1

[a]ground state dipole moment obtained from DFT

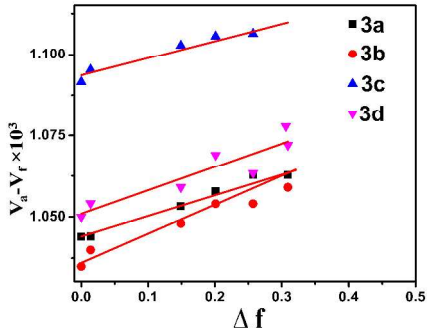

Figure 3. Lippert-Mataga plots for 3**a-d**.

Anion Binding Studies

All the compounds showed similar changes in absorption profile in the presence of fluoride ions (Figure 3 and supporting information). Upon addition of fluoride ion, the intensity of characteristic boryl absorption band at 315 nm decreased; concomitantly the intensity of the band at ~230 nm ($\pi \rightarrow \pi^*$ absorption of mesitylene unit) increased. This indicates that the coordination of the F^- ion to the boron centre of triarylborane moiety disrupts the $\pi \rightarrow p_\pi$ conjugation between the boron centre and the attached π conjugated system. These results are in line with those reported for TABs[17]. Fluorescence emission studies revealed that upon addition of TBAF, the broad emission band of **3a**, **3b**, **3c** and **3d** show gradual quenching as observed for triarylborane based fluoride sensors.

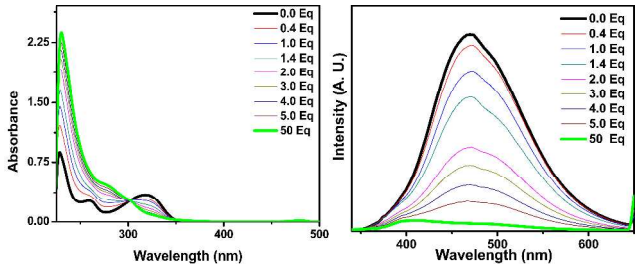

Figure 4: Absorption (left) and emission (right) spectra of **3b** (10 μM in CH_2Cl_2, λ_{ex} = 315 nm) in the presence of TBAF(1×10^{-3} M)

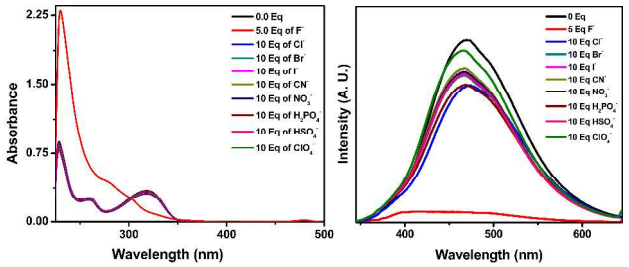

Figure 5: Absorption (left) and emission (right) spectra of **3b** (10 μM in CH_2Cl_2, λ_{ex} = 315 nm) in the presence of various anions (1×10^{-3}M)

Table 4: Stern–Volmer quenching constant of **3a-d**

Compounds	Quenching constant(K_{SV})
3a	1.8×10^5
3b	1.3×10^5
3c	1.6×10^5
3d	2.3×10^5

High selectivity is mandatory for a superior sensor. Achieving high selectivity for anions of interest over other potentially competing species is an challenging task in the area of anion probe development. To evaluate the selectivity of the new hybrid sensors **3a**, **3b**, **3c** and **3d,** spectrophotometric titrations were carried out in the presence of various anions (Figure 4 and ESI). As depicted in Figure 3, only the addition of F^- resulted in prominent decrease in fluorescence intensity at ~480 nm, whereas addition of an excess of anions such as Cl^- and $H_2PO_4^-$ caused very little change in the emission spectra. Other competing anions such as Br^-, I^-, NO_3^-, HSO_4^-, ClO_4^- and CN^- caused almost no changes in the emission intensity. This is quite remarkable considering the possible hydrogen bonding interaction between N-H of DPM unit of the host and the guest anions. This shows that the compounds **3a-d** are highly selective towards fluoride ions. The quenching constants of **3a-d** were calculated from Stern–Volmer plot (ESI and Table 4). The results indicate that **3d** shows the highest Stern–Volmer quenching constant (K_{SV}) and **3b** the least. Thus **3d** is the superior fluoride sensor among these four compounds.

NMR Titrations

To get further insight into the anion binding event, the ^{19}F and ^1H NMR titrations were carried out in $CDCl_3$. In ^{19}F NMR titrations (5×10^{-2} M), upon addition of TBAF to **3a-d**, a new peak at -172 ppm corresponding to F-BAr_3 was observed[28]. Addition of more than 1.25 Eq of fluoride ion gave rise to an additional peak at −81 ppm corresponding to F···H-N-R unit. Based on these results one can tentatively conclude that the initially fluoride prefers to bind at the triarylboron centre rather than the hydrogen bonding donor sites (dipyrromethane) in **3a-d**. However, the intensity of the peak corresponding to R_3B-F is still growing (with onset of peak corresponding to N-H—F) upon addition of more than 1eq of fluoride source. Addition of 1 eq of TBAF also resulted in a down-field shift of the N-H resonance of the receptors. The ^1H and ^{19}F NMR data show that there is a competition between the two binding sites (Ar_3B and pyrrole N-H), with exchange of the F^- anion between them. Thus, NMR data do not exclude the possibility of binding of fluoride to N-H units before saturating the Ar_3B moiety. The ^1H and ^{19}F NMR data also

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indicate that titration of the receptors 3**a-d** is complete when 3 eq of F^- were added. This result is consistent with one B-F and two N-H...F interactions (Chart 1 '**A'**).

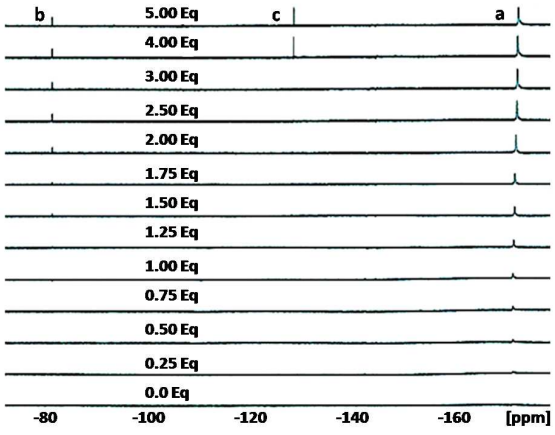

Figure 6: ^{19}F NMR titration spectra of **3b** solution in $CDCl_3$ (5×10^{-2}M) against increasing TBAF (2.1 M in $CDCl_3$) (0 to 5 Eq). **a** represents resonance of F- BAr_3, **b** represents resonance of N-H···F and **c** represents resonance of the anion source TBAF.

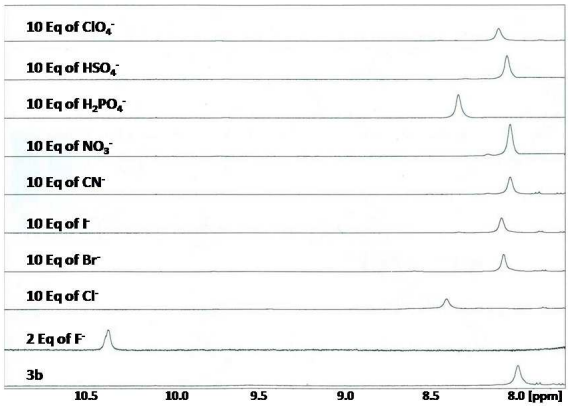

Figure 7: ^1H NMR of **3b** (5×10^{-2} M in $CDCl_3$) with various anions (2.1 M in $CDCl_3$)

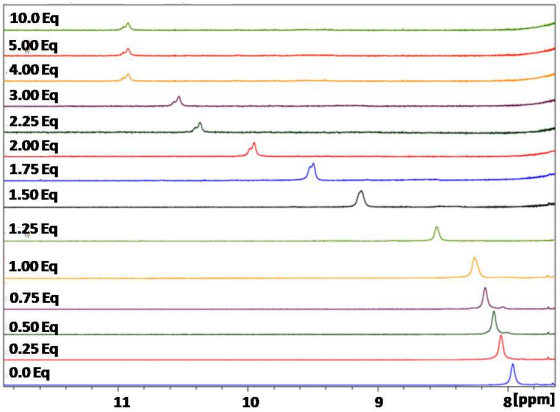

Figure 8: ^1H NMR titration spectra of **3b** solution in $CDCl_3$ (5×10^{-2}M) against increasing TBAF (2.1 M in $CDCl_3$) (0 to 10 Eq) – N-H region

To gain further insight into the possible fluoride adducts, variable temperature ^1H and ^{19}F NMR titrations were carried out in the range 20 to -50°C in $CDCl_3$. The ^1H NMR spectrum of a 1:1 mixture of receptor and TBAF shows a broad N-H signal at 8 ppm, which becomes sharp upon decreasing the temperature from 20 to -50 °C. For the 1:3 mixtures of receptor (1 eq) and TBAF (3 eq), this signal (at 8 ppm) is shifted down-field (**3a**: 10.3, **3b** is 11.0, **3c** is 10.3 and **3d** is 10.9 ppm) at 20° C. This signal is further shifted down-filed and progressively broadened upon decreasing the temperature from 20 to -40 °C. At -50° C this peak could not be observed. A new triplet at 16 ppm with a coupling constant of 123 Hz is appeares in the temperature range -10 to -50 ° C. The chemical shift and the coupling constant of this new peak are close to those observed for F_2H^- species reported elsewhere[34]. One can envisage the formation of HF_2 by two different routes. (1) reaction of adventious water in the medium with the fluoride source (ii) deprotonation of C-H of triarylmethine units in receptors **3a-b** . The observation of the signal corresponding to triarylmethine units in the ^1H NMR spectra of **3a-b** under titration conditions, excludes the possibility of C-H deprotonation (Figure S72 and S73). Hence the only plausible interpretation of the new triplet at 16 ppm is the formation HF_2^- ion due to adventious water in the medium[35]. This inference is also consistent with results of variable temperature ^{19}F NMR measurements carried out for 1:3 mixtures of receptor and TBAF. The proton coupled ^{19}F NMR shows two ^{19}F signals at -80.5 (doublet, $J_{N\text{-}H\text{-}F}$ = 54 Hz for **3a**, 53 Hz for **3b**, 53 Hz for **3c** and 53 Hz for **3d**) and broad signal at -172 ppm respectively. In proton decoupled experiment, compounds **3a-d** give rise to a singlet at -80.5 ppm, but there is no change in the peak at -172 ppm at 20 °C. Thus, the signal at -172 is assigned to Ar_3B-F unit and the peak at -80 ppm is attributed to N-H---F unit (Figure S37 to S44). Upon decreasing the temperature from 20 °C to -50 °C, in addition to -80 and -172 ppm peaks, a new signal at -156 ppm gradually gained in intensity and the peak at -172 disappeared completely. In proton decoupled ^{19}F NMR titrations, the peak at -156 ppm shows two singlets at -154 and -155 ppm respectively, whereas in proton coupled ^{19}F NMR spectrum, the peak at -154 become doublet ($J_{H\text{-}F}$ = 123 Hz) and the signal at -155 ppm remains singlet in the same region. The signal at -155 is attributable to Ar_3B-F and the doublet at -154 ppm is attributed to F_2H^-. As reported elsewhere the signal corresponding to F_2H^- ion could be observed only at low temperatures[36].

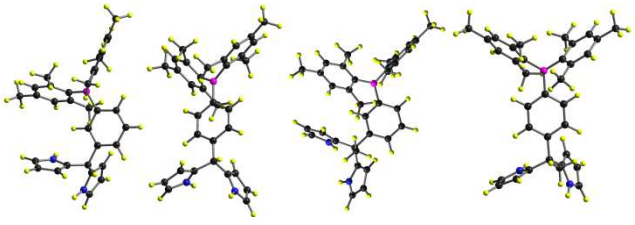

Figure 9: DFT B3LYP/6-31G(d) optimised structures of **3a-d** (from left to right respectively; Colour codes, C = Black, H = Yellow, N = Blue, B = Magenta)

DFT Computational Studies:

To understand the electronic structure of **3a-d**, DFT computational studies were performed. The hybrid B3LYP

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functional[30] has been used in all computations as incorporated in *Gaussian 09* package,[31] mixing the Hartree-Fock-type exchange with Becke's exchange functional[32] as proposed by Lee-Yang-Parr for the correlation contribution[33] We have considered 6-31G(d) basis set for all the atoms. Visualizations of the optimized structures and the MOs were performed using *Gaussview5.0*. The harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima. TD-DFT vertical excitation calculations were performed for **3a-d** based on their ground state optimized structures.

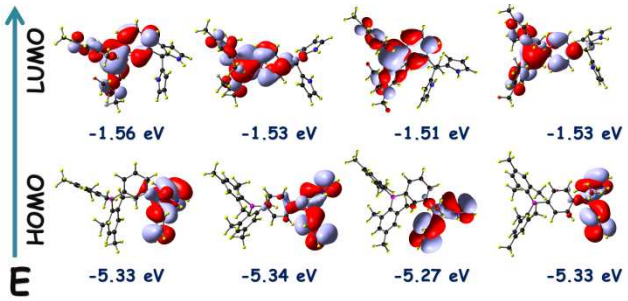

Figure 10: DFT B3LYP/6-31G(d) obtained FMOs (Frontier molecular orbitals) of **3a-d** (from left to right respectively, isovalue = 0.02)

The ground state optimized structures for compound **3a-d** are shown in figure 9. Evidently, the opposite orientations of the neighboring pyrrole moieties are consistent with the X-ray crystal structure of **3c**. The FMOs of the compounds are localised on individual chromophoric units indicating virtually no electronic communication between the two individual moieties. However, the HOMOs **3a-d** are concentrated on the pyrrolic moieties and the LUMOs are localised on the triarylborane moieties which apparently indicates the possibility of a dipyrromethane to $BMes_2$ (i.e. HOMO→LUMO) charge transfer process (~380-390 nm). However, TD-DFT (†ESI) vertical excitation calculations show that these transitions have low oscillator strengths with respect to $BMes_2$ centered π-pπ* transitions at ~350 nm and thus appears only as a very weak feature in their UV-Vis absorption spectra. The HOMO-LUMO band gaps (Figure 10) for **3a-d** are close to each other which would explain their identical UV-Vis absorption profile.

Conclusions

We have successfully synthesized and characterized four triarylboron decorated dipyrromethanes (**3a, 3b, 3c** and **3d**). Their anion sensing abilities were studied using UV/visible, fluorescence and NMR (^{1}H and ^{19}F) spectroscopy. DFT computational studies show that the individual chromophores in **3a-d** are electronically isolated. The new conjugates exhibit high selective response towards fluoride ions compared to other anions. The NMR measurements show that there is a competition between the two binding environments (Ar_3B and pyrrole N-H), with exchange of the F- anion between them.

Experimental Section

Methods and Materials

n-butyllithium (1.6 M in hexane), 3-bromobenzaldehyde, 4-bromobenzaldehyde, 1-(3-bromophenyl)ethanone, 1-(4-bromophenyl)ethanone, were purchased from Avra chemicals(India) and pyrrole was purchased from SRL (India). All reactions were carried out under an atmosphere of purified nitrogen using Schlenck techniques. THF and pyrrole were distilled over sodium. Chlorinated solvents were distilled over CaH_2 and subsequently stored over 4Å molecular sieves. The NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. All solution ^{1}H and ^{13}C spectra were referenced internally to the solvent signal. ^{11}B and ^{19}F NMR spectra were externally referenced to $BF_3.Et_2O$ (δ=0) in C_6D_6.UV-Visible absorption data were acquired on Lambda 750-Perkin Elmer UV-visible spectrophotometer. Solutions were prepared in a microbalance (± 0.1 mg) and volumetric glasswares and then charged in quartz cuvettes with sealing screw caps. Spectrophotometric titrations were performed on solutions of **3a**, **3b**, **3c** and **3d** in CH_2Cl_2. Tetrabutylammonium fluoride (TBAF) (1M) in THF, diluted in CH_2Cl_2 was added as the F- ion source and the absorption/fluorescence emission spectra of the samples were recorded. The excitation wavelength was λ_{ex} = 315 nm, the excitation and the emission slit widths were set at 3.0 nm, and the emission spectra were recorded. Absorption and emission spectra were recorded sequentially until no further changes were observed. Single-crystal X-ray diffraction studies were carried out with a Bruker SMART APEX diffractometer equipped with 3-axis goniometer. The data was integrated using SAINT, and an empirical absorption correction was applied with SADABS. The structure was solved by direct methods and refined by full matrix least-squares on F^2 using SHELXTL software[29]. All the non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms were refined isotropically on the positions calculated using a riding model. CCDC number for **3c:** 951177.

Synthesis of 1a

3-Bromobenzaldehyde (9.5 g, 51.41 mmol), triethylorthoformate (113.24 mmol) and catalytic amount of conc. HCl were dissolved in ethanol and the resultant solution was refluxed for 4 h. After all the 3-Bromobenzaldehyde was consumed, reaction mixture was brought to room temperature and extracted with mixture of cold water/ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The volatiles removed under reduced pressure afforded **1** as a colourless liquid. Yield: 14.2 g, 99%. ^{1}H NMR (399.99 MHz, $CDCl_3$) δ (ppm): 7.65 (s, 1H (*o*-Ph)), 7.35 (m, 2H (*o, m*-Ph)), 7.28 (d, *J* = 12 Hz 1H (*p*-Ph)) 5.48 (s, 1H (Methine C-H)), 3.76-3.63(m, 4H (-CH_2)), 1.28 (t, *J*= 6.8 Hz, 7.2 Hz, 6H (-CH_3)).

Synthesis of 1b

Compound **1b** was prepared following a procedure similar to that used for **1a.** The quantities involved and characterization data are as follows. 4-Bromobenzaldehyde (9.5 g, 51.41 mmol), triethylorthoformate (113.24 mmol), catalytic amount of con. HCl. Yield: 14.0 g, 98%. ^{1}H NMR (399.99 MHz, $CDCl_3$) δ (ppm): 7.49 (d, *J* = 6.8 Hz, 2H (*o*-Ph)), 7.35 (d, *J* = 8 Hz, 2H (*m*-Ph)), 5.46(s, 1H (Methine C-H)), 3.63-3.49(m, 4H (-CH_2)), 1.24 (t, *J*= 6.8 Hz, 7.2 Hz, 6H (-CH_3)).

Synthesis of 1c

Compound **1c** was prepared following a procedure similar to that used for **1a.** The quantities involved and characterization data are as follows. 3 – Bromoacetophenone (5.0 g, 25 mmol), $CH(OEt)_3$ (12.60 mL, 85 mmol), catalytic amount of HCl. Yield: 6.8 g,

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99%. ^{1}H NMR (399.99 MHz, $CDCl_3$), δ (ppm): 7.69 (s, 1H (*o*-Ph)), 7.44 (m, 2H (*o, m*-Ph)), 7.22 (d, J = 7.6 Hz, 1H (*p*-Ph)), 3.51-3.30 (m, 4H (-CH_2)), 1.52 (s, 3H (-CH_3)), 1.22 (t, J = 2.8 Hz, 7.2 Hz, 6H (-CH_3)).

Synthesis of 1d

Compound **1d** was prepared following a procedure similar to that used for **1a.** The quantities involved and characterization data are as follows. 4 – Bromoacetophenone (5.0 g, 25 mmol), $CH(OEt)_3$ (12.60 mL, 85 mmol), catalytic amount of HCl. Yield: 6.9 g, 99% ; ^{1}H NMR (399.99 MHz, $CDCl_3$), δ (ppm): 7.46 (d, J = 8 Hz, 2H (*o*-Ph)), 7.40 (d, J = 8 Hz, 2H (*m*-Ph)), 3.50-3.42 (m, 2H (-CH_2)), 3.37-3.29 (m, 2H (-CH_2)), 1.52 (s, 3H (-CH_3)), 1.23-1.18 (t, J = 4.8 Hz, J = 4.8 Hz, 6H (-CH_3)).

Synthesis of 2a

A solution of **1a** (2.5 g, 9.64 mmol) in dry THF was degassed by purging N_2 for 30 min followed by cooling to -78°C (Acetone/liq-N_2). *n*-butyllithium (6.6 mL (1.6 M solution in hexane), 10.61 mmol) was added over 30 min. After 1 h, a solution of bismesitylfluoroborane (2.9 g, 10.08 mmol) in 15 mL of dry THF was added over 10 min. The reaction mixture was allowed to warm to room temperature and stirring was continued for 12 h. After 12 h, 30 mL of 1N HCl was added and stirring was continued for another 4 h and extracted with ether. The combined organic layers were washed with brine solution and dried over anhydrous Na_2SO_4. Evaporation of the solvents under reduced pressure yielded crude product. Recrystallization of crude product in ethyl acetate gave pure **2a** as a colourless solid. Yield: 2.4 g, 64% ; ^{1}H NMR (399.99 MHz, $CDCl_3$), δ (ppm): 9.89 (s, 1H (-CHO)), 8.01 (m, 2H (*o*-Ph)), 7.77 (d, J = 6 Hz, 2H (*m*-Ph)), 7.53 (d, J = 7.2 Hz, 1H (*m*-Ph)) 6.83 (s, 4H (Mes C-H)), 2.31, 1.98 (s, 18H (Mes-CH_3)). ^{13}C NMR (100.00 MHz, $CDCl_3$), δ (ppm): 193.4, 142.5, 141.2, 139.7, 138.6, 136.6, 132.2, 129.3, 128.9, 23.9, 21.7. ^{11}B NMR (160 MHz, $CDCl_3$), δ (ppm): 75.7.

Synthesis of 2b

Compound **2b** was prepared following a procedure similar to that used for **2a.** The quantities involved and characterization data are as follows. Compound **1b** (2.5 g, 9.64 mmol), n-butyllithium (6.6 mL (1.6 M solution in hexane), 10.61 mmol), bismesitylfluoroborane (2.9 g, 10.08 mmol), 30 mL of 1N HCl. Recrystallization of crude product in ethyl acetate gave pure **2b** as a colourless solid. Yield: 2.0 g, 59%. ^{1}H NMR (399.99 MHz, $CDCl_3$), δ (ppm): 10.07 (s, 1H (-CHO)), 7.85 (d, J = 8 Hz, 2H (*o*-Ph)), 7.66 (d, J = 8 Hz, 2H (*m*-Ph)), 6.83 (s, 4H (Mes C-H)), 2.32, 1.98 (s, 18H (Mes-CH_3)). ^{13}C NMR (100.00 MHz, $CDCl_3$), δ (ppm): 193.3, 141.3, 139.9, 138.4, 136.4, 129.5, 128.8, 23.9, 21.7. ^{11}B NMR (160 MHz, $CDCl_3$), δ (ppm): 76.7.

Synthesis of 2c

Compound **2c** was prepared following a procedure similar to that used for **2a.** The quantities involved and characterization data are as follows. Compound **1c** (3.5 g, 12.81 mmol), *n* - butyllithium (8.8 mL (1.6 M solution in hexane), 14.09 mmol), bismesitylfluoroborane (4.1 g, 15.37 mmol), 20 mL of 2N HCl. Recrystallization of crude product in ethyl acetate gave pure **2c** as a colourless solid. Yield: 4.0 g, 85%. ^{1}H NMR (399.99 MHz, $CDCl_3$), δ (ppm): 8.07 (m, 2H (o, p-Ph)), 7.71 (d, J = 6.4 Hz, 1H (*o*-Ph)), 7.47 (d, J = 8 Hz, 1H (*m*-Ph)), 6.83 (s, 4H (Mes C-H)), 2.54 (s, 3H (-CH_3)), 2.31-1.98 (s, 18H (Mes-CH_3)). ^{13}C NMR (100.00 MHz, $CDCl_3$), δ (ppm): 199.2, 141.3, 139.6, 137.4, 136.3, 131.9, 128.9, 27.3, 24, 21.8. ^{11}B NMR (160 MHz, $CDCl_3$), δ (ppm): 71.7. HRMS (TOF-MS ES) m/z calcd for $C_{26}H_{29}BONa$ $(M + Na)^+$ 391.2209, found 391.2206.

Synthesis of 2d

Compound **2d** was prepared following a procedure similar to that used for **2a**. The quantities involved and characterization data are as follows. **1d** (3.5 g, 12.81 mmol), *n*-butyllithium (8.8 mL (1.6 M solution in hexane), 14.09 mmol), bismesitylfluoroborane (4.1 g, 15.37 mmol), dry THF (30 mL + 15 mL), HCl (20 mL, 2N). Recrystallization of crude product in ethyl acetate gave pure **8** as a colourless solid. Yield: 3.8 g, 80%. ^{1}H NMR (399.99 MHz, $CDCl_3$), δ (ppm): 7.90 (d, J = 8 Hz, 2H (o-Ph)), 7.59 (d, J = 8 Hz, 2H (*m*-Ph)), 6.83 (d, J = 6.4 Hz, 4H (Mes C-H)), 2.62 (s, 3H (-CH_3)), 2.31-1.97 (s, 18H (Mes-CH_3)). ^{13}C NMR (100.00 MHz, $CDCl_3$), δ (ppm): 199.1, 141.3, 139.7, 139.4, 136.3, 128.8, 128.6, 128.1, 27.3, 23.9, 22.8, 21.8. ^{11}B NMR (160 MHz, $CDCl_3$), δ (ppm): 74.1. HRMS (TOF-MS ES) m/z calcd for $C_{26}H_{29}BONa$ $(M + Na)^+$ 391.2209, found 391.2205.

Synthesis of compound 3a

Pyrrole (9.0 mL, 102.92 mmol) and **2a** (1.0 g, 2.82 mmol) were stirred at room temperature under nitrogen atmosphere for 30 min then one drop $BF_3{\cdot}Et_2O$ was added. The resultant mixture was stirred for another 6 h at room temperature and then quenched with 2N NaOH solution. The crude product was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. Column chromatography on a neutral alumina (ethyl acetate and pet ether in the ratio 0.2:9.8) afforded pure **3a** as a grey colour solid. Yield 0.8 g, 64%. ^{1}H NMR (399.99 MHz, $CDCl_3$), δ (ppm): 7.92(br, N-H), 7.45 (s, 1H (*o*-Ph)), 7.41 (d, J = 4.4 Hz, 1H (*m*-Ph)), 7.29 (m, 1H (*o, p*-Ph)), 6.79 (s, 4H (Mes C-H)), 6.67 (d, J = 1.6 Hz, 2H (β-H pyrrolic)), 6.13 (d, J = 3.2 Hz, 2H (α- H pyrrolic)), 5.82 (s, 2H (α-H pyrrolic)), 5.38 (s, 1H (meso C-H)), 2.30 (s, 6H (mes-CH_3)), 1.97 (s, 12H (Mes-CH_3)). ^{13}C NMR (100.0 MHz, $CDCl_3$), δ (ppm): 142.0, 141.2, 139.1, 137.0, 135.6, 133.1, 132.2, 129.8, 128.6, 117.6, 108.8, 107.6, 44.5, 23.9, 21.7. ^{11}B NMR (160 MHz, $CDCl_3$), δ (ppm): 69.6. HRMS (TOF-MS ES) m/z calcd for $C_{33}H_{34}BN_2$ (M^+) 469.2815, found 469.2825.

Synthesis of compound 3b

Compound **3b** was prepared following a procedure similar to that used for **3a**. The quantities involved and characterization data are as follows. Pyrrole (1.5 mL, 21.72 mmol), **2b** (0.2 g, 0.54 mmol), $BF_3{\cdot}Et_2O$ (one drop). The pure compound was obtained as a dirty white colour solid. Yield 0.1 g, 55 %. ^{1}H NMR (399.99 MHz, $CDCl_3$), δ (ppm): 7.82(br, N-H), 7.45 (d, J = 8 Hz, 2H (*m*-Ph)), 7.14 (d, J = 8 Hz, 2H (*o*-Ph)), 6.8 (s, 4H (Mes C-H)), 6.56 (d, J = 1.6 Hz, 2H (β-H pyrrolic)), 6.11 (d, J = 3.2 Hz, 2H (α- H pyrrolic)), 5.8 (s, 2H (α-H pyrrolic)), 5.38 (s, 1H (meso C-H)), 2.25 (s, 6H (mes-CH_3)), 2.01 (s, 12H (Mes-CH_3)). ^{13}C NMR (100.00 MHz, $CDCl_3$), δ (ppm): 146.7, 145.0, 142.3, 141.3, 139.2, 137.4, 132.8, 128.8, 128.6, 118.0, 108.9, 108.0, 44.6, 24.0, 21.8, 21.6. ^{11}B NMR (160 MHz, $CDCl_3$), δ (ppm): 68.1. HRMS (TOF-MS ES) m/z calcd for $C_{33}H_{34}BN_2$ (M^+) 469.2815, found 469.2816.

Synthesis of compound 3c

Compound **3c** was prepared following a procedure similar to that used for **3a**. The quantities involved and characterization data are as follows. Pyrrole (1.5 mL, 21.72 mmol), **2c** (0.2 g, .54.03 mmol) $BF_3{\cdot}Et_2O$ (one drop). Yield: 50 mg, 19%. ^{1}H NMR (399.99 MHz, $CDCl_3$), δ (ppm): 7.82 (s, br, 2H (N-H)), 7.48 (s, 1H (*o*-Ph)), 7.41 (d, J = 4.4 Hz, 1H (*m*-Ph)), 7.30 (m, 2H (*o, p*-

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Ph)), 7.13 (d, J = 4 Hz, 1H (*p*-Ph)), 6.84 (s, 4H (Mes C-H)), 6.67 (d, J = 2.8 Hz, 2H (β-H pyrrolic)), 6.18 (d, J = 2.8 Hz, 2H (α- H pyrrolic)), 5.92 (d, J = 1.6 Hz, 2H (β-H pyrrolic)), 2.35(s, 6H (mes-CH_3)), 1.97 (s, 12H (Mes-CH_3)), 1.34 (s, 3H (meso-CH_3)). ^{13}C NMR (100.00 MHz, $CDCl_3$), δ (ppm): 151.5, 142.2, 139.0, 137.4, 136.8, 128.6, 127.2, 117.4, 108.7, 106.8, 23.9, 21.7. ^{11}B NMR (160.4 MHz, $CDCl_3$), δ (ppm): 62.0. HRMS (TOF-MS ES) m/z calcd for $C_{34}H_{37}BN_2Na$ $(M + Na)^+$ 507.2947, found 507.2942 and 418.2677 (M^+–C_4H_4N).

Synthesis of compound 3d

Compound **3d** was prepared following a procedure similar to that used for **3a**. The quantities involved and characterization data are as follows. Pyrrole (1.5 mL, 21.72 mmol), **2d** (0.2 g, 0.54 mmol), $BF_3{\cdot}Et_2O$ (one drop). Yield: 45 mg, 17%. ^{1}H NMR (399.99 MHz, $CDCl_3$), δ (ppm): 7.83 (s, br, 1H (N-H)), 7.45 (d, J = 8 Hz, 2H (*o*-Ph)), 7.15 (d, J = 8 Hz, 2H (*m*-Ph)), 6.79 (s, 4H (Mes-CH)), 6.57 (t, J = 2.4 Hz, 2H (α-H pyrrolic)), 6.11 (d, J = 2.4 Hz, 2H (β-H pyrrolic)), 5.81 (s, 2H (β-H pyrrolic)), 2.27 (s, 6H (Mes-CH_3)), 1.99 (s, 12H (Mes-CH_3)), 1.32 (s, 3H (Meso-CH_3)). ^{13}C NMR (100.00 MHz, $CDCl_3$), δ (ppm): 171.9, 146.7, 145.0, 142.3, 141.3, 139.2, 137.3, 132.8, 128.8, 118.0, 108.9, 44.6, 42.0, 24.0, 21.8, 14.8. ^{11}B NMR (160 MHz, $CDCl_3$), δ (ppm): 64.2. HRMS (TOF-MS ES) m/z calcd for $C_{34}H_{37}BN_2Na$ $(M + Na)^+$ 507.2942, found 507.2950 and 418.2677 (M^+-C_4H_4N).

ACKNOWLEDGMENTS

PT thanks the Department of Science and Technology (DST), New Delhi, CSIR, New Delhi, and the ISRO-IISc Space Technology Cell for the financial support. Mr CAS thanks IISc for SRF and authors are grateful to Mr. Sanjoy Mukherjee for help in the theoretical calculations.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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DOI: 10.1039/C3DT52565A

Triarylborane-Dipyrromethane Conjugates Bearing Dual Receptor Sites: Synthesis and Evaluation of Anion Binding Site Preference

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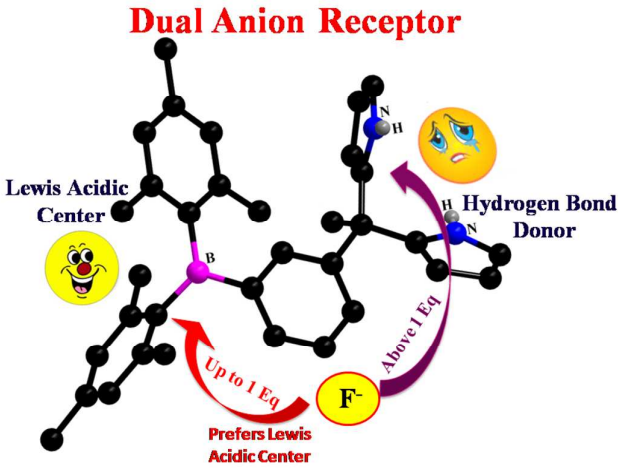

Synthesis and optical properties of four new triarylborane–dipyrromethane (TAB-DPM) conjugates (**3a-d**) containing dual binding sites (hydrogen bond donor and Lewis acid) have been reported. The titration results show that the anions bind to TAB-DPM conjugates via the Lewis acidic triarylborane centre in preference to hydrogen bond donor (dipyrromethane) units.