Tri-(2-picolyl)amine-modificated triarylborane: Synthesis, photophysical properties and distinguish for cyanide and fluoride anions in aqueous solution

Yufeng Zhang, Xianchao Du, Long Chen, Zixiu Li, Wenji Wang, Tianbao Li, Mao-Sen Yuan

PII: S1386-1425(19)30370-1
DOI: https://doi.org/10.1016/j.saa.2019.03.116
Reference: SAA 17006

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received date: 22 December 2018
Revised date: 30 March 2019
Accepted date: 30 March 2019

Please cite this article as: Y. Zhang, X. Du, L. Chen, et al., Tri-(2-picolyl)amine-modificated triarylborane: Synthesis, photophysical properties and distinguish for cyanide and fluoride anions in aqueous solution, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, https://doi.org/10.1016/j.saa.2019.03.116

Tri-(2-picolyl)amine-modificated triarylborane: synthesis, photophysical properties and distinguish for cyanide and fluoride anions in aqueous solution

Yufeng Zhang[‡], Xianchao Du[‡], Long Chen, Zixiu Li, Wenji Wang*, Tianbao Li* and Mao-Sen Yuan*

Corresponding author:

College of Chemistry & Pharmacy, Northwest A&F University, Yangling, Shaanxi 712100, P. R. China. E-mail: wjwang@nwsuaf.edu.cn; litianbao@nwsuaf.edu.cn; yuanms@nwsuaf.edu.cn

[‡] *These two authors contributed equally to this work.*

ABSTRACT

We designed and synthesized a tri-(2-picolyl)amine (TPA) functionalized triarylborane, 1-(6-(4-(dimesitylboryl)phenyl)pyridin-2-yl)-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine (**PB2**). The photophysical properties of **PB2** were thoroughly explored. Moreover, **PB2** can capture CN^- and F^- in aqueous solution through strong chelation induced by the synergy of a boron atom and metal ion gripped by TPA to display entirely different fluorogenic responses such as fluorescence enhancement for CN^- and fluorescence quenching for F^-. The results of TOF-MS-EI analysis and theoretical calculations indicate that the complexing of **PB2** with CN^- formed a 2-to-2 adduct with a stabilized configuration, resulting in strong emission. The complexing of **PB2** with F^- formed a 1-to-1 adduct with a loose configuration, resulting in weak emission. In pure water, the detection limit of **PB2** for CN^- is 0.79 μM, and in H_2O/THF (1:9 *v*/*v*) system, the detection limits of **PB2** for CN^- and F^- can reach 0.39 and 2.12 μM, respectively, indicating its potential application for effective detection and discrimination of CN^- and F^-.

KEYWORDS

Cyanide anions; Fluoride anions; Triarylborane; Fluorescent probe; Chalation

1. Introduction

The cyanide anion, whose toxic attack is rapid and low-dose, is known as highly poisonous anion for both biological systems as well as the environment. Cyanide anions mainly come from mining, electroplating, tanning industries, and synthetic fiber production [1]. Cyanide can bind to a heme unit of cytochrome *c* to inhibit cell respiration which leads to vomiting, twitch, coma, loss of consciousness , and even death [2]. Fluorine, an essential element in our body, is usually added to toothpaste for protecting teeth [3]. In addition, fluorine-containing pesticides and rubbers have also been widely used, and the fluoride from the decomposition of these materials will infiltrate into the soil and underground water [4]. Ultimately, people ingest fluorine from crops and drinking water. However, an excessive intake of fluorine will lead to dental and gastric disorders, skeletal fluorosis, urolithiasis, and even death [5]. Therefore, developing a simple and effective detection strategy for on-site detection of trace amounts of cyanide and fluoride anions is highly desirable and significant.

At present, the usual methods to detect these two anions include selective electrode methods, ion chromatography, and chromatography-mass spectrometry (GC-MS) [6]. These traditional detection methods have their own advantages, but the drawbacks, such as the high detection limit and complex sample preparation, are also extremely obvious [7]. In comparison with instrumental analysis, systems based on chromogenic and fluorogenic methods are much simpler and easier to operate [7,8]. Borane-based organic compounds have attracted much attention because of their intriguing photophysical properties and they have been exploited as fluorescent, colorimetric, or ratiometric probes for certain nucleophilic anions. This is attribute to the vacant *p* orbital and inherent Lewis acidic nature of trivalent organoboron [9]. In particular, triarylboranes containing two mesityl groups are widely explored as chemosensors for cyanide and fluoride anions. Their utility is ascribed to their moisture-stability and to their high steric hindrance which prevents large anions from approaching boron [10].

However, the design and development of organoboron-based water-tolerance fluorescence sensors for cyanide and fluoride is very challenging because of three counts: the poor solubility of triarylboranes in aqueous solution, the high hydration enthalpy of fluoride, and the difficulty in distinguishing between cyanide and fluoride [11]. Successful examples demonstrating that fluorescence sensors can respectively identify cyanide and fluoride in aqueous solution remain exceedingly rare. In the past few years, the Gabbaï group developed a series of cationic boranes that can bind fluoride anions in organic or protic solvents including water [12]. They utilized boranes decorated with peripheral ammonium, phosphonium, sulfonium, stibonium, or telluronium groups to form onium, which has promoted Lewis acidity and complexing capacity to capture fluoride in aqueous solution [10b,12b,13]. Among them, two structural isomers, 4-[bis(2,4,6-trimethylphenyl)boranyl]-*N*,*N*,*N*-trimethylaniline ([*p*-$(Mes_2B)C_6H_4(NMe_3)]^+$ and 2-[bis(2,4,6-trimethylphenyl)boranyl]-*N*,*N*,*N*-trimethylaniline ([*o*-$(Mes_2$-$C_6H_4(NMe_3)]^+$, exhibited the ability to identify CN^- and F^- respectively in aqueous solution (H_2O/DMSO 95:5 vol.) [14]. The Wang group designed a bipy functionalized dimesitylboron molecule, 5,5′-bis($BMes_2$)-2,2′-bipy, to enhance the electron accepting ability of boron via π-conjugation with bipy and metal chelation, and this compound can form a 1:1 adduct with F^- in the presence of methanol [15]. Enlightened by the above work, in this paper, tri-(2-picolyl)amine (TPA), a pyridine-based ligand that can bind to a variety of metal ions with high affinity, was chosen to functionalize PhB(Mes_2). One purpose of such a design is to improve the water solubility of the fluorescence probe via the multiple pyridyl rings and the chelate metal ion. In addition, the conterminous pyridyl group of PhB(Mes_2) will be a plus factor in enhancing the Lewis acidity of boron due to the electronegative nitrogen atoms [11b,16]. Furthermore, TPA was anticipated to be powerful for further promoting the electron-accepting ability of the boron center by metal chelation [10]. Above all, we designed the bifunctional borane/TPA molecule with the expectation that it can trap fluoride between the boron atom and the TPA-binding metal ion via synergy between the Coulombic effect and Lewis acidity, thus making it compatible with aqueous environments. Herein, two structural isomers of triarylboranes, 1-(6-(3-(dimesitylboryl)phenyl)pyridin-2-yl)-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine (**PB1**) and 1-(6-(4-(dimesitylboryl)phenyl)pyridin-2-yl)-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine (**PB2**), were synthesized.

PB2 exhibited gratifyingly ability for identifying fluoride and cyanide anions in aqueous medium with different colorimetric responses.

2. Experimental section

2.1 Synthesis and characterizations of the subject compounds

Solvents for reactions and spectral measurements were dried and distilled before use. The reagents used for reactions were purchased from J&K Scientific Ltd. ^{1}HNMR spectra were recorded at 25 ˚C on Bruker Avance 500 MHz spectrometer using $CDCl_3$ as solvent. ^{13}CNMR spectra were recorded at 25 ˚C on Bruker Avance 125 MHz spectrometer using $CDCl_3$ as solvent. Element analyses (C, H and N) were performed using a PE 2400 autoanalyser. Mass spectrometry analyses were performed by a Bruker Biflex III matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometer.

Synthesis of 1-(6-(3-(dimesitylboryl)phenyl)pyridin-2-yl)-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine (PB1). The mixture of 1-(6-bromopyridin-2-yl)-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine (**4**) (0.20 g, 0.48 mmol), 2-(3-(dimesitylboryl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6**) (0.204 g, 0.48 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), toluene (6 mL), ethanol (2 mL) and 1 M K_2CO_3 aqueous solution (1 mL) in the round-bottom flask were heated to 80 ˚C, and constantly stirred under an argon atmosphere for 8 h. The mixture was then cooled to room temperature and poured into water (100 mL). After extraction with DCM, the organic phase was dried over Na_2SO_4. Purification by column chromatography on silica gel and elution with dichloromethane-methanol (20:1, v/v) yielded **PB1** (0.216 g, 73.2%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, J = 4.6 Hz, 2H), 8.30 – 8.27 (m, 1H), 8.07 (s, 1H), 7.73 – 7.64 (m, 5H), 7.59 (d, J = 7.4 Hz, 1H), 7.51 (td, J = 7.3, 3.3 Hz, 3H), 7.18 (ddd, J = 6.7, 4.9, 1.9 Hz, 2H), 6.86 (s, 4H), 3.98 (s, 6H), 2.34 (s, 6H), 2.06 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.64, 159.15, 156.89, 149.10, 140.90, 139.18, 138.71, 137.05, 136.97, 136.41, 134.40, 130.97, 128.62, 128.25, 123.00, 121.97, 121.22, 118.99, 60.23, 60.05, 23.56, 21.26. TOF-MS-EI: m/z 614.3643 $[M]^+$.

Synthesis of 1-(6-(4-(dimesitylboryl)phenyl)pyridin-2-yl)-*N*,*N*-bis(pyridin-2-

ylmethyl)methanamine (**PB2**)**.** A similar synthetic and purification procedure as for **PB2** was followed for **PB1** using 2-(4-(dimesitylboryl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) as the precursor. **PB2** (0.231 g, 78.4%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 2H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.68 (ddd, *J* = 19.1, 9.3, 5.0 Hz, 7H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 5.2, 3.0 Hz, 2H), 6.88 (s, 4H), 4.00 (s, 6H), 2.36 (s, 6H), 2.07 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.57, 159.39, 156.38, 149.12, 142.42, 140.89, 138.72, 137.14, 136.79, 136.46, 128.21, 126.93, 126.44, 122.98, 122.01, 121.72, 119.20, 60.25, 60.17, 24.90, 23.51, 21.26. TOF-MS-EI: m/z 614.3654 $[M]^+$.

2.2 Photophysical properties measurement

UV-vis absorption spectra for the solutions and the solid-state were recorded with a Shimadzu UV-2550 spectrophotometer. Photoluminescence (PL) spectra were recorded using a Shimadzu RF-5301PC spectrofluorimeter. The fluorescence quantum yield (Φ) in solution was determined using rhodamine B in ethanol as a reference according to a previously reported method. Steady-state fluorescence spectra and decay curves were obtained using an Edinburgh FLS920 fluorescence spectrometer equipped with a time-correlated single photon counting (TCSPC) card. Reconvolution fits of the decay profiles were performed with F900 analysis software to obtain the lifetime values.

2.3 Theoretical calculation

By using the Gaussian 09 program, the Time-Dependent Density Functional Theory (TD-DFT) and the B3LYP scheme in conjunction with the 6-31G(d) basis set has been used to carry out the study of compounds **PB2**, $\mathbf{[K]^+[PB2{\cdot}F]^-}$ and $\mathbf{[K_2]^{2+}[2PB2{\cdot}(CN)_2]^{2-}}$. The molecular geometries of **PB2**, $\mathbf{[K]^+[PB2{\cdot}F]^-}$ and $\mathbf{[K_2]^{2+}[2PB2{\cdot}(CN)_2]^{2-}}$ for electronic structure calculation was obtained by DFT-B3LYP/6-31G(d) optimization. To include the solvent effects of THF, the Polarizable Continuum Model (PCM) was used.

3. Results and discussion

3.1 Synthesis

The probe molecules **PB1** and **PB2** were prepared according to the synthetic routes shown in Scheme 1. The 1,4-dibromobenzene and 1,3-dibromobenzene were used as the starting materials. After respective single-boronation of them with Mes_2BF followed by borylation of Mes_2BPhBr with bis(pinacolato)diboron, the corresponding $Mes_2BPhB(OR)_2$ (**2** and **6**) were obtained. 2-Bromo-6-(bromomethyl)pyridine (**3**) was prepared via bromomethylation of 2-bromo-6-methylpyridine. A subsequent reaction of **3** with di-(2-picolyl)amine afforded 1-(6-bromopyridin-2-yl)-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine (**4**). The final products **PB1** and **PB2** were readily synthesized through a conventional Suzuki reaction by reacting compound **4** with corresponding **6** and **2**. All of the compounds are stable in ambient air and H_2O, in both solution and in the solid state. Details of the synthesis, and purification processes, along with ^1H and ^{13}C NMR spectroscopy data and HR-MS results, can be found in the ESI.

3.2 Photophysical properties

The UV-visible absorption and PL spectra of **PB1** and **PB2** are shown in Figure 1. **PB1** exhibited two UV-visible absorption bands at 295 and 325 nm in THF solution. These bands can be assigned to the π–π^* intramolecular charge transfer (ICT) from TPA location to a benzene ring and π–p_π(B) ICT from TPA to the dimesitylboryl group, respectively. Different from **PB1**, **PB2** showed only one major UV-visible absorption band at 330 nm with a higher extinction coefficient. This indicated a greater degree of ICT from TPA to the dimesitylboryl group in comparison with **PB1**. The meso-position substitution of TPA in **PB1** lead to a rough ICT path from TPA to boron, resulting in a doublet-band absorption feature of **PB1**. Contrary to the absorption spectra, the PL spectra of **PB1** displayed a single-band emission at 389 nm with a quantum efficiency Φ of 0.21, and **PB2** displayed a doublet-band emission at 397 and 415 nm with a quantum efficiency Φ of 0.28. We think that the emission at 389 and 397 nm should be attributed to the short-distance ICT from TPA to benzene, and the emission at 415 nm originates from the long-distance ICT from TPA to dimesitylboryl group [17].

3.3 Sensing and differentiating F^- and CN^-

To examine our design concept and to assess the detection performance of **PB1** and **PB2** for F^- and CN^-, we firstly inspected whether they can work well for capturing and discriminating CN^- and F^- in a THF/H_2O system. Titration experiments were carried out in an aqueous solution of H_2O/THF (1:9 *v*/*v*) by using KCN and KF as the cyanide or fluoride anion source, respectively. The changes in the fluorescent spectra of **PB1** and **PB2** upon the addition of KCN and KF are shown in Figure 2. Very weak fluorescent quenching was observed for **PB1** upon the titration of CN^- even up to six equivalents (Figure 2a). And for the titration of F^-, the fluorescent spectra of **PB1** hardly changed, indicating the poor complexation ability of **PB1** to F^- and CN^- in a water-containing system. However, it is worth noting that the addition of KCN to **PB2** caused a significant enhancement of the fluorescence peak at 389 nm, and the PL intensity of **PB2** became saturation when the concentration of KCN reached 2.5×10^{-5} M (2.5 equivalents) with a quantum efficiency Φ of 0.59. In contrast, the incremental addition of KF to **PB2** displayed a gradual decease of the fluorescence intensity, and the fluorescence was almost entirely quenched ($\Phi = 0.03$) when the accumulated quantity of F^- reached 2.5 equivalents of **PB2** (Figure 2d). We found that whether enhancement for CN^- or decline of the fluorescent intensity for F^-, the spectral shape of **PB2** behaved the same and changed from doublet-band (397 and 415 nm) to a single-band (397 nm). The disappearance of the fluorescent band at 415 nm indicated the termination of the long-distance ICT from TPA to the dimesitylboryl group due to the $F^- \rightarrow B$ coordination, saturating the electron acceptor. In addition, visual fluorescent decline or enhancement of the **PB2** solution can be readily observed by the naked eye upon the addition of F^- and CN^-, respectively. The vivid fluorescent changes suggest that **PB2** can be used as a colorimetric sensor for F^- and CN^-.

The UV-visible absorption spectra of **PB2** exhibited a very similar change for CN^- and F^-, as shown in Figures S1 and S3 in SI. With the addition of incremental amounts of CN^- or F^-, the absorption of

PB2 at 330 nm gradually decreased until it finally disappeared, and in the meantime, a new absorption band at 300 nm arose, which further indicated that the π–p_π(B) charge transfer was interrupted after B bound with these anions. Binding constants (*K*) of **PB2** with KCN and KF in H_2O/THF (1:9 *v*/*v*) were determined based on the absorbance titration to be approximately 2.6×10^4 M^{-1} and 5.5×10^3 M^{-1} (Figures S2 and S4 in SI), respectively. The detection limits of probe **QB** for KCN and KF were estimated to be 0.39 and 2.12 μM, respectively, based on a signal-to-noise ratio (S/N) of 3 under the test conditions. We also investigated the selectivity of **PB2** for CN^- and F^- by measuring the changes in the PL spectra upon addition of an excess amount of various other anions, such as Cl^-, Br^-, NO_3^-, AcO^-, $H_2PO_4^-$, ClO_4^-, HSO_4^- and HS^-. As shown in Figure 3, **PB2** did not show any affinity toward these anions, indicating the highly selectivity and distinguishing ability of **PB2** for CN^- and F^-. The competitive experiments in the presence of CN^- and F^- were also carried out. The results manifested that fluoride anion did not interfere with the sensitivity of the probe **PB2** towards cyanide anion. However, the cyanide anion seriously interfered with the sensitivity of the probe **PB2** towards fluoride anion (Figure S10 in SI). On the other hand, the effect of pH on the sensing of **PB2** for CN^- and F^- in H_2O/THF (1:9 vol.) solutions has also been explored (see Figure S11 in SI). The probe **PB2** can be used to detect CN^- and F^- in a wide range of pH values (5.5–12).

Motivated by these favorable results, we then investigated the capturing ability of **PB2** for CN^- and F^- when increasing concentration of water (Figure S11 in SI). As shown in Figure 4, in pure water, the emission band at 389 nm was gradually enhanced upon adding KCN to **PB2** solution and reached saturation at 3.0 equivalents of **PB2**, with a binding constant of 4.6×10^4 M^{-1} and detection limit of 0.79 μM (Figures S6 and S9). However, no obvious changes in the PL spectra can be observed even upon the addition of 10 equivalents of fluoride anions to **PB2**. This suggests the inadequate capacity of **PB2** to complex fluoride in pure water because of the high hydration of the fluoride anion. But for all that, **PB2** clearly exhibited the excellent ability for sensing and discriminating CN^- and F^- in aqueous solution. As shown as Table 1, The low detection limits of **PB2** for these two anions in aqueous solution are inaccessible for most of organic fluorescent probes [18-23].

3.4 Sensing mechanism

PB2 exhibited different fluorescent responses for CN^- and F^-, enhancement and quenching respectively. To make certain of the reason and mechanism for the different fluorescent changes of **PB2** for CN^- and F^-, the reaction mixtures of **PB2** with respective KCN and KF were analyzed by using the TOF-MS-EI technique. The results revealed that a 2-to-2 adduct product including two **PB2** and two KCN molecules formed in the reaction system of **PB2** with KCN (Figure 5a), and the reaction of **PB2** with KF formed a 1-to-1 adduct confirmed by the molecular ion peak of 672.3267 (Figure 5b), which is consistent with our previous studies [10a]. For a better understanding of the PL spectral behaviors before and after **PB2** is bound to these two anions, theoretical calculations were performed using TD-DFT methods. The geometry of the 2-to-2 adduct ($[K_2]^{2+}[PB2{\cdot}(CN)_2]^{2-}$) of **PB2** with KCN was reasonably surmised based on our recent research results and was further optimized. We thought that two KCN molecules were simultaneously or successively captured by two **PB2** molecules via teamwork (Figure 6). The KCN was firmly chelated by boron and TPA, which were respectively affiliated with two individual **PB2** molecules. The C-terminal of KCN points towards the boron atom and is bound through the coordination effect, and the potassium is gripped by TPA segment of another **PB2** molecule. Another single KCN in the 2-to-2 adduct exhibit an identical coordination pattern, but a staggered construction. The **PB2**-KCN adduct $[K_2]^{2+}[PB2{\cdot}(CN)_2]^{2-}$ showed a very stable molecular configuration and the intramolecular single-bond rotations and configuration vibrations were deeply restricted to avoid nonradiative decay, resulting in the strong emission upon being excited. Therefore, **PB2** exhibited a turn-on fluorescence response for KCN. In addition, after complexing CN^- with the electron-deficient boron atom, the intramolecular charge transfer (ICT) from TPA to boron was blocked and the ICT path from TPA to an adjacent benzene ring was rebuilt (Figure 6), leading to the disappearance of the fluorescent band at 415 nm and the enhancement of fluorescent band at 397 nm. As for the coordination geometry of **PB2** with KF, the results of the theoretical calculation indicate that KF is chelated by the boron and TPA from the same single **PB2** molecule (Figure 6), which conformed to our anticipation. The probe **PB2** can capture the KF from the aqueous solution by itself. However, different from the **PB2**-KCN adduct $[K_2]^{2+}[PB2\cdot(CN)_2]^{2-}$, the **PB2**-KF adduct $[K]^{+}[PB2\cdot F]^{-}$ behaves a loose molecular configuration. The coordination of **PB2** with KF may aggravate the molecular configuration vibrations upon being excited to mainly result to the nonradiative decay. Therefore, **PB2** exhibited a turn-off fluorescence response for KF.

4. Conclusion

In conclusion, we successfully designed and synthesized a fluorogenic chemodosimeter **PB2** for the detection and discrimination of CN^- and F^- in aqueous solution with high sensitivity (3.19 μM for CN^- and 3.19 μM for F^-). The probe molecule **PB2** is composed of two segments, $PhB(Mes_2)$ and tri-(2-picolyl)amine (TPA). The photophysical properties of **PB2** were explored. Moreover, **PB2** can capture KCN and KF through strong chelation induced by the synergy of boron binding anions and TPA binding metal ion in THF/H_2O solution to exhibit entirely different fluorogenic responses, fluorescence enhancement for KCN and fluorescence quenching for KF. The results of TOF-MS-EI analysis and theoretical calculations indicate that the complexing of **PB2** with KCN formed a 2-to-2 adduct with a stabilized configuration, resulting in strong emission, and the complexing of **PB2** with KF formed a 1-to-1 adduct with a loose configuration, resulting in weak emission.

Acknowledgments

We gratefully acknowledge the National Natural Science Foundation of China (21202132, 21675126 and 21874108), China Postdoctoral Science Foundation (2016M592837) for funding.

References

[1] (a) R. Koenig, Wildlife deaths are a grim wake-up call in eastern europe, Science 287 (2000) 1737—1738;

(b) W.C. Lin, S.K. Fang, J.W. Hu, H.Y. Tsai, K.Y. Chen, Ratiometric fluorescent/colorimetric cyanide-selective sensor based on excited-state intramolecular charge transfer-excited-state intramolecular proton transfer switching, Anal. Chem. 86 (2014) 4648—4652;

(c) R. Jackson, R.P. Oda, R.K. Bhandari, S.B. Mahon, M. Brenner, G.A. Rockwood, B.A. Logue, Development of a fluorescence-based sensor for rapid diagnosis of cyanide exposure, Anal. Chem. 86 (2014) 1845—1852.

[2] (a) H.R. Bhat, P.C. Jha, Selective Complexation of cyanide and fluoride ions with ammonium boranes: a theoretical study on sensing mechanism involving intramolecular charge transfer and configurational changes, J. Phys. Chem. A 121 (2017) 3757—3767;

(b) Y. Shiraishi, M. Nakamura, N. Hayashi, T. Hirai, Coumarin-spiropyran dyad with a hydrogenated pyran moiety for rapid, selective, and sensitive fluorometric detection of cyanide anion, Anal. Chem. 88 (2016) 6805—6811;

(c) S. Goswami, S. Paul, A. Manna, Carbazole based hemicyanine dye for both "naked eye" and 'NIR' fluorescence detection of CN^- in aqueous solution: from molecules to low cost devices (TLC plate sticks), Dalton Trans. 42 (2013) 10682—10686.

[3] M. Kleerekoper, The role of fluoride in the prevention of osteoporosis, Endocrinol. Metab. Clin. North Am. 27 (1998) 441—452.

[4] L. Xiong, J. Feng, R. Hu, S. Wang, S. Li, Y. Li, G. Yang, Sensing in 15 s for aqueous fluoride anion by water-insoluble fluorescent probe incorporating hydrogel, Anal. Chem. 85 (2013) 4113—4119.

[5] (a) C.A.N. Kobayashi, A.D.L. Leite, T.L.D. Silva, L.D.D. Santos, F.C.S. Nogueira, K.S. Santos, R.C.D. Oliveira, M.S. Palma, G.B. Domont, M.A.R. Buzalaf, Proteomic analysis of urine in rats chronically exposed to fluoride, J. Biochem. Mol. Toxicol. 25 (2015) 8—14;

(b) J.D. Featherstone, R. Glena, M. Shariati, C.P. Shields, Dependence of in vitro demineralization of apatite and remineralization of dental enamel on fluoride concentration, J. Dent. Res. 69 (1990) 620—625.

[6] (a) Y. Yang, Q. Zhao, W. Feng, F. Li, Luminescent chemodosimeters for bioimaging, Chem. Rev. 113 (2013) 192—270;

(b) J.P. Hutchinson, C.J. Evenhuis, C. Johns, A.A. Kazarian, M.C. Breadmore, M. Macka, E.F. Hilder, R.M. Guijt, G.W. Dicinoski, P.R. Haddad, Identification of inorganic improvised explosive devices by analysis of postblast residues using portable capillary electrophoresis instrumentation and indirect photometric detection with a light-emitting diode, Anal. Chem. 79 (2007) 7005—

7013;

(c) Michael C. Breadmore, Anne S. Palmer, Mark Curran, Miroslav Macka, a. Nebojsa Avdalovic, Paul R. Haddad, On-column ion-exchange preconcentration of inorganic anions in open tubular capillary electrochromatography with elution using transient-isotachophoretic gradients. 3. implementation and method development, Anal. Chem. 74 (2002) 2112—2118.

[7] M. Sun, S. Wang, Q. Yang, X. Fei, Y. Li, Y. Li, A new colorimetric fluorescent sensor for ratiometric detection of cyanide in solution, test strips, and in cells, RSC Adv. 4 (2014) 8295—8299.

[8] (a) Y. Shen, X. Zhang, Y. Zhang, H. Li, Y. Chen, An ICT-modulated strategy to construct colorimetric and ratiometric fluorescent sensor for mitochondria-targeted fluoride ion in cell living, Sens. Actuators B 258 (2018) 544—549;

(b) D. Udhayakumari, Chromogenic and fluorogenic chemosensors for lethal cyanide ion. A comprehensive review of the year 2016, Sens. Actuators B 259 (2018) 1022—1057;

(c) L.E. Santos-Figueroa, M.E. Moragues, E. Climent, A. Agostini, R. Martinez-Manez, F. Sancenon, Chromogenic and fluorogenic chemosensors and reagents for anions. A comprehensive review of the years 2010-2011, Chem. Soc. Rev. 42 (2013) 3489—3613;

(d)Y. Chen, W. Shi, Y. Hui, X. Sun, L. Xu, L. Feng, Z. Xie, A new highly selective fluorescent turn-on chemosensor for cyanide anion, Talanta 137 (2015) 38—42.

[9] (a) C. Wang, J. Jia, W.N. Zhang, H.Y. Zhang, C.H. Zhao, Triarylboranes with a 2-dimesitylboryl-2'-(N,N-dimethylamino)biphenyl core unit: structure-property correlations and sensing abilities to discriminate between F^- and CN^- ions, Chem. Eur. J. 20 (2014) 16590—16601;

(b) S. Yamaguchi, a. Seiji Akiyama, K. Tamao, Tri-9-anthrylborane and its derivatives: new boron-containing π-electron systems with divergently extended π-conjugation through boron, J. Am. Chem. Soc. 122 (2000) 6335—6336;

(c) X.Y. Wang, F.D. Zhuang, J.Y. Wang, J. Pei, Incorporation of polycyclic azaborine compounds into polythiophene-type conjugated polymers for organic field-effect transistors, Chem. Commun. 51 (2015) 17532—17535;

(d) G.R. Kumar, S.K. Sarkar, P. Thilagar, Aggregation-induced emission and sensing characteristics of triarylborane-oligothiophene-dicyanovinyl triads, Chem. Eur. J. 22 (2016) 17215—17225;

(e) K. Dhanunjayarao, V. Mukundam, K. Venkatasubbaiah, Ratiometric sensing of fluoride anion through selective cleavage of Si-O bond, Sens. Actuators B 232 (2016) 175—180;

(f) C.D. Entwistle, T.B. Marder, Boron chemistry lights the way: optical properties of molecular and polymeric systems, Angew. Chem. Int. Ed 41 (2002) 2927—2931;

(g) Y. Kubo, M. Yamamoto, M. Ikeda, M. Takeuchi, S. Shinkai, S. Yamaguchi, K. Tamao, A colorimetric and ratiometric fluorescent chemosensor with three emission changes: fluoride ion sensing by a triarylborane- porphyrin conjugate, Angew. Chem. Int. Ed. 42 (2010) 2036—2040.

[10] (a) M.S. Yuan, X. Du, Z. Liu, T. Li, W. Wang, E.V. Anslyn, J. Wang, Di-(2-picolyl)-N-(2-quinolinylmethyl)amine-functionalized triarylboron: Lewis acidity enhancement and fluorogenic discrimination between fluoride and cyanide in aqueous solution, Chem. Eur. J. 24 (2018) 9211—9216;

(b) C.R. Wade, A.E.J. Broomsgrove, S. Aldridge, F.P. Gabbaï, ChemInform abstract: fluoride ion complexation and sensing using organoboron compounds, Chem. Rev. 110 (2010) 3958—3984.

[11] (a) V.K. Gupta, N. Mergu, L.K. Kumawat, A.K. Singh, A reversible fluorescence “off–on–off” sensor for sequential detection of aluminum and acetate/fluoride ions, Talanta 144 (2015) 80—89;

(b) H. Zhao, L.A. Leamer, F.P. Gabbaï, Anion capture and sensing with cationic boranes: on the synergy of Coulombic effects and onium ion-centred Lewis acidity, Dalton Trans. 42 (2013) 8164—8178;

(c) D.R. Bai, X.Y. Liu, S. Wang, Charge-transfer emission involving three-coordinate organoboron: V‐shape versus U‐shape and impact of the spacer on dual emission and fluorescent sensing, Chem. Eur. J. 13 (2010) 5713—5723.

[12] (a) M. Hirai, F.P. Gabbaï, Lewis acidic stiborafluorenes for the fluorescence turn-on sensing of fluoride in drinking water at ppm concentrations, Chem. Sci. 5 (2014) 1886—1893;

(b) C.R. Wade, F.P. Gabbaï, Colorimetric turn-on sensing of fluoride ions in H2O/CHCl3 mixtures by pyridinium boranes, Dalton Trans. (2009) 9169—9175；

(c) C.H. Chen, F.P. Gabbaï, Exploiting the strong hydrogen bond donor properties of a borinic acid functionality for fluoride anion recognition, Angew. Chem. Int. Ed. 57 (2018) 521—525.

[13] (a) H. Zhao, F.P. Gabbaï, A bidentate Lewis acid with a telluronium ion as an anion-binding site, Nat. Chem. 2 (2010) 984—990;

(b) Y. Kim, F.P. Gabbaï, Cationic boranes for the complexation of fluoride ions in water below the 4 ppm maximum contaminant level, J. Am. Chem. Soc. 131 (2009) 3363—3369.

[14] T.W. Hudnall, F.P. Gabbaï, Ammonium boranes for the selective complexation of cyanide or fluoride ions in water, J. Am. Chem. Soc. 129 (2007) 11978—11986.

[15] Y. Sun, N. Ross, S.B. Zhao, K. Huszarik, W.L. Jia, R.Y. Wang, D. Macartney, S. Wang, Enhancing electron accepting ability of triarylboron via pi-conjugation with 2,2'-bipy and metal chelation:

5,5'-bis(BMes(2))-2,2'-bipy and its metal complexes, J. Am. Chem. Soc. 129 (2007) 7510—7511.

[16] (a)Y. Deng, Y. Sun, D. Cao, Y. Chen, Z. Liu, Q. Fang, Two-photon excited fluorescence properties and anions recognition of a trivalent organoboron compound, J. Mol. Struct. 1000 (2011) 145—149;

(b) S.K. Sarkar, P. Thilagar, A borane-bithiophene-BODIPY triad: intriguing tricolor emission and selective fluorescence response towards fluoride ions, Chem. Commun. 49 (2013) 8558—8560;

(c) P. Chen, R.A. Lalancette, F. Jäkle, π-Expanded borazine: an ambipolar conjugated B-π-N macrocycle, Angew. Chem. Int. Ed. 51 (2012) 7994—7998;

(d) X. Yin, K. Liu, Y. Ren, R.A. Lalancette, Y.L. Loo, F. Jäkle, Pyridalthiadiazole acceptor-functionalized triarylboranes with multi-responsive optoelectronic characteristics, Chem. Sci. 8 (2017) 5497—5505.

[17] J. Lei, F. Qi, Y. Mao-Sen, L. Zhi-Qiang, S. Yu-Xiang, C. Hong-Feng, Switching high two-photon efficiency: from 3,8,13-substituted triindole derivatives to their 2,7,12-isomers, Org. Lett. 12 (2010) 5192—5195.

[18] J.L. Fillaut, H. Akdas-Kilig, E. Dean, C. Latouche, A. Boucekkine, Switching of reverse charge transfers for a rational design of an OFF-ON phosphorescent chemodosimeter of cyanide anions, Inorg. Chem. 52 (2013) 4890—4897.

[19] R. Wang, J. Li, G. Li, C. Hao, Y. Zhang, S. Wang, J. Zhao, Q. Liu, Z. Shi, Synthesis of 1-amino-12-hydroxyl-perylene tetra-(alkoxycarbonyl) for selective sensing of fluoride, Dyes Pigments 156 (2018) 225—232.

[20] K. Dhanunjayarao, V. Mukundam, K. Venkatasubbaiah, Ratiometric sensing of fluoride anion through selective cleavage of Si-O bond, Sens. Actuators B 232 (2016) 175—180.

[21] S.K. Padhan, M.B. Podh, P.K. Sahu, S.N. Sahu, Optical discrimination of fluoride and cyanide ions by coumarin-salicylidene based chromofluorescent probes in organic and aqueous medium, Sens. Actuators B 255 (2018) 1376—1390.

[22] H. Li, R.A. Lalancette, F. Jakle, Turn-on fluorescence response upon anion binding to dimesitylboryl-functionalized quaterthiophene, Chem. Commun. 47 (2011) 9378—9380.

[23] L. Wang, L. Li, D. Cao, Dual binding site assisted chromogenic and fluorogenic discrimination of fluoride and cyanide by boryl functionalized BODIPY, Sens. Actuators B 228 (2016) 347—359.

Caption for Table

Table 1. Several organic fluorescent probes and their sensing properties for F^- and CN^-.

Caption for Scheme

Scheme 1. Synthetic routes to **PB1** and **PB2**.[a] [a]Reaction conditions: (a) 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane), KOAc, $Pd(PPh_3)_2Cl_2$, 1,4-dioxane, reflux, 4 h; (b) NBS, AIBN, CCl_4, reflux, 4 h; (c) bis(pyridin-2-ylmethyl)amine, NaOH, DCM, 0 ˚C, overnight; (d) $Pd(PPh_3)_4$, toluene, ethanol, 1 M K_2CO_3 aqueous solution, 80 ˚C, 8 h.

Captions for Figures

Figure 1. Absorption (a) and normalized PL (b) spectra of **PB1** and **PB2** in THF (10 μM).

Figure 2. Changes in the fluorescence spectra of **PB1** (10 μM) in H_2O/THF (1:9 vol) upon addition of KCN (a) and KF (b); Changes in the fluorescence spectra of **PB2** (10 μM) in H_2O/THF(1:9 vol) upon addition of KCN (c) and KF (d). Inset: Plot of emission intensity as a function of the concentrations of CN^- or F^-; the visual fluorescence color of probe **PB2** upon addition of KCN and KF under a 365nm UV lamp.

Figure 3. Fluorescence changes of **PB2** in H_2O/THF (1:9 vol.) solutions (10 μM) upon addition of various anions (3 equivalents) using their potassium salt as the anions source.

Figure 4. Changes in the fluorescence spectra of **PB2** (10 μM) in pure water upon addition of KCN (a) and KF (b).

Figure 5. TOF-MS-EI of the adducts of **PB2** with KCN (a) and KF (b).

Figure 6. Schematic illustration of intramolecular charge-transfer (ICT) before and after **PB2** binding with KCN and KF.

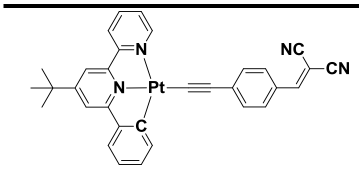
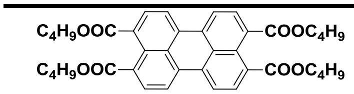
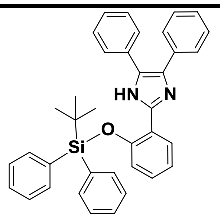
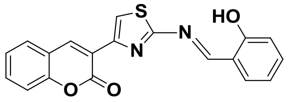
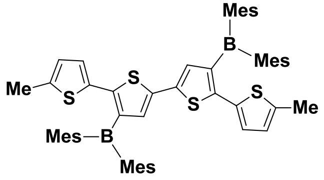
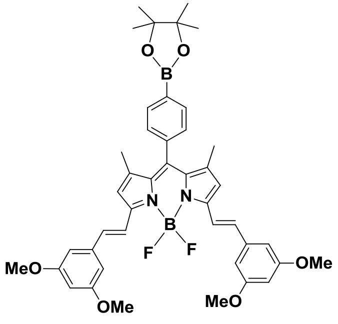
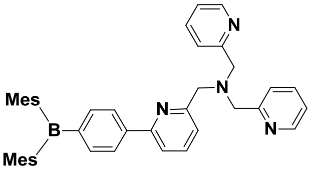
Probes	Response	LODS	Solvents	Sensing ions	References
	turn on	6 μM	CH_2Cl_2	CN^-	[18]
	turn off	1.18 μM	CH_2Cl_2	F^-	[19]
	turn on	no data	DMSO	F^-	[20]
	turn on	0.72 μM	CH_3CN	F^-	[21]
	turn on	2.7 μM	CH_3CN/H_2O (1:1, vol)	CN^-	
	turn on	no data	THF	F^- & CN^-	[22]
	turn off	2.96 μM	THF/H_2O (98:2, vol)	F^-	[23]
	ratio	5.23 μM		CN^-	
	turn off	2.12 μM	THF/H_2O (9:1, vol)	F^-	This work
	turn on	0.39 μM		CN^-	
	turn on	0.79 μM	water	CN^-	

Table 1

Highlights:

> A tri-(2-picolyl)amine-modificated triarylborane was synthesized. > The photophysical properties of this compound were explored. > The triarylborane can capture and differentiate CN^- and F^- in aqueous solution. > It exhibited fluorescent enhancement for CN^- and fluorescent quenching for F^-. > The sensor can form 2-to-2 adduct with KCN and 1-to-1 adduct with KF.