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A highly emissive cruciform triarylborane as a ratiometric and solid state fluorescence sensor for fluoride ions

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ABSTRACT

We disclosed a novel cruciform tri-coordinate organoboron compound, 2′,5′-bis{[(4-dimesitylboryl)phenyl]ethynyl}-1′,4′-bis[(4-*N*,*N*-diphenylamino)phenyl]-[1,1′:4′,1′]terphenyls, which displays a characteristic intramolecular charge transfer transition and is highly emissive both in solutions and solid state. The complexation with fluoride ions induces a large blue shift in fluorescence, enabling ratiometric fluorescence sensing of fluoride. In addition, its prompt response to fluoride ions was also observed even in the solid state.

The selective sensing of fluoride ion is of great interest owing to its important roles in a wide range of biological, medical, and chemical processes and applications, such as dental care,[1] treatment of osteoporosis,[2] fluorination of water supplies,[3] and even in chemical and nuclear warfare agents.[4] The design principles of fluoride probes are typically based on the hydrogen bonding formation between the active N–H group of organic chromophores and fluoride ions.[5] Recently, specific Lewis acid/base interactions have been adopted as a new efficient approach for fluoride sensing. One intriguing example is the complexation of tri-coordinate boron compounds with fluoride anions, which would disrupt the p_π–π^* conjugation between the boron center and the attached π-conjugated system and thus lead to a significant change in the UV/Vis absorption, fluorescence, and two-photon excited fluorescence.[6–12] In addition, these organoboron compounds possess high selectivity for fluoride binding over other anions, such as chloride, bromide, and iodide, owing to the steric hindrance of bulky substituents on the boron center, which not only ensures stability to water including atmospheric moisture but also prevents the complexation of the boron center with other large Lewis bases. Hereby, tri-coordinate conjugated organoboron compounds have attracted increased attention as efficient fluoride ion sensors. Among the various analytical methods, fluorescent sensing is highly desirable because of its high sensitivity. Most of the reported fluorescent fluoride sensors of organoboron compounds are based either on fluorescent quenching[7b] or on fluorescence enhancement,[6b,11a,c] few on ratiometric fluorescence, where the detection sensitivity may be increased by measuring the ratio changes of the fluorescence intensities at two different wavelengths. To develop ratiometric response probes, one seductive strategy is to design cruciform chromophores possessing spatially separated frontier molecular orbitals, for which the analyte binding would affect either HOMO or LUMO to a different degree and thus induce a significant change in emission and absorption spectra.[13] Herein, we designed a new cruciform tri-coordinate organoboron compound, 2′,5′-bis{[(4-dimesitylboryl)phenyl]ethynyl}-1′,4′-bis-[(4-*N*,*N*-diphenylamino)phenyl]-[1,1′:4′,1′]terphenyls **1** (Fig. 1), in which the electron-withdrawing [(4-dimesitylboryl)phenyl]ethynyl branch and the electron-donating 4-(*N*,*N*-diphenylamino)-phenyl branch are connected perpendicularly with via a central benzene core. We envisioned that the HOMO would be delocalized over the electron-donating 4-(*N*,*N*-diphenylamino)phenyl arm

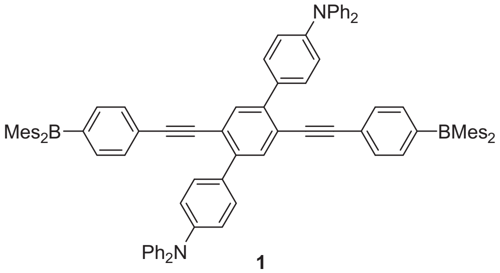

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Figure 1. Structure of cruciform triarylborane **1**.

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while the LUMO would be delocalized over the electron-withdrawing [(4-dimesitylboryl)phenyl]ethynyl axis and **1** would display a characteristic intramolecular charge transfer (CT) emission. The complexation of **1** with fluoride would increase LUMO level independently and interrupt the intramolecular CT transition, resulting in a remarkable blue shift in fluorescence. In fact, we found that **1** was highly emissive in solutions and could retain high fluorescence efficiency with large blue shift in fluorescence spectra after binding with fluoride ions, enabling ratiometric fluorescence sensing of fluoride ions. Moreover, it was observed that this cruciform triarylborane displayed intense emission as well as prompt fluorescence response to fluoride ions even in the solid state.

The synthetic route to the cruciform triarylborane **1** is shown in Scheme 1. It was readily prepared in two steps, using 1,4-dibromo-2,5-diethynylbenzene **2** as the starting material.[14] Thus, the Pd(0)-catalyzed Sonogashira coupling reaction of **2** with 1-iodo-4-dimesitylborylbenzene produced the key precursor 1,4-dibromo-2,5-bis[(4-dimesitylboryl)phenyl]ethynyl)benzene **3** in 68% yield. The following Pd(0)-catalyzed Suzuki coupling reaction of **3** with 4-(*N*,*N*-diphenylamino)phenylboronic acid afforded the cruciform triarylborane **1** in 34% yield.[15] The obtained compound **1** is very stable in air and water and can be purified by silica-gel column chromatography.

The photophysical property data of compound **1** are summarized in Table 1 and the UV/Vis absorption and emission spectra are shown in Figure 2. In cyclohexane, in addition to the intense absorption below 400 nm, **1** shows a relatively weaker shoulder band at the longer wavelength (λ_{abs} = 411 nm; log ε = 3.39). To clarify the origin of this shoulder band, theoretical calculations were performed by using time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G(d) level of theory. According to the calculation results, the present cruciform triarylborane **1** exhibits a disjoint frontier molecular orbital structure, in which the HOMO and LUMO are mainly delocalized over the electron-donating 4-(*N*,*N*-diphenylamino)phenyl moiety and the electron-withdrawing 4-[(dimesitylboryl)phenyl]ethynyl framework, respectively (Fig. 3). The shoulder absorption band at 411 nm is assignable to the intramolecular CT transition from the HOMO to the LUMO. These calculation results clearly suggest a polarized structure in the excited state. In the fluorescence spectra, **1** displays extremely strong greenish blue fluorescence at 470 nm with a quantum yield close to unity. Notably, the fluorescence is highly dependent on the polarity of the solvent while the absorption shows only trivial solvent dependence. With increasing polarity of solvent, the fluorescence maximum is red shifted remarkably from 470 nm in cyclohexane to 498 nm in toluene, and 540 nm in THF, indicating the intramolecular CT character in the excited state, which is in good accordance with the theoretical calculation results.

Table 1
Photophysical properties of **1**

	λ_{abs}/nm (log ε)	λ_{em}/nm[b]	Φ_F[c]
Cyclohexane	352 (4.10), 411 (sh[a], 3.39)	470	0.98
Toluene	359 (4.59), 406 (sh[a], 3.85)	498	0.98
THF	358 (4.85), 418 (sh[a], 4.12)	540	0.43

[a] Shoulder band.
[b] Excited at the longest absorption maxima.
[c] Calculated using fluorescein as standard.

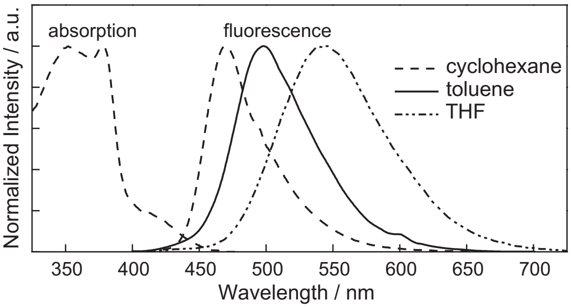


Figure 2. UV/Vis absorption and fluorescence spectra of **1**.

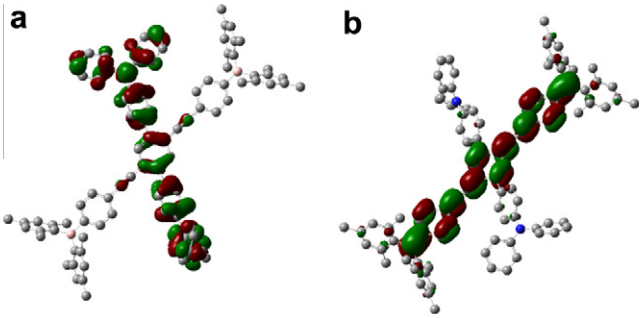
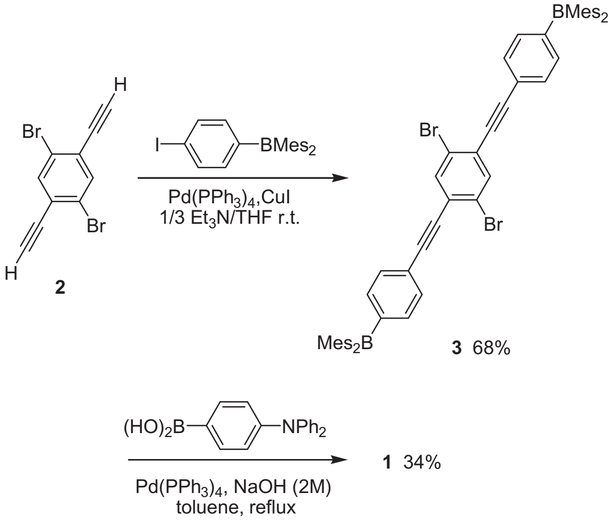


Figure 3. Pictorial drawings of (a) HOMO and (b) LUMO of **1** calculated at the B3LYP/6-31G(d) level of theory.



Scheme 1. Synthesis of cruciform triarylborane **1**.

In the course of purification of **1** by flash column, we noticed that it emitted strong yellowish green fluorescence after evaporation of solvent, similar to that in toluene. This observation prompted us to investigate its photophysical properties in the solid state in details (Fig. 4). It was found that in addition to strong emission in powder form, **1** exhibited remarkably intense yellowish green emission for thin film, which was prepared by spin-coating from a solution of **1** in dichloromethane (3 mg/mL). Moreover, a spin-coated poly(methyl methacrylate) (PMMA) film doped with **1** also shows brilliant bluish green fluorescence. In view of the absorption and emission spectra, it maintains almost the same spectra in thin film and PMMA film as those in toluene solution, indicating formation of neither aggregation in the ground state nor an excimer in the excited state, presumably owing to the suppressed intermolecular interaction as a result of the nonplanar structures of central *para*-terphenyl framework in the cruciform structure[16] and the steric bulkiness of dimesitylboryl groups. The suppressed intermolecular interaction is supposed to be an important factor contributing to the intense solid state fluorescence.

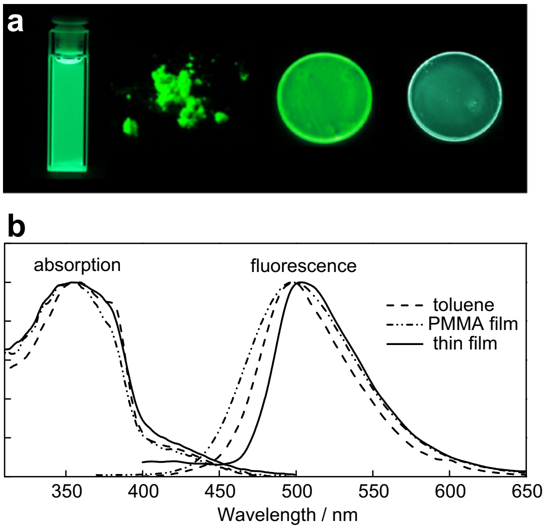


Figure 4. (a) Photographs of **1** under irradiation at 365 nm, arranged in the following order: in toluene, powder, thin film and PMMA film. (b) UV/Vis absorption and fluorescence spectra of **1** in toluene and in the solid state.

Considering the characteristic intramolecular CT emission of the present cruciform triarylborane **1**, we envisioned that the co-ordination of a fluoride ion to the boron center would interrupt the strong intramolecular CT transition, leading to a significant change in the fluorescence spectra. On basis of this idea, we investigated the fluoride sensing ability of **1**. The titration experiment of **1** with fluoride ion was carried out in THF by using *n*-Bu_4NF (TBAF) as the fluoride source. The fluorescence change of **1** (2.38 μM) upon addition of TBAF is shown in Figure 5. Although **1** contains two boron atoms, no stepwise changes were observed. As the concentration of TBAF increased, the emission at 540 nm decreased gradually, and a new blue-shifted band appeared at 442 nm. This change became saturated when the concentration of TBAF amounted to 29.0 μM. The presence of a clear isobestic point might suggest that only one new species was formed during the titration process. The molar ratio analysis showed that the spectral change was attributed to the formation of a 1:2 complex of **1** with two equivalents of F^- ions (see the Supplementary data). The binding constant was determined to be $3.27 \times 10^{10}\ M^{-2}$, which is comparable to those of other tri-coordinate organoboron compounds.[6–12] Notably, the complexation with fluoride ions did not cause any decrease in the fluorescence efficiency ($\Phi_F = 0.43$ for **1**; $\Phi_F = 0.83$ for $\mathbf{1}\cdot F_2^{2-}$) and the difference at the two wavelengths is very large, ca. 100 nm. This situation provides the opportunity for a ratiometric fluorescence sensing. Figure 6 shows a correlation between intensity ratios of fluorescence intensity at 442 nm with those at 540 nm (I_{442}/I_{540}) versus fluoride concentration. The ratios of emission intensities at 442 and 540 nm (I_{442}/I_{540}) exhibit a dramatic change from 0.02:1 to 13.6:1. Such a large change of emission intensity ratios at two wavelengths is desirable for ratiometric fluorescent probes, as the sensitivity and the dynamic range of ratiometric probes are controlled by the emission ratio. Moreover, a dramatic change of emission was observed from yellow to sky-blue, thus enabling colorimetric fluoride ion sensing by naked eyes. In contrast to the remarkable changes in the fluorescence, only trivial changes were observed in the absorption spectra after addition of excess fluoride anions (Fig. S-2).

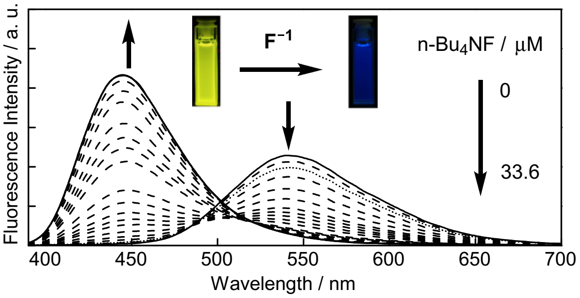


Figure 5. Fluorescence spectra change of **1** (2.38 μM in THF) upon addition of TBAF (λ_{ex} = 370 nm). Inset: emission color change upon addition of TBAF.

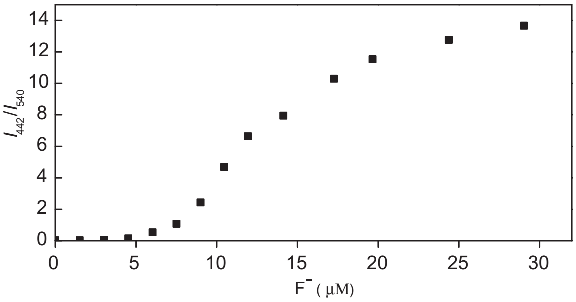


Figure 6. Plot of fluorescence intensity ratios between 442 and 540 nm (I_{442}/I_{540}) versus concentration of F^- in THF.

The realization of solid state detection is quite meaningful for the sensor in its practical application in portable sensing devices. Since **1** maintains intense fluorescence in the solid state, its fluoride sensing in the solid state was also investigated. We prepared spin-coated PMMA film doped with the probe compound **1** (0.5 mg of **1** and 500 mg PMMA). The cruciform triarylborane **1** in polymer matrix responded to TBAF solution immediately. Figure 7 shows the patterned film images of two characters of Chinese abbreviation for Shandong University, which were inscribed by using a writing brush with a THF solution of TBAF under UV light. Evident emission color change was observed upon exposure to fluoride. In addition, the polymer film is stable under ambient light and temperature over weeks with no obvious change in response. Thereby it was showed that compound **1** exhibited excellent fluorescence sensing performance even in the solid state, which will be very useful for the fabrication of sensing devices with fast and convenient detection for fluoride ions.

In conclusion, we have designed and synthesized a novel cruciform triarylborane **1**, in which the electron-withdrawing [(4-dimesitylboryl)phenyl]ethynyl branch and the electron-donating 4-(*N*,*N*-diphenylamino)phenyl branch are connected perpendicularly with via a central benzene core. This compound displays a characteristic intramolecular CT transition and is highly emissive both in solutions and in the solid state. Binding of fluoride ions leads to the remarkable fluorescence spectra and color changes, enabling colorimetric and ratiometric fluoride ion sensing. In addition, this triarylborane also displays prompt response to fluoride ions even in the solid state.

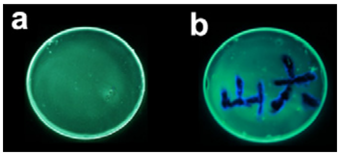


Figure 7. Photographs of (a) PMMA film dope with **1** under irradiation at 365 nm and (b) the patterned film images of two characters of the Chinese abbreviation for Shandong University inscribed by using a writing brush with fluoride ion under irradiation at 365 nm.

Acknowledgments

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Supplementary data

Supplementary data (experimental procedures, analytical data and NMR spectra for all new compounds, theoretical calculations of **1**, the molar ratio analysis and binding constant determination of titration of **1** with fluoride ions) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.05.076.

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15. *Preparation and characterization data of* **1**: To a mixture of 1,4-dibromo-2,5-bis{[(4-dimesitylboryl)phenyl]ethynyl}benzene **3** (93.2 mg, 0.1 mmol), 4-(diphenylamino)phenyl boronic acid (60.0 mg, 0.21 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) were added degassed toluene (10 ml) and NaOH (2M, 0.2 ml) successively under a stream of nitrogen. The reaction mixture was refluxed overnight. The mixture was cooled to room temperature and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (petroleum ether/CH_2Cl_2 3:1, $R_f = 0.18$) to afford 35 mg (0.034 mmol) of **1** in 34% yield as yellowish green solids: mp >300 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.00 (s, 24H), 2.33 (s, 12H), 6.84 (s, 8H), 6.97 (t, J = 6.9 Hz, 4H), 7.19 (m, 20H), 7.30 (d, J = 7.8 Hz, 4H), 7.43 (d, J = 7.8 Hz, 4H), 7.59 (d, J = 8.7 Hz, 4H), 7.71 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.2, 23.4, 91.9, 94.4, 121.6, 123.0, 124.5, 126.6, 128.3, 129.3, 130.3, 130.8, 133.3, 133.4, 136.1, 138.9, 140.8, 141.6, 142.2, 147.6, 147.7; HRMS (FTMS): (M^+) 1258.6734; calcd for $C_{94}H_{82}N_2B_2$: 1258.6731.
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