C_S-Symmetric Triarylborane Substituted Bisthiazole for Selective Detection of F^- and CN^- ions

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Graphical Abstract

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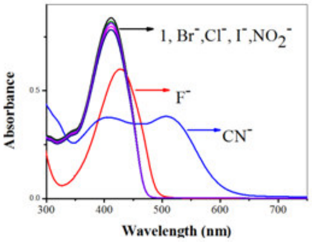

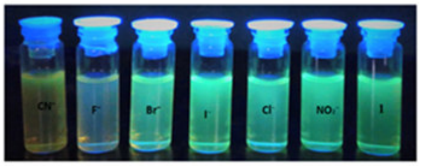

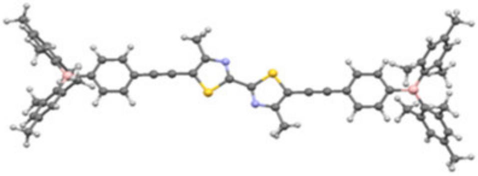

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C_S-Symmetric Triarylborane Substituted Bisthiazole for Selective Detection of F^- and CN^- ions

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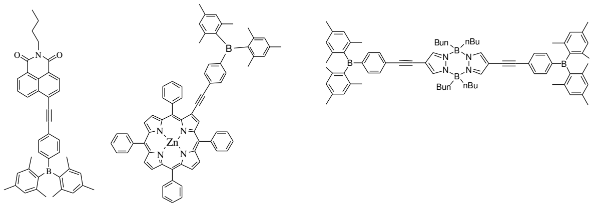
ABSTRACT

Triarylborane substituted bisthiazole **1** was designed and synthesized by the Sonogashira cross–coupling reaction for selective detection of F^- and CN^- ions in the presence of Cl^-, Br^-, I^- and NO_2^- anions. The detection limits for F^- and CN^- was found to be 5.7×10^{-6} M and 2.1×10^{-6} M respectively. The time dependent density functional theory (TD-DFT) calculation at B3LYP on the bisthiazole triarylborane **1** was studied for F^- and CN^- ions. In the case of **1** Boron is electron deficient, the addition of F^- ion should increase the electron density on Boron which was confirmed by electrostatic potential surfaces of bisthiazole triarylborane dyad **1**, **1-F**.

In recent years considerable effort has been made in the design and synthesis of anion probes due to their application in wide range of chemical, environmental, industrial and biological processes.[1] The fluoride ion is primarily used in dental care and the treatment of osteoporosis.[2,3] However, excessive amounts of fluoride ions in human body result in dental and skeletal injuries, bone diseases, lesions of the thyroid, liver and other organs.[4] On the other hand cyanide ion is widely used in synthetic fertilizers, dyes and textiles, petrochemical elution, pesticides, automobiles, pharmaceuticals and electroplating.[5] Therefore there is a need of sensor which can detect these anions. The literature reveals that a variety of triarylborane based molecular systems has been explored in organic electronics.[6] The triarylborane containing molecular systems have empty p_π–orbital on the boron centre which can effectively communicate with the neighboring π-electron system.[7] This makes triarylborane derivatives a potential candidate for optoelectronics applications.[8-21] The triarylborane molecular systems exhibit high Lewis acidity and steric hindrance due to the bulky mesityl groups. The acidity of the triarylborane moiety can be tuned by substituting the electron donating and electron withdrawing groups.[22] The electron-withdrawing group conjugated with the triarylborane increases the Lewis acidity of the triarylborane. Our research group is involved in the design and synthesis of anion sensors based on triarylborane containing molecular systems. We have reported the F^- and CN^- ion sensing behavior of triarylborane functionalized naphthalimide, porphyrin, and pyrazabole (Chart 1).[23]

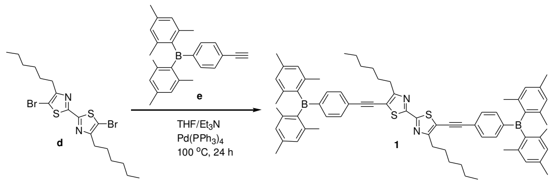


~~Chart 1.~~ Structures of previously reported triarylborane systems.

The bisthiazole is a strong acceptor and bisthiazole systems are studied in Organic photovoltaics (OPVs), dye sensitized solar cells (DSSC).[24] In triarylborane substituted bisthiazole the bisthiazole drags electron density from triarylborane unit and increases its Lewis acidity. In this contribution, we report triarylborane functionalized bisthiazole for the selective detection of F^- and CN^- anions.

The triarylborane substituted bisthiazole 1 was synthesized by the Pd–catalysed Sonogashira cross–coupling reaction of bisthiazole as shown in Scheme 1. The starting material 5, 5'-dibromo-4,4'-dihexyl-[2,2']bithiazolyl (**d**) and (4–ethynylphenyl)–dimesitylborane (**e**) was synthesized by the reported procedures.[25, 26]

The triarylborane substituted bisthiazole **1** was synthesized by the Sonogashira cross–coupling reaction of bisthiazole **d** with (4–ethynylphenyl)dimesitylborane e using the $Pd(PPh_3)_4$ as a catalyst in tetrahydrofuran (THF) solvent, triethylamine as a base at 100 °C for 24h, which resulted the triarylborane substituted bisthiazole **1** in 74% yield (Scheme 1). The triarylborane substituted bisthiazole **1** was characterised by ^1H NMR, ^{13}C NMR and HRMS techniques. In the ^1H NMR spectra of triarylborane substituted bisthiazole **1**, the aromatic protons of triarylborane exhibit multiplet between 7.49 – 7.54 ppm and one singlet at 6.84 ppm.



Scheme 1. Synthesis of triarylborane substituted bisthiazole dyad 1.

The electronic absorption and emission spectra of **1** was recorded in THF. The triarylborane substituted bisthiazole **1** show red shifted absorption band at 416 nm compared to the bisthiazole intermediate **d** (353 nm) which can be attributed to the π–π* electronic transition.

The triarylborane substituted bisthiazole **1** show emission maximum at 474 nm and 503 nm and the quantum yield of 0.26 (Fig 1).

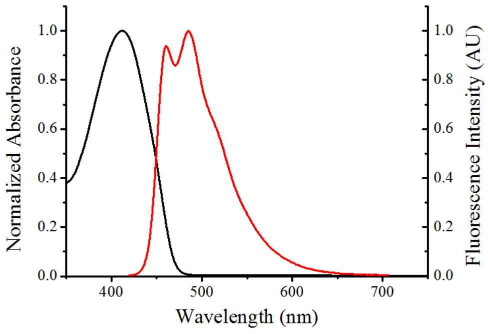
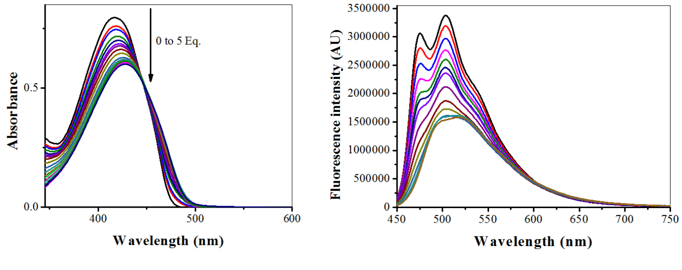


Fig 1. Normalized electronic absorption and emission spectra (λ_{ex} 416 nm) of triarylborane substituted bisthiazole 1 (2.1×10^{-5} M) in THF solvent.

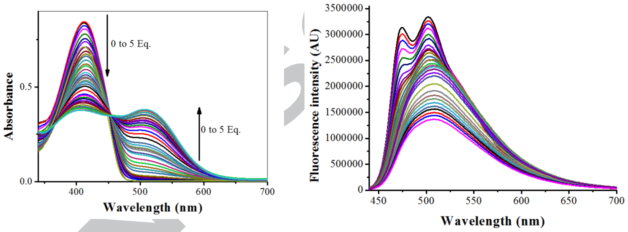
The anion sensing ability of the triarylborane substituted bisthiazole **1** was investigated by the absorption and emission studies, using various anions (F^-, Cl^-, Br^-, I^-, NO_2^- and CN^-). The anions were used in their tetrabutylammonium salts in THF solvent. The absorption and emission studies show no significant change in the presence of Cl^-, Br^-, I^- and NO_2^- anions (Fig S5 and Fig S6), while F^- and CN^- exhibit profound effect. Upon addition of fluoride ion the intensity of absorption band at 416 nm gradually decreased and shifted to 429 nm (Fig 2). One isobestic point was observed at 446 nm. The bisthiazole triarylborane dyad **1** exhibits fluorescence at 474 nm and 503 nm upon excitation at 410 nm in THF solvent. Job's plot analysis at 416 nm revealed a 1:2 stiochiometry between triarylborane substituted bisthiazole **1** and fluoride ions (Fig S7).The emission studies show no significant change in the presence of Cl^-, Br^-, I^- and NO_2^- anions (Fig S5), whereas F^- and CN^- show significant effect. Upon addition of fluoride ion to **1**, its emission intensities at 474 nm and 503 nm gradually decreased and become a broad emission centred at 511 nm. The addition of F^- ion results in red shifted in emission at 511 nm and fluorescence was quenched by 2.3 folds (Fig 2) and fluorescence quantum yield of formed complex is 0.12. To investigate the selectivity of **1** towards fluoride, the changes in the absorbance and emission spectra of **1** was monitored in the presence of other competing anions such as Cl^-, Br^-, I^-, NO_2^- and CN^- (Fig S8). Except for fluoride, no significant changes could be observed upon addition of other anions (5 equiv.).



(a) **(b)**

Fig 2. (a) Absorption and (b) fluorescence titration spectra of triarylborane substituted bisthiazole **1** (2.1×10^{-5} M) with TBAF in THF solvent.

After addition of cyanide ion, there was a gradual decrease in the intensity of the absorption band at 416 nm and a new band at 510 nm was developed (Fig 3). One isosbestic point was observed at 453 nm. Job's plot analysis at 416 nm revealed a 1:2 stoichiometry between triarylborane substituted bisthiazole **1** and cyanide ions (Fig S9). Upon addition of cyanide ion to **1**, its emission intensities at 474 nm and 503 nm gradually decreased and become a broad emission peak centering at 506 nm. The fluorescence was quenched upto 2.9 folds (Fig 3) and fluorescence quantum yield of formed complex is 0.08. To investigate the selectivity of **1** towards cyanide, the changes in the absorbance and emission spectra of **1** was monitored in the presence of other competing anions such as Cl^-, Br^-, I^-, NO_2^- and F^- (Fig S10). Expect for cyanide, no significant changes could be observed upon addition of other anions (5 equiv.).The detection limit of **1** for F^- and CN^- was calculated based on the fluorescence titration data and found to be 5.7×10^{-6} M and 2.1×10^{-6} M respectively.



(a) **(b)**

Fig 3. (a) Absorption and (b) fluorescence titration spectra of bisthiazole triarylborane **1** (2.1×10^{-5} M) with TBACN in THF solvent.

The binding constant of the complex formed in solution was estimated by using the standard Benesi–Hildebrand equation 1.
Where I_0 is the intensity before addition of anion, I is the intensity in the presence of F^-/ CN^-, I_1 is intensity upon saturation with anion,

$$\frac{1}{I - I_0} = \frac{1}{I_1 - I_0} + \frac{1}{(I_1 - I_0)K_a[M]} \qquad \text{Eq.1}$$

and K_a is the binding constant of the complex formed. The binding constant towards the F^- and CN^- ion were found 11,100 M^{-1} and 12,464 M^{-1} using the above equation (Fig S10 and Fig S11).
In order to gain further insight into the F^- and CN^- binding, ^{1}H-NMR titration studies were performed on **1**. The comparison of ^{1}H–NMR spectra of **1** before and after addition of fluoride anion is shown in Fig 4. The aryl protons of triarylborane show multiplet between 7.49 –7.54 ppm and one singlet 6.84 ppm (Chart S1). From the chart S1 and Fig 4 it can be observed the phenyl protons (H-1) singlet signal at 6.84 ppm are shielded upon addition of fluoride anion and the new signal was observed at 6.57 ppm. In the case of cyanide sensing aryl protons of triarylborane singlet signal at 6.84 ppm was shielded upon addition of cyanide anion and it was observed at 6.59 ppm (Fig S13).

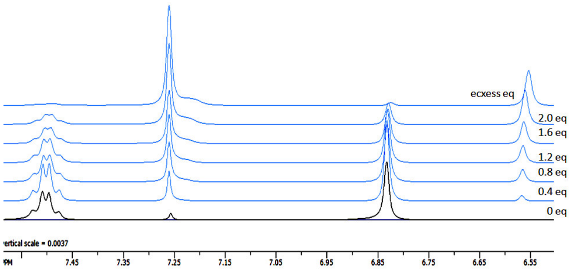


Fig 4. ^{1}H–NMR titration spectra of bisthiazole triarylborane dyad **1** with TBAF in CDCl$_3$.

In order to understand the anion sensing behaviour of the bisthiazole substituted triarylborane **1** the time dependent density functional (TD-DFT) calculation was performed. The quantum chemical calculations were performed using the Gaussian 09 program.[27] The structures of **1**, **1-F**, and **1-CN** were optimized using B3LYP level The 6-31G** basis set for C, N, H, B, S used for all the calculations (See Fig S1). The solvent calculations were carried out in the tetrahydrofuran (THF) using the polarized continuum model (CPCM) of Gaussian 09 software.[28]

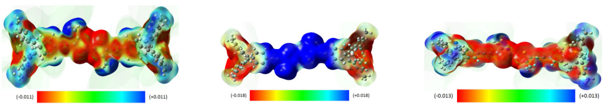
The **1**, **1-F** and **1-CN** experimental and computed (TD–DFT: B3LYP) (UV–vis) absorption data are represented in Figure S2. The strong absorption band of **1**, **1-F** and **1-CN** calculated at B3LYP levels are 495 nm, 524 nm and 507 nm respectively. The experimental values for this transition are 416 nm, 428 nm and 503 nm for **1**, **1-F** and **1-CN** respectively. The experimental values are in good agreement with the TD–DFT/B3LYP values.

In bisthiazole triarylborane dyad **1** the HOMO → LUMO transition contributes to the lowest excited state by 98% and oscillator strength is 2.73. After addition of fluoride ion the **1-F** shows HOMO-1 → LUMO+1 transition contribute to the lowest excited state by 30% and in case of **1-CN** shows major contribution (59%) between HOMO-1→LUMO+1 (Table 1) and these transitions are shown Fig S3.

Table 1. Computed vertical transition energies and their Oscillator strengths (*f*) and major contributions for the **1, 1-F** and **1-CN**.

Bisthiazole triarylborane	TD-DFT/ B3LYP (DCM)		
	λmax	f	Major contribution (%)
1	495 nm	1.7002	HOMO→LUMO (98%)
1F	524 nm	0.3902	HOMO-1→ LUMO+1 (30%)
1CN	507 nm	1.6259	HOMO-1→LUMO+1 (59%)

The electrostatic potential surface of bisthiazole substituted triarylborane dyad **1**, **1-F** and **1-CN** are shown in Fig 5. In **1** the bisthiazole groups show negative potential (-0.011) whereas the triarylborane moiety show positive potential (+0.011) confirming bisthiazole is acting as a acceptor. Since Boron is electron deficient, the addition of F$^-$ should increase the electron density on Boron which was confirmed by the negative potential (-0.019) of triarylborane unit from the electrostatic potential surfaces of bisthiazole triarylborane dyad **1F**.



1 **1F** **1CN**

Fig 5. The electrostatic potential surfaces of bisthiazole triarylborane dyad **1**, **1-F** and **1-CN**.

The Fig 6 shows the energy level digram of the frontier molecular orbitals (FMO) of bisthiazole triarylborane dyad **1, 1-F** and **1-CN** obtained using computational calculation. The HOMO-LUMO gap in **1, 1-F** and **1-CN** is a function of anion groups. In bisthiazole triarylborane dyad **1** the HOMO-LUMO gap is 2.84 eV. After addition of F$^-$ anion the HOMO and LUMO energy gap was decreased to 0.15 eV. The addition of CN$^-$ further reduced the HOMO-LUMO gap to 0.13 eV. The HOMO-LUMO gap in bisthiazole triarylborane dyad **1, 1-F** and **1-CN** follows the order **1CN > 1F >1**.

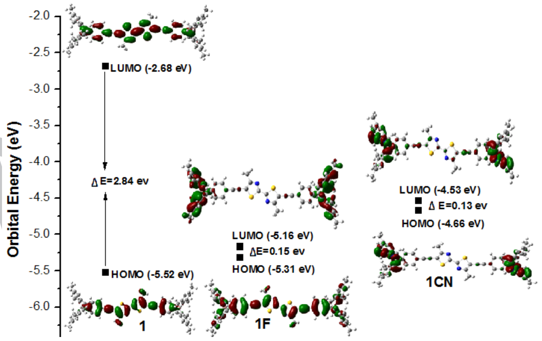


Fig 6. The energy level diagram of the frontier molecular orbitals of bisthiazole triarylborane dyad 1, 1-F and 1-CN calculated using B3LYP level of TD-DFT theory.

In summary, we have designed and synthesized new bisthiazole triarylborane based fluorescent chemosensor for the selective detection of F$^-$ and CN$^-$ anions. The bisthiazole triarylborane selective detects F$^-$ and CN$^-$ ions the presence of Cl$^-$, Br$^-$, I$^-$, NO$_2^-$ ions and exhibits colorimetric and fluorometric response. The computational and Photophysical properties show strong electronic communication between the triarylborane and bisthiazole unit. The NMR titration studies further confirmed the selective detection of F$^-$ and CN$^-$ anions. The ease of synthesis and simplicity in sensing of triarylborane bisthiazole can be used for onsite anion sensing of F$^-$ and CN$^-$ anions.

Supporting Information

General experimental methods, synthesis procedures, copies ^{1}H NMR, ^{13}C NMR and HRMS spectra, UV-vis and fluorescence spectra, TD-DFT graphs and Benesi–Hildebrand plots are provided.

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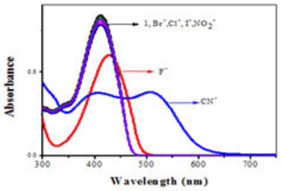
1) Synthesis of Bisthiazole based triarylborane is reported.
2) The results are explained by using theoretical TD-DFT calculations.
3) The binding constant towards the F^- and CN^- ion are respectable.

TOC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CN⁻
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400
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600
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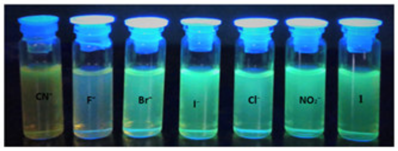
Wavelength (nm)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