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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# Truxene-cored π-expanded triarylborane dyes as single- and two-photon fluorescent probes for fluoride

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***Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX***

**DOI: 10.1039/b000000x**

Fluoride anion ($F^-$) significantly affects chemical, biological, and environmental processes. Fluoride recognition and detection have received increasing attention. Convenient, effective, and sensitive fluorescent probes for $F^-$ should urgently be designed and synthesized. In this study, we describe a strategy for constructing two triarylborane-based fluoride fluorescent probes: 2,7,12-tri(2-(5-(dimesitylboryl)thiophen-2-yl)ethynyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**C3B3**) with π-3A(acceptor) configuration and 2,7-di(*N*,*N*-diphenylamino)-12-(5-(dimesitylboryl)thiophen-2-yl)-5,5′,10,10′,15,15′-hexaethyltruxene (**N2SB**) with 2D(donor)-π-A configuration. The loss of color of the tetrahydrofuran solution of these probes from greenish yellow suggests that they can conveniently monitor $F^-$ at a low concentration (10 μM) with apparatus-free. The different structural features of these probes varied their fluorescent responses to $F^-$. The single-photon fluorescence intensity of **C3B3** declined 90% upon the addition of 4.5 equivalents of $F^-$ to its tetrahydrofuran solution. However, the single-photon fluorescence intensity of **N2SB** was enhanced six-fold to 2.5 equivalents of the $F^-$. Under the experimental conditions, the detection limit of the two probes for $F^-$ can reach to (12–13) μM (**C3B3)** and (3–5) μM (**N2SB)**. The ability of the two probes in detecting $F^-$ in their toluene solution in the two-photon mode was also investigated. The sensitive two-photon fluorescence responses of both probes make them excellent two-photon fluorescence probes.

## Introduction

Given the significance of anions in biological and environmental processes, identifying anions is attracting considerable interest.[1–2] Fluoride ion ($F^-$), the smallest anion, significantly affects the treatment of osteoporosis and dental health.[3] $F^-$ is often added to drinking water, toothpaste, and some drugs. However, chronic exposure to high levels of this anion can lead to skeletal fluorosis, urolithiasis, or even cancer.[3–4] Therefore, detecting and monitoring this small anion is very important. The ion-selective electrode, ion chromatography, and standard Willard–Winter methods are usually used to quantitatively analyze fluoride.[5–8] However, all these methods have complicated procedures, high costs, or low mobility.[9] Thus, highly selective, sensitive, convenient, and rapid fluoride detection methods should be developed.

Numerous efforts have been devoted to discovering effective fluorescent probes for $F^-$ because the fluorescent probe method detects analytes with outstanding sensitivity, is neither invasive nor damaging, and has a short response time ($<10^{-9}$ s).[10–11] Furthermore, this method can realize "naked-eye" detection and provide both qualitative and quantitative information with simple equipment. Several synthetic fluorescent probes for $F^-$ have been designed and studied. At the forefront of this research, hydrogen bond-based or fluoride desilylation reaction-based fluorescent probes have been explored thoroughly and have exhibited unique advantages in some respects.[1,9,10,12–17] Lewis acid and base interaction–based trivalent organoboron compounds as $F^-$ fluorescent probes have received increasing attention because of their selectivity for $F^-$ and the wide scope of their use.[18] Having a vacant $p_z$ orbital, trivalent organoboron is inherently electron-poor and forms strong binding with the most electronegative $F^-$.[19] The big steric hindrance of triarylboron compounds around the boron atom can improve the sensing selectivity of the smallest anion. Since Yamaguchi *et al*. first reported the fluoride ion sensing of trianthrylborane,[20,21] several researchers have extended and reinforced this research.[22–41] Gabbaï *et al*. successfully chelated cationic arylborane-based $F^-$ probes that can tolerate aqueous media.[22–24] Wang *et al*. demonstrated an N-π-B charge-transfer system with a fluorescent signal-on feature.[25,26] Jäkle *et al*. developed bora-cyclophanes with high affinity for $F^-$.[27] Most of these reported triarylboron-containing fluorescent probes exhibit good selectivity and sensitivity to $F^-$. However, either low emission efficiency or complex molecular design limits the application of most of these probes.[35] Furthermore, these probes were mostly designed based on single-photon (SP) fluorescence technology, which has relatively low signal/noise ratios and strong photobleaching. Compared with SP fluorescence, two-photon (TP) fluorescence excited by simultaneously absorbing two long-wavelength photons through a virtual state offers intrinsic high three-dimensional resolution, increased penetration

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depth, reduced photodamage, and self-absorption.[42] Some reported triarylboron compounds have exhibited excellent TP fluorescence.[43–46] However, the studies of triarylboron compounds as TP fluorescence probes for fluoride are very limited.

Several TP compounds have been used as TP fluorescent probes in TP microscopy to image the distribution of ions in cellular processes.[47,48] However, common organic compounds emit very weak TP fluorescence and have low values of TP absorption cross-section ($\delta$), a fundamental parameter for evaluating TP absorption. Research on the structure–property relationship reveals that the TP absorption and fluorescence of an organic molecule are correlated to its three structural characteristics: π-conjugation length, molecular symmetry, and the donor/acceptor strength of the chromophore.[47,49] For instance, π-conjugated motifs with a strong donor/acceptor generally emit excellent TP fluorescence, and coplanar octupolar molelules with $C_3$-symmetry exhibit a large TP cross section arising from cooperative enhancement during the molecular three branches. These factors should be considered in designing a TP fluorescent probe, aside from the prime selective binding site for the analyte. Thus, connecting triarylboron to a special organic π-system is a promising design for both SP and TP $F^-$ fluorescent probes. After binding with $F^-$, the $F^-$ → boron (B) coordination disrupts the $p_\pi$(B)-π conjugation, changes the intramolecular charge transfer, and ultimately significantly changes the optical properties.

In this study, we used truxene (10,15-dihydro-5*H*-diindeno[1,2-*a*;1',2'-*c*]fluorene), a heptacyclic polyarene with $C_3$-symmetric configuration and a rigid planar skeleton, as the π-conjugated central core. After the π-conjugation of truxene at its 2,7,12-positions was expanded through two different strategies, the big π-system was connected to the dimesitylboryl group as the $F^-$ recognition site to form two π-expanded triarylborans: 2,7,12-tri(2-(5-(dimesitylboryl)thiophen-2-yl)ethynyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**C3B3**) with $C_3$-symmetric π-3A(acceptor) configuration and 2,7-di(*N*,*N*-diphenylamino)-12-(5-(dimesitylboryl)thiophen-2-yl)-5,5′,10,10′,15,15′-hexaethyltruxene (**N2SB**) with asymmetric 2D(donor)-π-A configuration (Scheme 1). These triarylborans remarkably changed color and SP/TP fluorescence upon the addition of $F^-$ to their organic solution. The different molecular designs of these compounds make them exhibit different spectrophotometric responses to $F^-$. The SP fluorescence intensity of **C3B3** was quenched (i.e., turned off) upon the addition of $F^-$ to its solution. However, the SP fluorescence of **N2SB** was enhanced (i.e., turned on) by $F^-$ titration.

## Experimental

### Chemicals

The solvents used in the synthesis were purified by standard procedures. Dried tetrahydrofuran (THF) and toluene were purified and distilled from sodium prior to use in spectrum experiments. 2-Thiopheneboronic acid, 2-ethynylthiophene, tetrakis(triphenylphosphine)palladium, tetrabutylammonium fluoride (TBAF), 18-crown-6-ether, and dimesitylboron fluoride were purchased from J&K Scientific. 5,5′,10,10′,15,15′-Hexaethyltruxene (compound **1**), 2,7,12-triiodo-hexaethyltruxene (compound **2**), 2,7,12-tri(2-thiophenylethynyl)-hexaethyltruxene (compound **3**), 2-bromo-hexaethyltruxene (compound **4**), 2-bromo-7,12-diiodo-hexaethyltruxene (compound **5**), 2-bromo-7,12-di(*N*,*N*-diphenylamino)-hexaethyltruxene (compound **6**), and 2,7-di(*N*,*N*-diphenylamino)-12-(2-thiophenyl)-hexaethyltruxene (compound **7**) were synthesized in our laboratory (for their synthesis and characterization, see Supporting Information).[50,51] All the other chemicals were obtained from local commercial suppliers and used without further purification.

### Apparatus

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance spectrometer (500 MHz for $^1$H and 125 MHz for $^{13}$C). C, H, N, and S were analyzed by using a PE 2400 autoanalyzer. Mass spectrometry analyses were performed by a Bruker Biflex III matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometer. SP absorption spectra were recorded on a Shimadzu UV1800 spectrometer, and SP fluorescence spectra were recorded on a Shimadzu RF-5301PC fluorescence spectrometer. TP fluorescence were obtained by using a Tsunami 3941-M3-BB femtosecond Ti:sapphire laser with a 532 nm Millennia Pro 5 semiconductor laser instrument as an excited source. An Ocean USB2000 fluorescence spectrometer was used to record TP fluorescence spectra.

### Synthesis of C3B3

*n*-BuLi (2.4 M solution in *n*-hexane, 1.50 mL, 3.60 mmol) was added to a stirred solution of compound **3** (0.90 g, 1.08 mmol) in dried THF (40 mL) under nitrogen at −78 °C for 5 min. This mixture was then naturally warmed to room temperature. After further reaction for 4 h, the reactants were cooled to –78 °C again, and dimesitylboron fluoride (1.00 g, 3.15 mmol) in THF (5 mL) was injected for 5 min. After further reaction for 2 h in the same temperature, the temperature was allowed to naturally rise to room temperature, and the mixture was continuously stirred for 2 d. The reactants were then diluted with ethyl acetate, washed with water, and dried over $Mg_2SO_4$. Removing the solvents yielded a crude product. Purification by column chromatography on silica gel and elution with dichloromethane-petroleum ether (1:5, v/v) yielded **C3B3** (0.48 g, 42%) as a light green powder (melting point [m.p.] = 222 °C to 224 °C). $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 0.22–0.25 (t, $J$ = 7.5, 18 H), 2.10–2.32 (m, 42 H), 2.35 (s, 18 H), 2.97–3.02 (m, 6 H), 6.88 (s, 12 H), 7.41–7.43 (d, $J$ = 10, 6 H), 7.54–7.56 (d, $J$ = 10, 3 H), 7.61 (s, 3 H), and 8.32–8.34 (d, $J$ = 10, 3 H). $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 152.9, 145.3, 141.1, 140.9, 140.1, 138.8, 138.5, 135.3, 133.6, 129.8, 128.2, 125.3, 124.6, 120.7, 97.6, 83.6, 57.0, 29.5, 23.5, 21.3, and 8.5. MALDI-TOF: $m/z$ 1572.7 [$M^+$], 1543.6 [M-29]$^+$. Elemental anal. calcd. for $C_{111}H_{111}B_3S_3$: C, 84.72; H, 7.11; and S, 6.11. Found: C, 84.91; H, 7.02; and S, 6.12.

### Synthesis of N2SB

*n*-BuLi (2.4 M solution in *n*-hexane, 0.20 mL, 0.48 mmol) was added to a stirred solution of compound **7** (0.20 g, 0.22 mmol) in dried THF (20 mL) under nitrogen at −78 °C. This mixture was then naturally warmed to room temperature. After further reaction for 4 h, the reactants were cooled to –78 °C again, and dimesitylboron fluoride (0.10 g, 0.32 mmol) in THF (5 mL) was

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injected. After further reaction for 2 h at the same temperature, the temperature was allowed to naturally rise to room temperature, and the mixture was continuously stirred for 2 d. The reactants were then diluted with ethyl acetate, washed with water, and dried over $Mg_2SO_4$. Removing the solvents yielded a crude product. Purification by column chromatography on silica gel and elution with dichloromethane-petroleum ether (1:10, v/v) yielded **N2SB** (81 mg, 31%) as a light green powder (m.p. = 188 °C to 190 °C). $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 0.23–0.27 (m, 18 H), 1.89–2.18 (m, 18 H), 2.33 (s, 6 H), 2.87–2.97 (m, 6 H), 6.86 (s, 6 H), 7.00–7.05 (m, 6 H), 7.18–7.19 (m, 6 H), 7.27–7.30 (m, 6 H), 7.46–7.47 (m, 1 H), 7.56–7.57 (m, 1 H), 7.69–7.71 (d, $J$ = 10, 6 H), 8.08–8.10 (d, $J$ = 10, 1 H), 8.14–8.16 (d, $J$ = 10, 1 H), and 8.24–8.26 (d, $J$ = 10, 1 H). $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm) $\delta$ 157.6, 154.2, 153.8, 147.9, 146.5, 143.2, 141.9, 141.4, 140.9, 138.6, 138.5, 135.3, 129.3, 128.2, 125.2, 124.9, 124.3, 122.8, 120.0, 119.7, 117.6, 56.8, 56.7, 29.5, 29.4, 29.2, 23.5, 21.3, 8.7, and 8.6. MALDI-TOF: $m/z$ 1173.9 [$M^+$], 1144.8 [M-29]$^+$. Elemental anal. calcd. for $C_{85}H_{83}BN_2S$: C, 86.85; H, 7.12; N, 2.38; and S, 2.73. Found: C, 86.67; H, 7.02; N, 2.37; and S, 2.65.

**Absorption and SP fluorescence titration of C3B3 with F$^-$**

A 1.0 mM solution of **C3B3** was prepared by dissolving 7.9 mg **C3B3** in 5.0 mL THF at room temperature. This 50.0 μL solution was then diluted to a total volume of 5.0 mL with THF to obtain a 10 μM solution for spectrophotometric experiments. A 1.8 mM THF solution of TBAF was prepared by diluting a 1.0 M THF solution of TBAF purchased from J&K Scientific. The 10 μM THF solution of **C3B3** with a volume of 2.0 mL was placed in a 1 cm standard quartz cell and titrated by stepwise adding a 5.0 μL THF solution of TBAF at a concentration of 1.8 mM to a total volume of 50.0 μL (4.5 equivalents). After every addition of TBAF, the mixture was stirred for 2 min. Absorption and SP fluorescence emission spectra were then measured at room temperature. The excitation wavelength of the fluorescence emission spectra was 365 nm, with an emission wavelength range of 370 nm to 700 nm. The fluorescence quantum yield (Φ) was determined by using rhodamine B in ethanol as the reference according to a previously reported method.[52]

**Absorption and SP fluorescence titration of N2SB with F$^-$**

The F$^-$ titration experiments of **N2SB** by absorption and SP fluorescence were conducted according to the same procedures as **C3B3**. A total of 2.5 equivalents of TBAF was added to the **N2SB** THF solution. The excitation wavelength of the fluorescence emission spectra was 355 nm, with an emission wavelength range of 360 nm to 700 nm.

**TP fluorescence titration of C3B3 with F$^-$**

The 5 μM toluene solution of **C3B3** was prepared through dilution for its 1.0 mM THF solution. This solution with a volume of 2.0 mL was placed in a 1 cm standard quartz cell and titrated by stepwise adding a 5.0 μL THF solution of TBAF at concentration of 1.8 mM to a total volume of 25.0 μL (4.5 equivalents). After every addition of TBAF, the mixture was stirred for 2 min. TP fluorescence emission spectra were then measured at room temperature at an excitation wavelength of 725 nm. To reduce reabsorption to TP fluorescence, the exciting laser beam was focused as closely as possible to the sample cell wall by a lens.

**TP fluorescence titration of N2SB with F$^-$**

The F$^-$ titration experiments of **N2SB** by TP fluorescence were conducted according to the same procedures as **C3B3**. A total of 2.5 equivalents of TBAF was added to the **N2SB** THF solution.

**Measurement of TP absorption cross section**

To investigate the changes in the TP absorption of **N2SB** and **C3B3** before and after binding with F$^-$, their TP absorption cross sections ($\delta$) were measured by the TP fluorescence method by using rhodamine B as the reference.[52,53] The TP property of rhodamine B has been well characterized in literature. This method is based on the supposition that TP fluorescence intensity is proportional to the $\delta$ of the product and fluorescent quantum yield Φ. The sample was dissolved and diluted with toluene to prepare a 5 μM toluene solution, and TP fluorescence intensity was measured. The intensities of the TP fluorescence of the reference (5 μM, in methanol) and the sample at the same excitation wavelength were determinted. The TP absorption cross section was calculated according to

$$\delta = \delta_r(F_s\Phi_r n_r c_r)/(F_r\Phi_s n_s c_s)$$

where $s$ and $r$ stand for the sample and the reference, respectively; $\delta$ is the value of the TP absorption cross section, $F$ is the TP fluorescence integral intensity of the solution emitted at the exciting wavelength, Φ is the fluorescence quantum yield, $n$ is the refractive index of the solution, and $c$ is the concentration of the solution. The $\delta_r$ of the reference was obtained from literature.[52,53]

**Theoretical calculation**

To describe the optical changes before and after **N2SB** bound with F$^-$, the orbital energy of **N2SB** and its F$^-$ complexes **[N2SB-F]**$^-$ were calculated by using the Gaussian 09 program at the B3LYP Time-Dependent Density Functional Theory (TD-DFT). The 6-31G* was used to treat all atoms. Given that the molecular sizes of **N2SB** and [**N2SB-F**]$^-$ were too large and we wanted to keep the computation feasible, all ethyl groups in the 5-, 10-, and 15-positions of truxene and the methyl groups in the mesityl groups were replaced by H-atoms. To include the solvent effects of THF, the Polarizable Continuum Model was used.[24,54]

## Results and discussion

**Synthesis of C3B3 and N2SB**

As shown in Scheme S1 (Supporting Information), the 5,5′,10,10′,15,15′-hexaethyltruxene (compound **1**) reported in our previous study was used as the starting material. After the full iodization of **1**, three iodine atoms were connected to the 2-, 7-, and 12-positions of hexaethyltruxene, and triiodo-hexaethyltruxene (compound **2**) was prepared. A conventional Sonogashira cross-coupling reaction was then conducted by using compound **2** and 2-ethynylthiophene as the reactants to obtain $C_3$-symmetric 2,7,12-tri(2-thiophenylethynyl)-hexaethyltruxene (**3**). Given the high activity of the $\alpha$-H of thiophene, compound **3** can directly react with $n$-butyllithium and dimesitylboron fluoride in an orderly manner to synthesize the object octupolar **C3B3**.

As to the synthesis of **N2SB**, an asymmetric halide 2-bromo-7,12-diiodo-hexaethyltruxene (**5**) was prepared by quantitatively brominating and iodinating compound **1**. Selective Ullmann

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condensation was then processed between diphenylamine and compound **5** to obtain 2-bromo-7,12-di(*N*,*N*-diphenylamino)-hexaethyltruxene (**6**), which stems from the different reactions between aryl bromide and aryl iodide. After a conventional Suzuki reaction with 2-thiopheneboronic acid and an ultimate boronation with dimesitylboron fluoride, compound **6** was translated to **N2SB**.

### Photophysical properties

The UV-visible absorption and SP fluorescence spectra of **C3B3** and **N2SB** are shown in Figure 1. For comparison, the UV-visible absorption and SP fluorescence spectra of 2,7,12-tri(dimesitylboryl)-hexaethyltruxene (**B3**), a known compound reported in our previous study,[50] are also shown in Figure 1. **B3** is essentially colorless because no absorptions exist in the visible spectral range. When three 2-ethynylthiophene moieties are embedded into the three branches of **B3** between dimesitylboryl and truxene to form π-expanded **C3B3**, the absorption peak positions exhibited a notable red shift to the visible spectral range (390 nm to 430 nm), and **C3B3** was a greenish yellow in either solid state or solution. We optimized the molecular structure of **B3** to obtain a colored probe, which exhibits an obvious color change before and after complexing with $F^-$ to reach visible "naked-eye" detection. **C3B3** featured two major UV-visible absorption bands at 377 and 405 nm in THF solution, which can be assigned to the $\pi$–$\pi^*$ electron transition from thiophene to truxene and to the $\pi$–$p_\pi$(B) electron transition from truxene to the dimesitylboryl group, respectively. As to **N2SB**, three charge-transfer bands appeared in its absorption spectrum. The absorption maxima ($\lambda_{abs}$) at 363 nm was mainly attributed to the $p_\pi$(N)–$\pi$ electron transition from the diphenylamino group to truxene.[50] The other two shoulder bands at 388 and 407 nm were attributed to the $\pi$–$p_\pi$(B) electron transition from truxene to the dimesitylboryl group and to the $p_\pi$(N)–$\pi$–$p_\pi$(B) electron transition from the diphenylamino groups to the dimesitylboryl group via the π bridge, respectively. The UV-visible absorption spectra of both **C3B3** and **N2SB** exhibited obvious vibronic features, which suggest that these probes have rigid planar frameworks. By contrast, **C3B3** displayed a blue emission in THF with a maximal emission wavelength of 429 nm (Figure 1b) and a quantum efficiency Φ of 0.63, about twice that of **B3**. **N2SB** emitted green light at 525 nm in THF and exhibited a large Stokes shift stemming from its polar 2D–π–A molecular structure but a relatively low quantum efficiency Φ of 0.22.

The spectral phenomena indicate that the structural optimizations, including the extension of the π–conjugation, the introduction of a donor, and the establishment of a planar configuration, can effectively facilitate intramolecular charge transfer and improve molecular photophysical properties. These effects are ultimately beneficial to the detection sensitivity of these compounds and their convenience as fluorescent probes.

### $F^-$ sensing by SP spectrophotometric response

The responses of **C3B3** and **N2SB** to $F^-$ were investigated through UV-visible absorption and SP fluorescence spectra in their THF solutions. The changes in the UV-visible absorption spectra of **C3B3** with the addition of incremental amounts of $F^-$ from TBAF are shown in Figure 2a. The absorption of **C3B3** at 405 nm gradually decreased and finally disappeared during $F^-$ titration in THF, in contrast to the only slight decrease in intensity of 377 nm. The spectral changes confirm the electron transition modes of the two absorption peaks. The absorption peak vanished at 405 nm, suggesting that the $\pi$–$p_\pi$(B) electron transition was interrupted after B bound with $F^-$. Similarly, **N2SB** exhibited a sensitive response to $F^-$. Two $\pi$–$p_\pi$(B) and $p_\pi$(N)–$\pi$–$p_\pi$(B) absorption bands of **N2SB** at 388 and 407 nm in the visible spectral range decreased gradually in intensity and completely faded upon the addition of 2.5 equivalents of $F^-$ to the **N2SB** solution (Figure 2b). The absorption peak at 365 nm slightly increased and blue shifted to 363 nm. Corresponding to the spectral changes, the vivid color changes of the THF solution (10 μM) of the two probes from greenish yellow to colorless were easily observed with the naked eye. Thus, both probes can be utilized as convenient colorimetric probes for $F^-$.

As to the fluorescent emission spectra of **C3B3** and **N2SB**, both of them exhibited remarkable fluorescent response to $F^-$, which is an advantage to compare with those weak-fluorescent probes, e.g., ionic compound-based fluorescent probes.[41] It is noteworthy that **C3B3** displayed entirely different responsive characteristics to $F^-$ from **N2SB**. The blue emission band of the THF solution of **C3B3** was gradually quenched and the detection signal turned off during $F^-$ titration (Figures 2c and 2d). By contrast, aside from a 100 nm blue-shift (from 530 nm to 430 nm) of emission wavelength upon the addition of $F^-$, the fluorescent intensity of **N2SB** drastically increased to an ultimate six-fold enhancement. Correspondingly, the fluorescent color of the THF solution of **N2SB** remarkably changed from weak green to strong blue. For a better understanding of spectral behavior before and after **N2SB** bound with $F^-$, theoretical calculations were performed on **N2SB** and its $F^-$ complexes [**N2SB-F**]$^-$ by using TD-DFT methods and the Polarizable Continuum Model.[24,54] The results of these calculations are shown in Figure 3. Before and after binding with $F^-$, the localized positions of the lowest unoccupied molecular orbitals (LUMOs) of **N2SB** significantly changed and transferred from the dimesitylboryl portion to the truxene–thiophene backbone. Meanwhile, the energy level of the LUMO of **N2SB** remarkably increased, and the energy gap of [**N2SB-F**]$^-$ between the highest occupied molecular orbital (HOMO) and the LUMO increased by 0.78 eV (0.029 au) compared with that of **N2SB**. The results corresponded to the vanishing of the lowest energy absorption band at 407 nm and the 100 nm blue-shift of fluorescence emission after the addition of $F^-$ to **N2SB**. Moreover, the oscillator strength *f* of the lowest-lying allowable transition (excited state 1) of [**N2SB-F**]$^-$ was 0.5702, far greater than that of **N2SB** (0.0106; Supporting Information). These calculation results explain why **N2SB** exhibited a turn-on fluorescence change.

Signal detection is practically more effective with turn-on probes, especially with those displaying distinct color changes concurrently.[25] Aside from being highly sensitive, turn-on probes cannot be disturbed by external factors. Figures 2e and 2f plots the absorbance ($A/A_0$ at 405 nm) and fluorescent intensity ($I/I_0$ at 430 nm), respectively, of the two probes as a function of $F^-$ concentration. The slope of the $A/A_0$ – [$F^-$] or $I/I_0$ – [$F^-$] plot can be used as a measure of sensitivity. The slope of turn-on probe **N2SB** in Figure 2f is estimated to be about 10 times that of turn-off probe **C3B3** in Figure 2f and 8 times that of **N2SB** in Figure

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2e. If we consider the quenching to half of the fluorescent intensity of the turn-off probe or the doubling of the same intensity of the turn-on probe to be sufficient signal changes, the detection limit of the two fluorescent probes for $F^-$ can reach 12 μM to 13 μM for **C3B3** and 3 μM to 5 μM for **N2SB** under the experimental conditions.

**Binding constants with $F^-$ and selective optical response**

The binding constants of **C3B3** and **N2SB** with $F^-$ were determined from the absorption titration data (Supporting Information) to be approximately $3.5 \times 10^5$ $M^{-1}$ and $3.2 \times 10^{14}$ $M^{-3}$ (the total binding constant for the three fluoride ions), respectively, which indicates their enough high complexation with $F^-$.

We investigated the selectivity of **N2SB** for $F^-$ by measuring the changes in the fluorescence spectra upon the addition of an excess amount of various other anions as the $Bu_4N^+$ salts. From the data shown in Figure 4, adding 3 equivalents of $F^-$ significantly increased the emission at 430 nm. It was also evident that **N2SB** exhibited appropriate complexation with $CN^-$, which is similar to previously reported triarylboranes.[27,28] But it did not show any affinity for the other anions, such as $Cl^-$, $Br^-$, $NO_3^-$, $H_2PO_4^-$, $AcO^-$, $HSO_4^-$ and $ClO_4^-$. Thus, **N2SB** is highly selective to $F^-$. **C3B3** exhibited almost the same selectivity to $F^-$ as **N2SB** because of their similar mechanism for sensing $F^-$.

**$F^-$ sensing by TP spectrophotometric response**

We also investigated the TP spectrophotometric response of **C3B3** and **N2SB** to $F^-$ (Figure 5). The TP fluorescence intensity of **C3B3** gradually decreased upon the addition of $F^-$, a reduction similar to its spectrophotometric response in the SP mode. However, the response of **N2SB** differed from its turn-on SP fluorescent change: TP fluorescence was quenched upon the addition of $F^-$. This phenomenon may indicate that different mechanisms are involved in SP and TP fluorescence.[34,46] The changes in the TP fluorescence intensity of both **C3B3** and **N2SB** were almost linear with $F^-$ concentration within certain limits (Figure 5c). Thus, $F^-$ concentration can be measured based on the titration curve.

Assuming that the TP fluorescence quantum efficiency of a molecule is constant under similar experimental conditions, the TP fluorescence intensity of this molecule definitively depends on its TP absorption strength. Thus, changes in TP absorption reflect changes in TP fluorescence intensity to some extent. Therefore, we further determined the TP absorption cross sections ($\delta$) of the two probes and their $F^-$ complexes by using the TP fluorescence technique at 710 nm to 800 nm. **C3B3** had a significantly larger $\delta$ than **N2SB** and exhibited a $\delta_{max}$ of 441 GM at 725 nm (Figure 5d). Upon the addition of $F^-$, the $\delta$ values of both **C3B3** and **N2SB** were markedly reduced, indicating that their $F^-$ complexes were not TP fluorescence–active. Thus, the TP fluorescence intensity of **N2SB** decreased with the titration of $F^-$.

## Conclusions

In summary, we have successfully designed and synthesized two truxene-based π-expanded triarylboranes as $F^-$ fluorescent probes. The excellent luminescent properties and high selectivity of these compounds guarantee that they can effectively monitor $F^-$ in organic solution. Moreover, the different feature structures of these compounds make them exhibit different SP fluorescence responses to $F^-$. The SP fluorescence intensity of **C3B3** was quenched upon the addition of $F^-$ to its solution and is thus a turn-off fluorescent probe. By contrast, **N2SB** exhibited a six-fold fluorescence enhancement upon the addition of $F^-$ and is thus a turn-on fluorescent probe. Under the experimental conditions, the detection limit of the two probes for $F^-$ reached 12 μM to 13 μM for **C3B3** and 3 μM to 5 μM for **N2SB**. Furthermore, the dramatic loss of color of these probes from greenish yellow at a concentration of 10 μM provides them the capacity for "naked-eye" detection of $F^-$. The high TP absorption cross sections ($\delta$) and strong TP fluorscence of the two triarylboron compounds make them excellent TP fluorescent probes for $F^-$ in organic solution. However, the two triarylboranes are incapable of detecting $F^-$ in aqueous solution, which will be the goal of our efforts in the next work.

## Acknowledgements

This study was supported by the National Natural Science Foundation of China (21202132, 21175107 and 21375106), the Natural Science Foundation of Shaanxi (2012JQ2017), the Ministry of Education of the People's Republic of China (NCET-08-602 0464), the Fundamental Research Funds for the Central Universities (Z109021106 and Z109021303), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, the State Education Ministry, and the Northwest A&F University.

## Notes and references

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† Electronic Supplementary Information (ESI) available: synthesis, theoretical calculation, calculation of association constants and additional spectra. See DOI: 10.1039/b000000x/

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## Caption to Scheme 1

**Scheme 1** Schematic illustration of F− sensing processes of **C3B3** and **N2SB** and their SP fluorescent changes. The color and area of the light spots represent the color and intensity of SP fluorescence, respectively.

## Captions to Figures

**Fig. 1** Normalized linear absorption (a) and SP fluorescence (b) spectra of **B3** (black), **C3B3** (pink), and **N2SB** (olive) in THF (10 μM).

**Fig. 2** Absorption (a and b) and SP fluorescence (c and d) spectra for titrations of **C3B3** and **N2SB** (10 μM in THF) with *n*-$Bu_4NF$ solution of THF. Plot of absorbance ($A/A_0$ at 405 nm, e) and fluorescent intensity ($I/I_0$ at 430 nm, f) of **C3B3** and **N2SB** as a function of $F^-$ concentration.

**Fig. 3** Molecular orbital diagrams of HOMO and LUMO of **N2SB** and [**N2SB-F**]$^-$ with their relative energy according to TD-DFT calculation.

**Fig. 4** Fluorescence changes of **N2SB** upon addition of various anions (3 equivalents).

**Fig. 5** TP fluorescence spectra (a and b, $\lambda_{ex}$ = 725 nm) for titrations of **C3B3** and **N2SB** (5 μM in toluene) with THF solution of *n*-$Bu_4NF$. Plot of fluorescence intensity ($I/I_0$ at 480 nm) of **C3B3** and **N2SB** as a function of $F^-$ concentration (c) and TP excitation spectra of **C3B3** and **N2SB** with and without $F^-$ (d).

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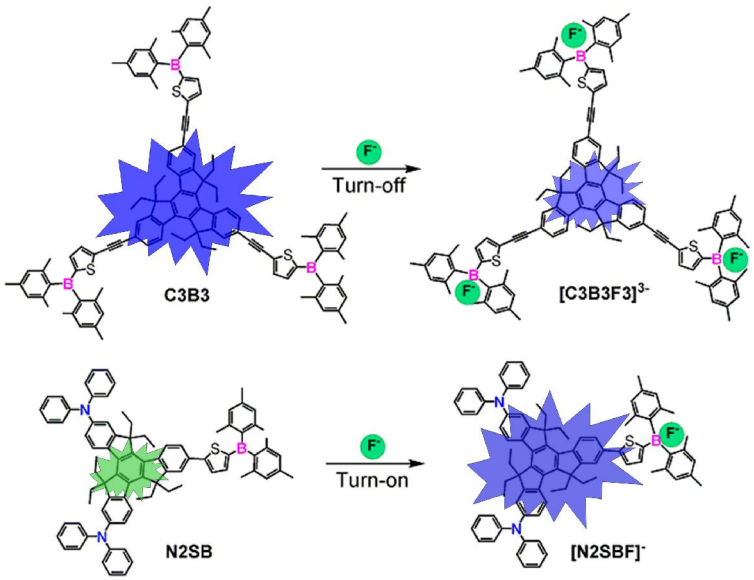


**Scheme 1**

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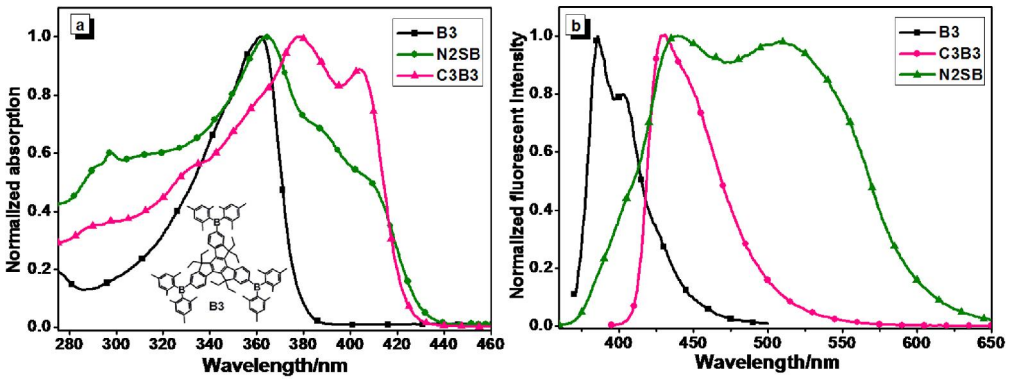


**Fig. 1**

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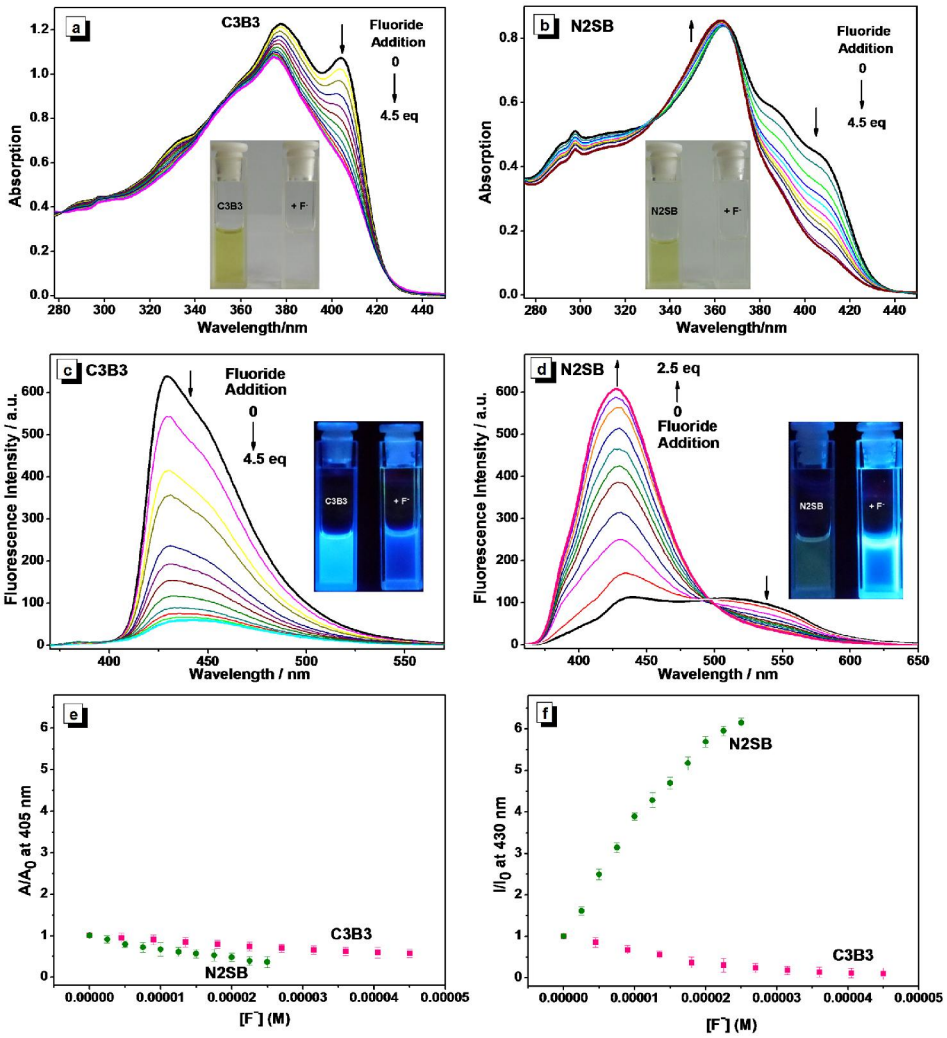


**Fig. 2**

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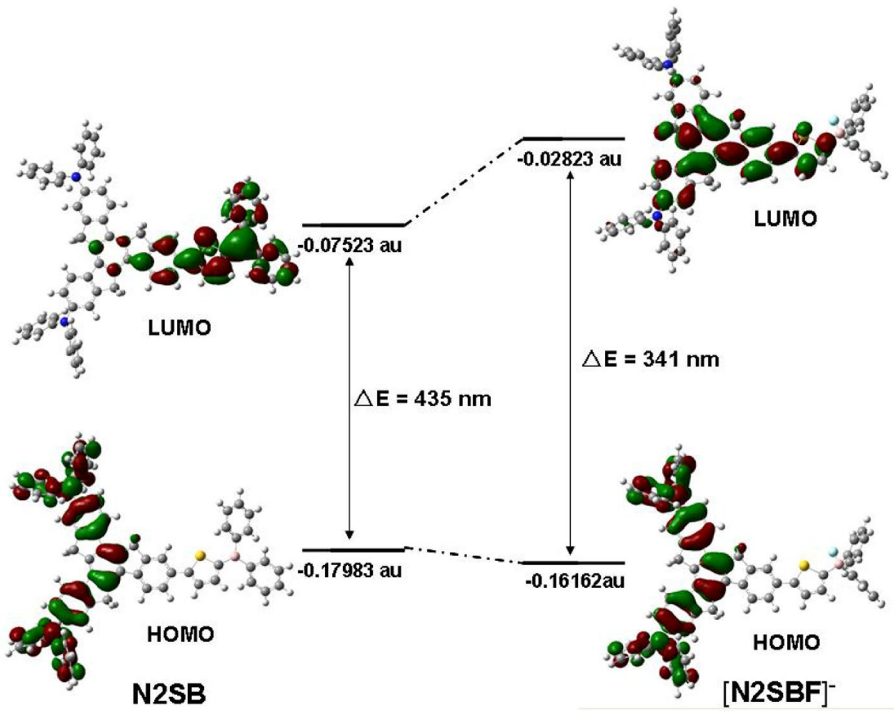


**Fig. 3**

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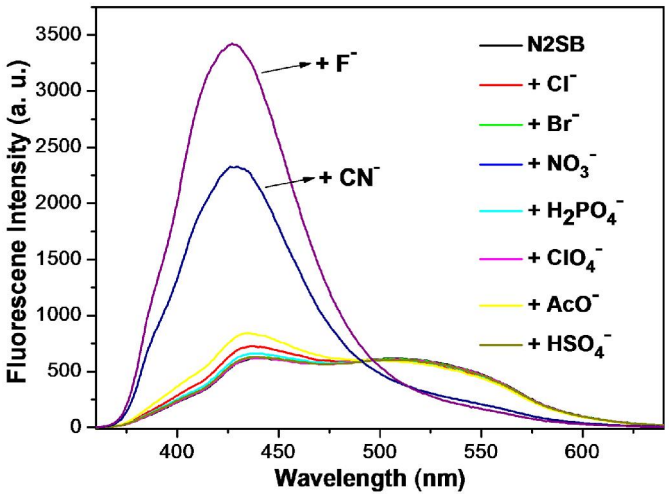


**Fig. 4**

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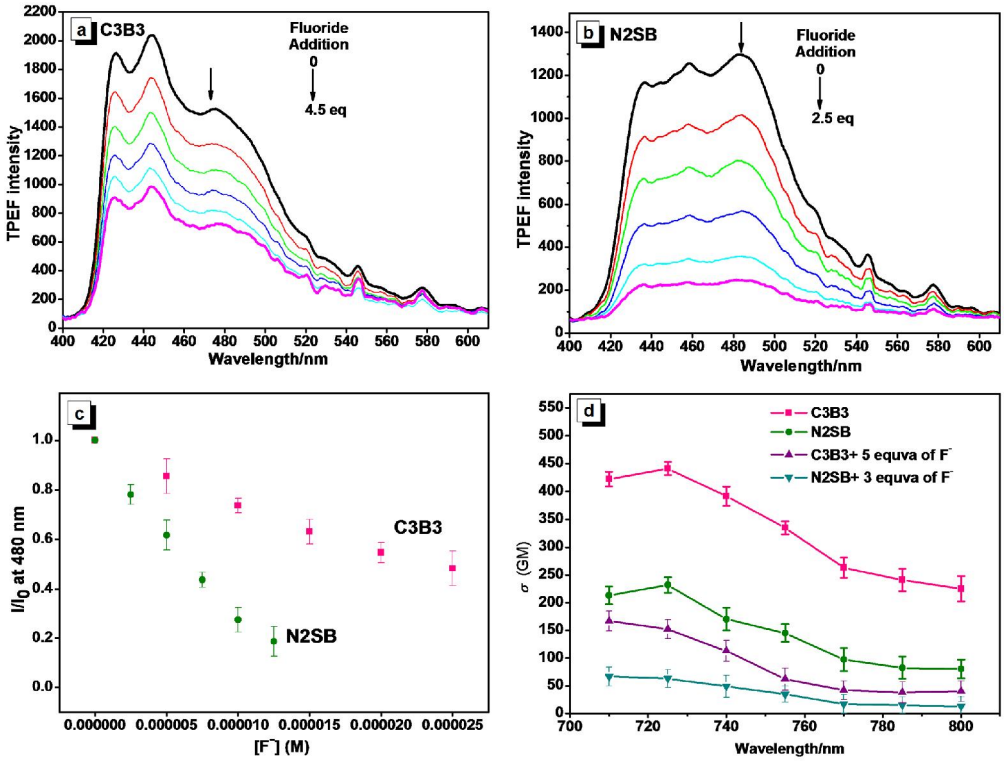


**Fig. 5**

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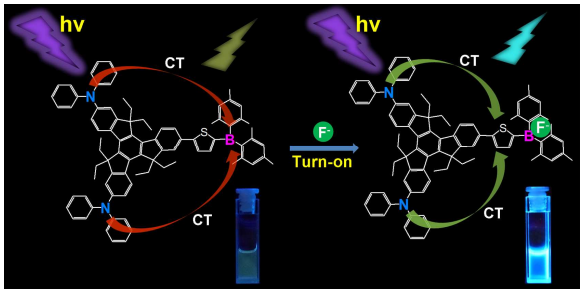
# Graphical Abstract




Two triarylboranes were synthesized and they exhibited high selectivity and sensitivity to fluorid as both single-photon and two-photon fluorescent probes.

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