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Turn-on colorimetric sensing of fluoride ions by a cationic triarylborane bearing benzothiazolium

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ABSTRACT

A cationic triarylborane Lewis acid bearing benzothiazolium moiety, 2-(4′-dimesitylborylphenyl)-3-methylbenzo[*d*]thiazol-3-ium ([**2**]$^+$) was prepared from a neutral borane (**2a**) and their crystal structures were determined from X-ray diffraction studies. While **2a** shows a blue-shift with a small decrease in the UV–vis absorption band upon fluoride binding to the boron atom, [**2**]$^+$ undergoes a red-shift of the absorption band which tails over visible region, giving rise to the color change of the solution from colorless to yellow. The fluoride binding constant in THF/H_2O (9/1, v/v) is calculated to be 1.3×10^4 M^{-1} that is much greater than that of a neutral borane **2a** ($K = 4.2 \times 10^2$ M^{-1}). DFT calculation results suggest that the absorption process in the fluoroborate (**2F**) is involved with π(Mes)→π^*(phenylbenzothiazolium) intramolecular charge transfer and the greater elevation of the π(Mes) donor level is responsible for the turn-on colorimetric response of [**2**]$^+$.

1. Introduction

The recognition and quantification of fluoride anions in chemical and physiological systems are of great interest because they play important roles in dental health and in treating osteoporosis but are toxic when exposed to overdoses [1–3]. A number of fluoride sensors based on optical and electrochemical methods have been developed for the detection of fluoride [4–11]. Among them, triarylborane compounds have been particularly intriguing because of their high fluorophilicity [5,6,8,9,12–29]. Moreover, optical changes in color [13,28,30], absorption, or fluorescence [19,27,31–33] before and after a binding event of fluoride to the boron center of triarylboranes have provided a simple and easy detection of fluoride. While most of triarylborane sensors for fluoride developed to date have successfully operated in organic media, such sensors showed a limited binding response in the presence of water that interferes with the fluoride binding. Since fluoride anion is present in abundance in aqueous media, detection of fluoride in aqueous or water-compatible media is of great importance in real applications. To address this issue, many efforts have been devoted to enhance the Lewis acidity of triarylborane to overcome hydration of fluoride. Some of the plausible strategies are involved with the introduction of electron-withdrawing groups such as *o*-carborane cages [34,35] and cationic substituents [30,36–46] into triarylboranes or with the use of metal chelation [31,47], all of which were found to be effective in enhancing the Lewis acidity of a boron center. In particular, the cationic triarylboranes have been shown to increase largely the fluorophilicity of the boron center enough to be operating in aqueous media due to the favorable Coulombic attractions that assist B–F dative interactions [38,39,41,43–45].

On the other hand, development of a new design principle that may lead to the efficient detection of fluoride at a low level of concentration has been also equally regarded important from an analytical point of view. In most cases, triarylboranes are conjugated with aromatic fluorophore (or chromophore) through the empty p_π orbital of boron atom. Fluoride binding disrupts the extended conjugation because of population of the boron p_π orbital, thus giving rise to the quenching of the absorption or fluorescence intensity of the triarylboranes. When triarylborane displays an initial absorption in the visible region, which makes the solution colored, disappearance of the color can be accompanied by the fluoride binding [28]. Although such turn-off responses have been widely observed in the usual triarylborane-based sensors, turn-on sensors have also attracted great attention due to their better suitability for practical uses [48–54]. For example, Wang et al. reported a turn-on fluorescence sensor that utilizes intramolecular electron transfer from triarylamine donor to triarylborane acceptor [32] and also investigated turn-on phosphorescence responses

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using Ru(II)- [55] and Pt(II)-borane [31,56,57] conjugates. Huang et al. demonstrated that turn-on switching from phosphorescence to fluorescence can be achievable using Ir(III)-borane conjugate [58]. Yoon et al. reported a ratiometric fluorescence change as well as enhanced fluorophilicity in the bidentate receptor bearing *ortho*-boronic acid and imidazolium moiety [59]. Gabbaï et al. have shown that blocking of a PET (photo-induced electron transfer) process from organic fluorophores to borane by fluoride binding can induce a fluorescence turn-on response of phosphonium boranes which can be operating in aqueous solution [37]. We also reported very recently that metal-to-ligand charge transfer (MLCT) phosphorescence can be effectively turned on by preventing a PET process from MLCT state to the auxiliary borane ligand upon fluoride binding [60]. In addition to the turn-on response of emission mentioned above, Gabbaï et al. reported a colorimetric turn-on sensor based on cationic pyridinium boranes, which can extract fluorides biphasically in water/$CHCl_3$ mixture [30]. They have shown that the turn-on color change is attributed to the intramolecular charge transfer (CT) from borate to pyridinium moiety, which has been newly induced in the visible region after fluoride binding.

Since the colorimetric turn-on response may provide the most simple naked eye detection of fluoride, the cationic boranes that can exhibit a colorimetric turn-on response, as well as can operate in aqueous solution at a low level of fluorides will be promising in real applications. For this purpose, we have been interested in the heterocyclic benzothiazole which has been widely used in dyes and can be easily converted into a cationic form [61–63]. In particular, benzothiazole and benzothiazolium derivatives have been effectively utilized as a colorimetric or fluorescent signaling unit in metal cation sensing [64–69] and very recently in fluoride sensing [70,71]. Thus, if the cationic borane with benzothiazolium moiety induces a low-energy intramolecular CT (ICT) transition after fluoride binding, one may expect turn-on response toward fluoride as similarly demonstrated in the pyridinium boranes.

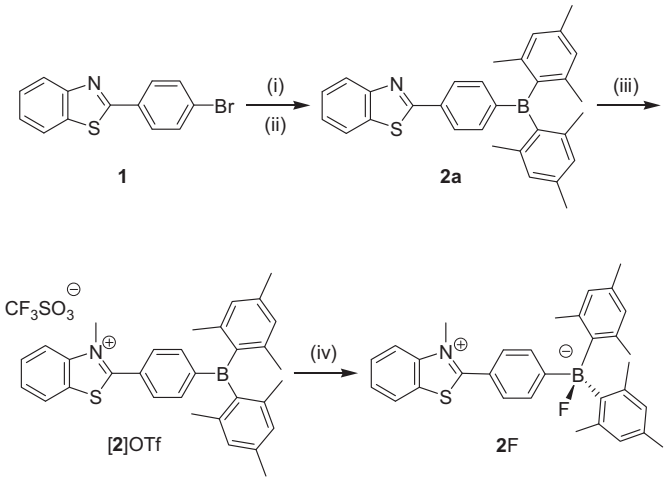
In this report, we prepared a triarylborane containing benzothiazolium moiety and investigated its fluoride binding properties in THF/H_2O (9/1, v/v) solution. The details of synthesis, characterization, and colorimetric turn-on sensing properties for fluorides at a low level of concentration (~4 ppm) are described.

2. Results and discussion

2.1. Synthesis and characterization

The reaction between the lithium salts derived from 2-(4-bromophenyl)benzo[*d*]thiazole (**1**) [72] and dimesityboron fluoride (Mes_2BF) in THF afforded the triarylborane containing benzothiazole moiety, 2-(4-bromophenyl)benzo[*d*]thiazole (**2a**) as a pale yellow solid in moderate yield (66%, Scheme 1). The identity of **2a** has been fully characterized by multinuclear NMR spectroscopy, elemental analysis, mass spectrometry, and X-ray diffraction methods. While the ^1H and ^{13}C NMR spectra show the expected resonances corresponding to the benzothiazole and Mes_2B moieties, the ^{11}B NMR signal detected at δ 73.8 ppm confirmed the presence of a three-coordinated boron center. Furthermore, X-ray diffraction studies revealed the molecular structure of **2a** (Fig. 1 and Table 1). The boron atom of the triarylborane moiety adopts a trigonal planar geometry ($\sum_{(C-B-C)} = 359.9°$), as consistent with the ^{11}B resonance. The phenyl and benzothiazole ring fragments forms a dihedral angle of 3.5(1)°, indicating a planar arrangement between the two rings.

Treatment of **2a** with excess MeOTf in Et_2O resulted in the formation of cationic tirarylborane ($[\mathbf{2}]^+$) containing benzothiazolium



Scheme 1. (i) *n*-BuLi, THF, −78 °C; (ii) Mes_2BF, THF, 25 °C; (iii) Methyl triflate, ether, 25 °C; (iv) TBAF, $CHCl_3$, 25 °C.

moiety (Scheme 1). While the formation of [**2**]OTf has been characterized by multinuclear NMR spectroscopy, elemental analysis, and mass spectrometry, X-ray diffraction studies unequivocally revealed the presence of *N*-methylated benzothiazolium moiety as well as a trigonal planar boron center ($\sum_{(C-B-C)} = 359.9°$) (Fig. 1, right), the latter of which is also consistent with the ^{11}B signal observed at δ 75.3 ppm. In contrast to the almost planar arrangement between the phenyl and benzothiazole ring fragments in **2a**, the two rings in $[\mathbf{2}]^+$ shows a large distortion ($\angle_{dihedral} = 51.8(2)°$) probably due to the steric hindrance between phenylene C–H and *N*-methyl group of the benzothiazolium moiety. To gain insight into the fluoride binding properties, the cationic $[\mathbf{2}]^+$ was further converted into its fluoride adduct (**2F**) from the reaction with one equiv of tetra-*n*-butylammonium fluoride (TBAF) in $CHCl_3$. The zwitterionic **2F** could be easily obtained as a yellow solid by simple filtration of a reaction mixture. While the ^1H and ^{13}C NMR spectroscopy and elemental analysis showed the formation of fluoride adduct, the ^{11}B NMR signal at δ 9.1 ppm confirmed the presence of a four-coordinated boron center. It is also notable that **2F** forms a yellow solution different from the colorless $[\mathbf{2}]^+$.

2.2. Fluoride sensing properties

To investigate fluoride sensing properties of $[\mathbf{2}]^+$, UV–vis titration experiments were carried out. The cationic borane $[\mathbf{2}]^+$ features a low-energy absorption band at 325 nm ($\log \varepsilon = 4.33$) in THF, as similarly observed in the usual Mes_2B-based triarylboranes (Fig. 2a) [5,8,25,28]. Upon addition of incremental amounts of fluoride, this band was gradually quenched while forming a new absorption band at the lower energy region (ca. 355 nm) which tails over visible region (450 nm). The absorption band after the addition of one equiv of fluoride was also found to be exactly matched with that of **2F**, confirming the binding of fluoride to the boron atom of $[\mathbf{2}]^+$.

To elucidate the absorption change of $[\mathbf{2}]^+$ after fluoride binding, the structures of $[\mathbf{2}]^+$ and **2F** were optimized using density functional theory (DFT) methods. To include the solvent effects of THF, the Polarizable Continuum Model (PCM) [73–75] was used. As shown in Fig. 3, the highest occupied molecular orbitals (HOMOs) of both compounds are mainly located on the mesityl groups while the lowest unoccupied molecular orbitals (LUMOs) are localized on the phenylbenzothiazolium moiety. Further inspection of LUMOs indicates that the empty $p_\pi(B)$ orbital of $[\mathbf{2}]^+$ largely contributes to LUMO delocalization, but no more conjugation in **2F** due to occupancy