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Triarylborane substituted naphthalimide as fluoride and cyanide ion sensor

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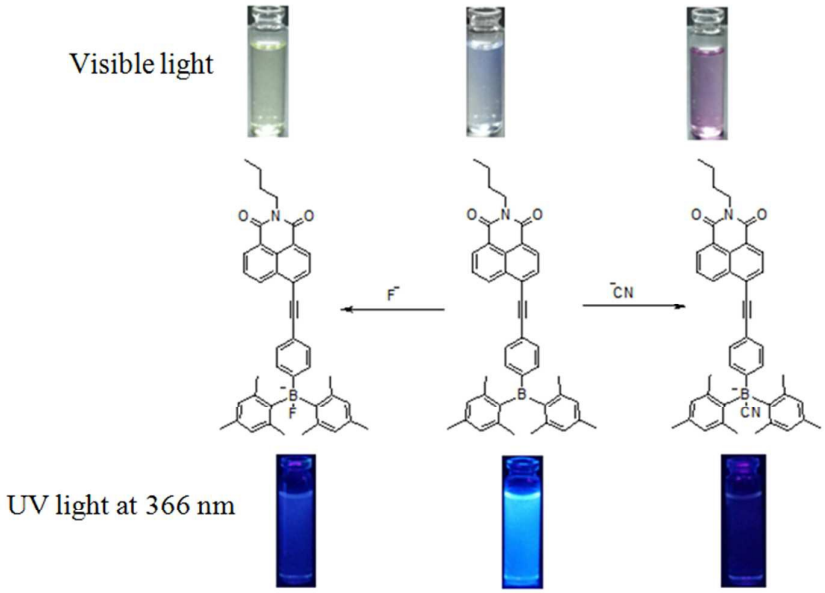
Table of Content graphic



Abstract: Triarylborane substituted naphthalimide **3** was designed and synthesized by the Sonogashira cross–coupling reaction. The electronic absorption and emission spectra of the triarylborane naphthalimide **3** show red shifted absorption and emission as compared to the 4–bromonaphthalimide **2**. The sensing behaviour of **3** was studied for different anions. The triarylborane naphthalimide **3** selectively detects F^- and CN^- ions in the presence of Cl^-, Br^-, I^- and NO_2^- ions. The effect of F^- and CN^- ions on the structure of **3** was studied by performing DFT calculations. The theoretical calculations show good agreement with the experimental results. The detection limits for F^- and CN^- were found to be 2.01×10^{-10} M and 3.94×10^{-10} M respectively.

Introduction:

The development of the molecular probes that can detect the anions has been of significant interest, due to the key roles of anions in a wide range of chemical and biological processes.[1] Among the range of anions, fluoride and cyanide are important because of their biological and environmental effect. The fluoride ion is widely used in dental care and the treatment of

osteoporosis.[2,3] More than the required amounts of fluoride ions in human body result in dental and skeletal fluorosis, bone diseases, lesions of the thyroid, liver and other organs.[4] Cyanide is widely used in many applications, such as synthetic fertilizers, dye and textile, pesticides, automobile, gold extraction, metallurgy, pharmaceuticals and electroplating.[5] Therefore, the development of effective and selective fluoride and cyanide probes are design and synthesis is necessary.

Triarylborane containing molecular systems are widely studied in optoelectronics.[6] The empty p_{π}–orbital on the boron centre makes these compounds excellent electron acceptors. This unique electronic property of the triarylborane enables their use in diverse fields such as non-linear optics, anion sensing, hydrogen activation and storage and in organic light-emitting diodes (OLEDs).[7-12]

Triarylborane molecular systems have received considerable attention as colorimetric and fluorometric sensors for fluoride and cyanide anions due to their high Lewis acidity and steric protection from the bulky mesityl groups. The Lewis acidity of the triarylborane group can be varied by the conjugation with various electronic donating and electron withdrawing groups.[13] The electron-withdrawing groups conjugation with the triarylborane increases the Lewis acidity of the triarylborane. In this context, we designed triarylborane substituted naphthalimide for the selective detection of fluoride and cyanide anions. Our group is engaged in design of anion sensors based on triarylborane containing molecular systems. Recently, our group has reported, pyrazabole, BODIPY and porphyrin based triarylborane molecular systems for the selective sensing of fluoride and cyanide anions.[14] In this contribution, we wish to report, a novel triarylborane naphthalimide for the selective detection of F^- and CN^- anions.

Results and Discussion:

The triarylborane naphthalimide **3** was synthesized by the Pd–catalysed Sonogashira cross–coupling reaction of the 4–bromonaphthalimide **2** with the (4–ethynylphenyl)dimesitylborane (Scheme 1). The 4–bromonaphthalimide was synthesized by the condensation reaction in between 4–bromo–1,8–naphthalic anhydride and n–butyl amine (Scheme S1). The (4–ethynylphenyl)–dimesitylborane was synthesized by reported procedure.[14a]

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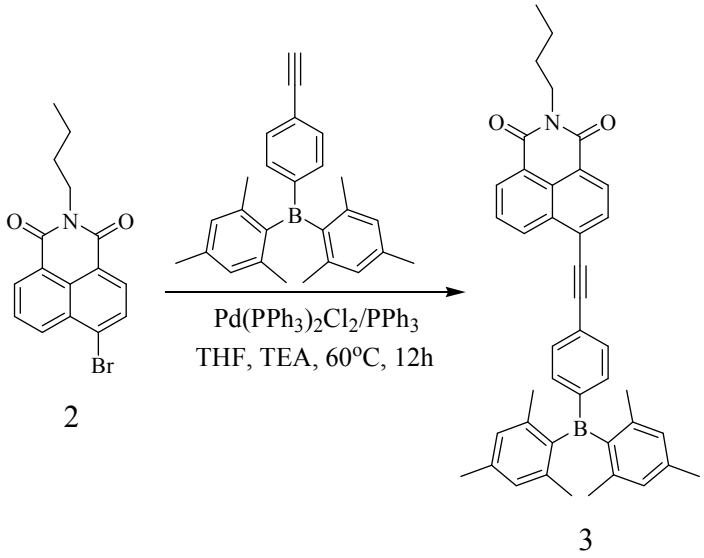

2 3

Scheme 1: Synthesis of triarylborane naphthalimide **3**.

The triarylborane naphthalimide **3** was synthesized by the Sonogashira cross–coupling reaction of 4–bromonaphthalimide **2** with (4–ethynylphenyl)dimesitylborane using the catalyst $Pd(PPh_3)_2Cl_2$, CuI in tetrahydrofuran (THF) solvent, triethylamine as base at 60 °C for 12h, which resulted **3** in 73% yield. The triarylborane naphthalimide **3** was well characterized by ^1H, ^{13}C NMR and HRMS spectroscopic techniques (Figures S1–S3). In the ^1H NMR spectra of **3**, five aromatic protons of naphthalene ring show four doublets and one triplet around 7.80–8.78 ppm. The phenyl protons of the triarylborane show two doublets at 7.60 ppm and 7.65 ppm and one singlet at 6.87 ppm. Thermal stability is one of the important parameter for the optoelectronic applications of the materials. The thermal property of **3** was investigated by thermogravimetric analysis (TGA) with a heating rate of 10 °C min^{-1} under an inert atmosphere (Figure S4). The thermal decomposition temperature (T_d) at 10% weight loss is 320 °C and show a sudden weight loss of 73% at 539 °C.

Photophysical properties:

The electronic absorption and emission spectra of the triarylborane naphthalimide **3** was recorded in THF at room temperature. The 4–bromonaphthalimide **2** absorbs at 342 nm with a shoulder at 356 nm attributed to the π–π* electronic transition, whereas **3** show red shifted absorption at 378 nm with a shoulder at 398 nm (Figure S5). The triarylborane naphthalimide **3** show emission maximum at 423 nm and with quantum yield of 0.92 (Figure S5).

Anion binding studies: The anion sensing ability of the triarylborane naphthalimide **3** was investigated by the absorption and emission studies, using various anions (F^-, Cl^-, Br^-, I^-, NO_2^- and CN^-) in THF solvent. The anions were used in their tetrabutylammonium salts. The absorption and emission studies show no significant change in the presence of Cl^-, Br^-, I^- and

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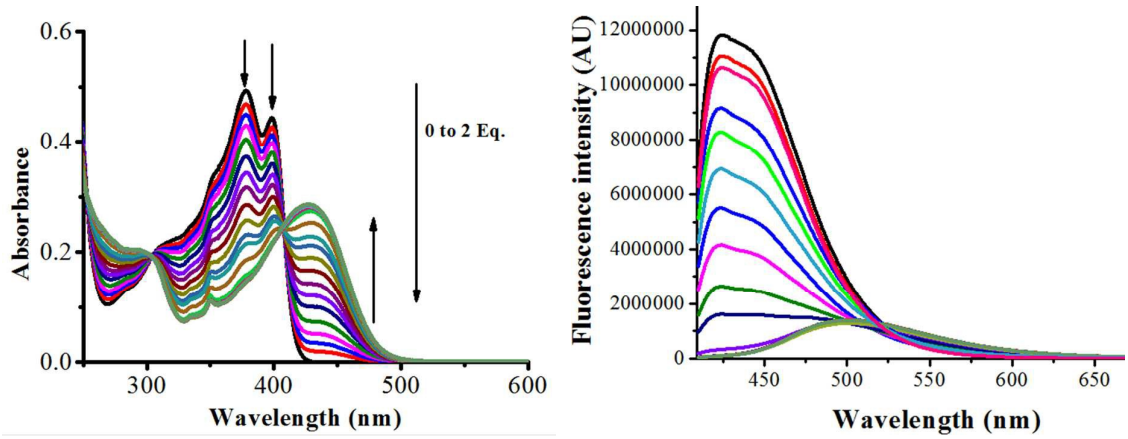
NO_2^- anions (Figures S6–S7). The triarylborane naphthalimide **3** show two absorption bands at 378 nm and 398 nm. After addition of fluoride ion, there is a gradual decrease in the intensity of the absorption bands at 378 nm and 398 nm, and a new band at 427 nm was developed (Figure 1). Two isosbestic points were observed at 304 nm and 407 nm. After gradual addition of the fluoride ions to the solution of **3** in THF, the emission intensity of **3** at 423 nm gradually decreased and it was shifted towards red region. The addition of F^- ion caused red shift in emission maxima at 501 nm and fluorescence was quenched to 9.4 folds (Figure 1).



a **b**

Figure 1: Absorption (a) and fluorescence (b) titration spectra of triarylborane naphthalimide **3** (1.66 x 10^{-5} M) with TBAF in THF solvent.

After addition of the cyanide ion, there is a gradual decrease in the intensity of the absorption bands at 378 nm and 398 nm, and two new bands at 420 nm and 580 nm were developed (Figure 2). Upon addition of Cyanide, two isosbestic points were observed at 299 nm and 406 nm. The gradual addition of cyanide ions to the solution of **3** in THF, the emission intensity of **3** at 423 nm gradually decreased and it was completely quenched with an increase in cyanide ion concentration (Figure 2). The addition of CN^- ion caused fluorescence quenching to 116 folds.

The detection limit of **3** for F^- and CN^- was calculated based on the fluorescence titration data. The detection limits for F^- and CN^- were 2.01 $\times 10^{-10}$ M and 3.94 $\times 10^{-10}$ M respectively. The binding constant of the complex formed in solution was estimated by using the standard Benesi−Hildebrand equation. The binding constant towards the F^- and CN^- ion were found to be 24928 M^{-1} and 43848 M^{-1} (Figures S8–S9).

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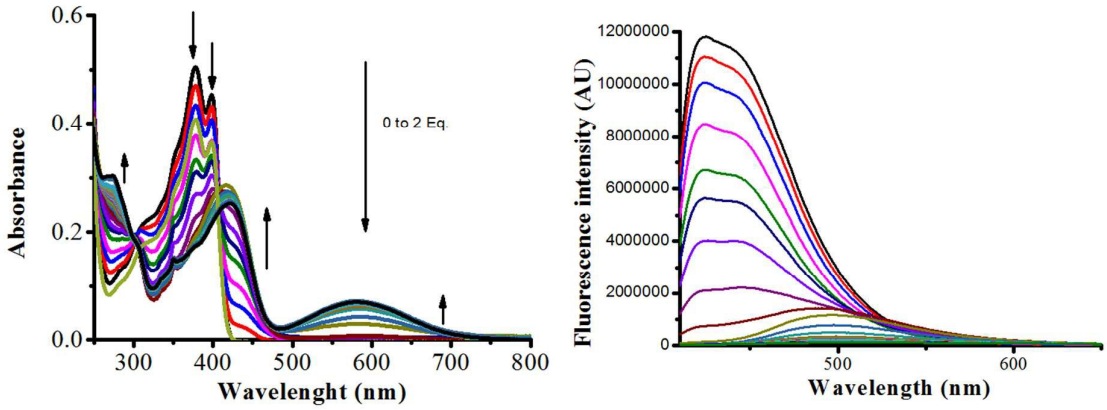

a **b**

Figure 2: Absorption (a) and fluorescence (b) titration spectra of triarylborane naphthalimide **3** (1.66 x 10^{-5} M) with TBACN in THF solvent.

In order to gain further insight in to the fluoride and cyanide binding, ^{1}H-NMR titration studies were performed. The proton NMR chemical shift assignment of triarylborane naphthalimide **3** is shown in Figure S10. The comparison of ^{1}H–NMR spectra of **3** before and after addition of fluoride ion is shown in Figure S11. From the Figure S10 and S11 it can be observed that upon addition of fluoride ion to the triarylborane naphthalimide results in down–field shift of naphthalimide H–1 proton and up–field shift of rest of the protons of naphthalimide ring. The phenyl protons (H–8) singlet signal at 6.84 ppm is shielded upon addition of fluoride anion and it was observed at 6.56 ppm. The ^{19}F-NMR of triarylborane naphthalimide **3,** upon binding with fluoride ion, showed two signals at –128.89 and –171.95 ppm. . The signal at –128.89 ppm corresponds to excess fluoride ion from TBAF and signal at –171.95 ppm corresponds to the boron attached fluoride (Figure S12). The ^{11}B-NMR of triarylborane naphthalimide **3,** upon binding with fluoride ion, Ar_3**B**–F boron signal was observed at –1.103 ppm (Figure S13). The ^{1}H–NMR titration, ^{19}F NMR and ^{11}B NMR results clearly confirms that the fluoride ion is binding at the boron centre of the triarylborane naphthalimide.[14a]

The comparison of ^{1}H–NMR spectra of triarylborane naphthalimide **3** before and after addition of cyanide anion is given in Figure S14. From the Figure S10 and Figure S14 it can be observed that upon addition of cyanide ion to the triarylborane naphthalimide results in down–field shift of naphthalimide H–1 proton and up–field shift of rest of the protons of naphthalimide ring. The phenyl protons (H–8) singlet signal at 6.84 ppm is shielded upon addition of cyanide anion and it is observed at 6.58 ppm. The ^{11}B-NMR of triarylborane

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naphthalimide **3,** upon binding with cyanide ion, Ar_3**B**–CN boron signal was observed at –1.045 ppm (Figure S15).The ^{1}H–NMR titration and ^{11}B NMR results clearly confirms that the fluoride ion is binding at the boron centre of the triarylborane naphthalimide.[14a]

Theoretical Study: In order to understand the structure and electronic properties of the triarylborane naphthalimide **3, 3–F** and **3–CN**, the density functional (DFT) calculations were performed by using Gaussian 09 program 6–31G(d, p) for C, N, H,O, B, F at B3LYP level.[15,16] The frontier molecular orbitals (HOMO to LUMO) of the triarylborane naphthalimide **3** and **3–F** and **3–CN** are shown in Figure 3. In **3** the HOMO is majorly localized on the naphthalimide part and partially localized on the phenyl and B–mesityl rings, whereas the LUMO is majorly localized on the naphthalimide part, phenyl ring and boron atom. In **3–F** and **3–CN** HOMO is localized on naphthalimide and phenyl ring. In **3–F** LUMO is localized on B–mesityl rings, boron and fluoride atoms, whereas in **3–CN**, LUMO is localized on B–mesityl rings, cyano and boron atom. These results indicate, in **3–F** and **3–CN,** HOMO→LUMO charge transfer is taking place, which was observed in experimental UV–visible titrations.

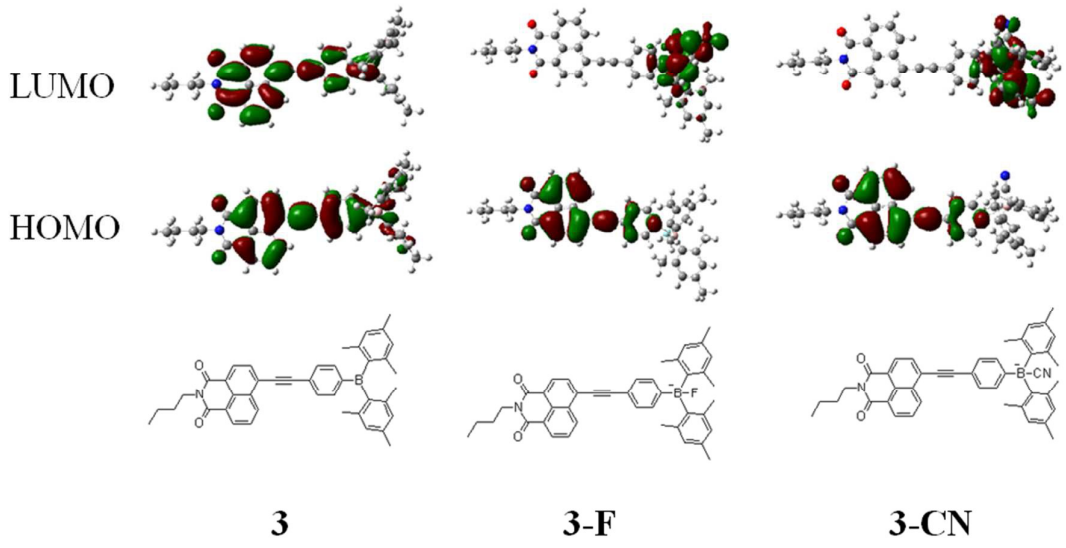

Figure 3: The frontier molecular orbitals (HOMO to LUMO) of the triarylborane naphthalimide **3**, **3–F** and **3–CN** calculated using B3LYP level of DFT theory.

The red shift in the absorption maxima of the triarylborane naphthalimide **3** upon binding with fluoride and cyanide can be understood in term of decrease in the HOMO–LUMO gap (Figure S16). Form the Figure S16, it is evident that the gap between HOMO and LUMO of triarylborane substituted naphthalimide **3** decreases on its binding with fluoride and cyanide ion. In the triarylborane substituted naphthalimide **3**, the boron atom has a vacant p_π–orbital.

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Hence, upon binding with the fluoride and cyanide ions the potential energy of the LUMO decreased comparatively than that of the HOMO. This ultimately leads to the decrease in the HOMO–LUMO, which is responsible for the red shift of absorption maximum of triarylborane substituted naphthalimide **3** on its binding with fluoride and cyanide ions. The differences in the HOMO–LUMO gap of the **3**, **3–F** and **3–CN** are 3.26 eV, 1.20 eV and 1.07 eV respectively.

Conclusions: In summary, triarylborane substituted naphthalimide **3** was designed and synthesized by the Sonogashira cross–coupling reaction for the selective detection of fluoride and cyanide ions. The triarylborane naphthalimide **3** show red shifted absorption maxima and quenching of fluorescence upon addition of fluoride and cyanide ions was observed. The photophysical properties and theoretical results show strong electronic communication between triarylborane and naphthalimide units. The triarylborane naphthalimide **3** detection limits for F^- and CN^- were found to be 2.01 $\times 10^{-10}$ M and 3.94 $\times 10^{-10}$ M respectively, which are far lower than the maximum level for fluoride and cyanide in drinking water according to WHO guidelines.

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Supporting Information

General experimental methods, copies ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{11}B NMR and HRMS spectra, UV–vis and fluorescence spectra, Benesi–Hildebrand plots and DFT data are provided.

Experimental data:

Synthesis of 6–{4–[Bis–(2,4,6–trimethyl–phenyl)–boranyl]–phenylethynyl}–2–butyl–benzo[*de*]isoquinoline–1,3–dione 3: 4-bromonaphthalimide **2** (76 mg, 0.22 mmol), (4–ethynylphenyl)dimesitylborane (80 mg, 0.22 mmol) were dissolved in THF-triethylamine (1:1, v/v, 20 mL) and the mixture was deareated for 20 min with argon bubbling and then $Pd(PPh_3)_2Cl_2$ (8 mg, 5 mol%) and CuI (2 mg, 5 mol%) were added. The solution was deaerated for further 5 min; after that, reaction was left under argon at 60 °C for 12h. After completion of reaction, the reaction mixture was cooled at room temperature and the solvent

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was evaporated. The crude product was dissolved in CH_2Cl_2 and purified by a column chromatography on silica gel using (9:1; hexane-ethylacetate) as an eluent.

3: Yield: 73 % (100 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* =8.031, 1H, aromatic), 8.65 (d, *J* =7.02, 1H, aromatic), 8.56 (d, *J* =7.53, 1H, aromatic), 7.96 (d, *J* =7.53, 1H, aromatic), 7.84 (t, *J* =7.78, 1H, aromatic), 7.64 (d, *J* =8.03, 1H, aromatic), 7.57 (d, *J* =8.03, 1H, aromatic), 6.84 (s,1H, aromatic), 4.19 (t, 2H, *J* =7.53, –NCH_2), 2.32 (s, 6H), 2.02 (s, 12H), 1.76–1.69 (m, 2H, –CH_2), 1.48–1.43 (m, 2H, –CH_2), 0.99 (t, *J* =7.27, 3H, –CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 164, 163.7, 140.8, 139.1, 136.1, 132.3, 131.6, 131.3, 130.9, 130.3, 128.3, 128.07, 127.5, 127.3, 125.3, 123, 122.3, 99.2, 88, 40.3, 30.2, 23.4, 21.2, 20.4, 13.8. HRMS (ESI–TOF): m/z calculated for $C_{42}H_{40}NO_2B$ 602.3232 $[M+1]^+$, measured 602.3238 $[M+1]^+$. Elemental analysis calcd. (%) for $C_{42}H_{40}NO_2B$ (601.31 g mol^{-1}): C 83.85, H 6.70, N 2.33; found: C 83.62, H 6.43, N 2.16.

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