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Highly Selective Two-Photon Chemosensors for Fluoride Derived from Organic Boranes

Zhi-Qiang Liu,[†,‡] Mei Shi,[†] Fu-You Li,*[,†] Qi Fang,*[,‡] Zhang-Hai Chen,[†,§] Tao Yi,[†] and Chun-Hui Huang[†]

Laboratory of Advanced Materials, Fudan University, 200433 Shanghai, P. R. China,
State Key Laboratory of Crystal Materials, Shandong University,
250100 Jinan, P. R. China, and Department of Physics, Fudan University,
200433 Shanghai, P. R. China

fyli@fudan.edu.cn; fangqi@icm.sdu.edu.cn

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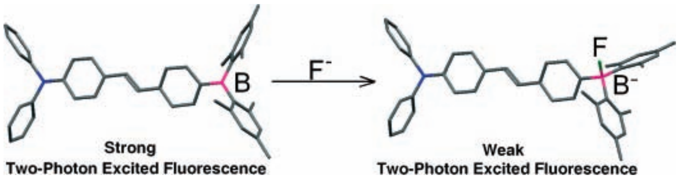
ABSTRACT



Three organoboron compounds are shown to be two-photon fluorescent sensors for fluoride anion with high sensitivity and selectivity. The recognition mechanism is attributed to the unique steric structure of the bulky dimesitylboryl group and the Lewis acid–base interaction between trivalent boron atom and fluoride anion.

Chemosensors that convert molecular recognition into highly sensitive and easily detected signals have been actively investigated in recent years. Since the fluoride anion is highly relevant to health and environmental issues,[1] a large number of synthetic chemosensors have been designed for this important analyte. Among them, either the specific Lewis acid−base interaction, such as the strong affinity of a boron atom toward fluoride ion,[2,3] or designed hydrogen bonding, such as urea with fluoride ion,[4] were adopted as efficient approaches. To the best of our knowledge, the output signals of these fluoride sensors are limited to the change of single-photon related absorption or emission properties.

Recently, two-photon laser scanning microscopy has been greatly developed in combination with suitable two-photon chemosensors to image the distribution of ions in cellular processes with deeper penetration and higher 3-D spatial selectivity than what the single-photon technique can attain.[5]

[†] Laboratory of Advanced Materials, Fudan University.

[‡] State Key Laboratory of Crystal Materials, Shandong University.

[§] Department of Physics, Fudan University.

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Up to now, only a few two-photon chemosensors have been found in the literature. They are crown ether derivatives which are responsive to metal ions[6] and quadrupolar dyes which are responsive to pH.[7] However, the sensitivity and selectivity achieved are far from what is expected.

Many three-coordinate organoboron compounds have been investigated for their potential applications in optoelectronics during the past dacades.[8] Marder et al.[9] and our group[10] have recently reported the remarkable two-photon excited fluorescence (TPEF) properties of some three-coordinated boron compounds, in which the dimesitylboryl group were adapted as electron acceptors. In this paper, we extended our results to use the boranes **1**−**3**[10] (Figure 1) as the two-photon excited fluorescent sensors for fluoride anion. In the presence of fluoride ion, the strong B−F interaction will interrupt the extended π-conjugation, thereby causing a dramatic change in the photophysical properties, including TPEF of the compounds **1**−**3**.

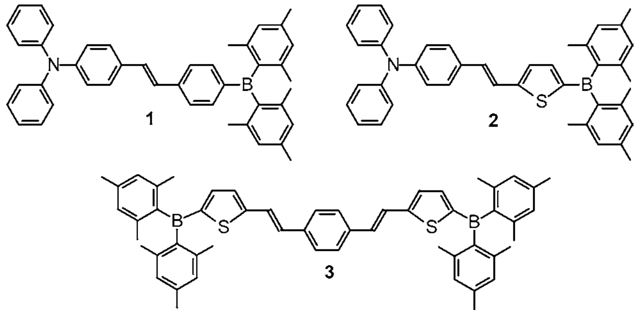

Figure 1. Molecular structures of compounds **1**−**3**.

In our present experiments, n-Bu$_4$NF (TBAF) as a fluoride source was gradually added to a THF solution of each borane. The complexation abilities of **1**−**3** with fluoride ion were investigated by the UV−vis absorption and fluorescence techniques. Here, **1F**, **2F**, and **3F** represent the corresponding borates of **1**, **2**, and **3**, respectively. The changes of their photophysical properties are summarized in Table 1. When TBAF was added to the THF solution of **1**, an apparent color change from green-yellow to colorless in ambient light, as shown in Figure 2a, can be observed by the naked eye.

Table 1. Photophysical Properties of **1**−**3** in THF[a]

	λ_{abs}/nm[b]	$\epsilon/10^4$	λ_{SPEF}/nm[c]	λ_{TPEF}/nm	δ/GM[d]
1	402	4.02	522	520	300
1F	363	4.18	411		
2	428	4.12	536	540	119
2F	385	3.85	450		
3	435	9.32	482,515	491,514	850
3F	435	5.23	493		
3F$_2$	417	4.94	490		

[a] All of the photon-physical properties were measured with 10 μM solutions. [b] Only the longest absorption peaks are shown. [c] Emission maximum wavelength excited at the absorption maximum. [d] TPA cross-sections were measured by the comparative TPEF method[11] at 800 nm.

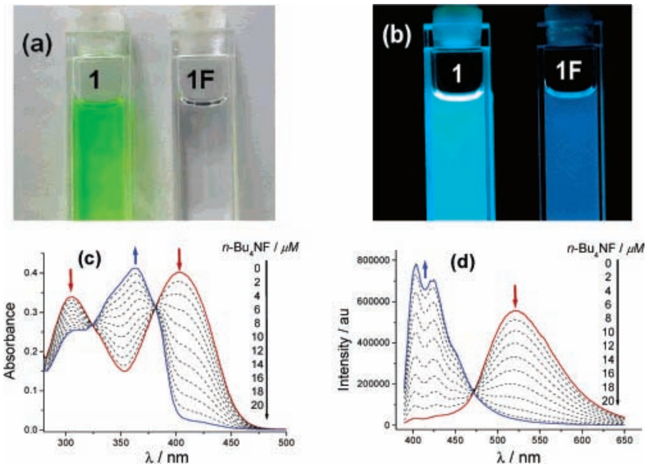

Figure 2. (Top) Color change (a) and fluorescence emission (b) response of **1** in THF (10 μM) on addition of 2 equiv of TBAF. Left to right: **1**, **1F**, the emission of **1** and **1F** (irradiated at 365 nm). (Bottom) Changes in UV−vis absorption (c) and emission spectra (d) of **1** (10 μM) at 20 °C in THF upon the addition of 2.0−20.0 μM of TBAF.

Notably, upon complexation with F$^-$, the characteristic strong absorption band of **1** at 400 nm completely disappeared, and a new band centered at 370 nm arose (Figure 2c). That is, a greater than 30 nm λ_{max}(abs) blue-shift occurred with this anion-binding event. The binding constant (K) of **1** for fluoride ion was determined from the absorption-titration curves to be $2.3(\pm0.3) \times 10^5$ M^{-1} at 20 °C in THF, which is comparable to those of compounds previously reported.[2]

As shown in Figure 2d, the single-photon excited fluorescence (SPEF) emission spectra of **1** also displayed obvious changes when fluoride ion was added. The strong emission band of **1** at 520 nm progressively decreased, and a new emission band centered at 411 nm increased. A blue-shift of λ_{max}(SPEF) of more than 110 nm occurred with the anion-binding event. Furthermore, for both **1** and its borate **1F** an intense fluorescence with quantum yield over 0.80 was identified. This means that **1** can serve as a good sensor for fluoride ion applied to the “fluorescent ratiometric method”, which may increase the sensitivity by measuring the ratio changes of the fluorescence intensities at two different wavelengths.[12]

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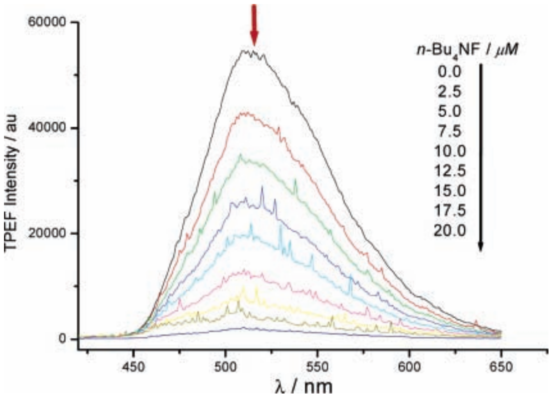

Figure 3. TPEF spectra changes of **1** (10 μM) at 20 °C in THF upon the addition of 2.0−20.0 μM of TBAF.

As shown in Figure 3, the TPEF intensity decreased gradually upon the addition of fluoride anion, hence it is possible to measure the fluoride anion concentration by the titration curve with the TPEF signal (see the Supporting Information). To our surprise, the TPEF spectrum of **1F** is quite different from SPEF of **1F**. No obvious TPEF signal is recorded under the excitation of fs laser from 730 to 800 nm, indicating that **1F** is not TPEF-active. Taking SPEF quantum yield of 0.82 for **1F** into account, we can estimate that the TPA cross-section of compound **1F** is very small under this condition. This fact may indicate that different mechanisms are involved in single and two-photon excited fluorescence of **1F**. Moreover, both the single and two-photon related photophysical properties of **2** show a similar response to the titration of TBAF with those of **1**.

On the basis of both SPEF and TPEF quenching data at 520 nm, the binding constants of **1** for fluoride anion were also calculated as 2.1(±0.4) × 10^5 and 2.8(±0.6) × 10^5 M^{-1}, respectively. Obviously, these results are similar to that measured by linear absorption in the range of experimental error.[6b] We can then presume that all the recorded changes in both absorption and emission spectra derived from the same intrinsic chemical event.

In contrast to the monoboron compound **1**, the more extended π-electron system **3** has been characterized as a strong TPEF emitter with a TPA cross-section as large as 1300 GM.[10a] For two symmetrical dimesityboryl moieties on the two end of the π-conjugated bridge, **3** is potentially capable of multistage sensing of fluoride ion.[2c]

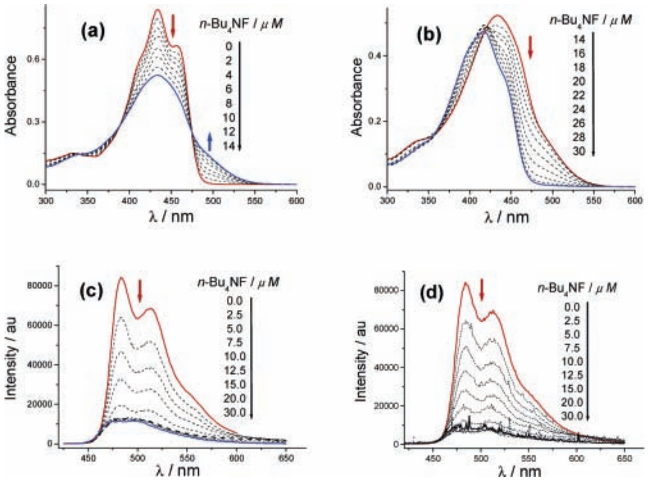

Figure 4. Changes in UV−vis absorption (a, b), SPEF (c), and TPEF (d) emission spectra of **3** (10 μM) at 20 °C in THF upon the addition of 2.0−30.0 μM of TBAF.

Figure 4 shows the spectral change of **3** in THF solution (10 μM) upon addition of TBAF. As the titration continued, the main absorption between 390 and 475 nm of **3** greatly decreased and the peak at 457 nm disappeared. As a result, the whole band degenerated to a broad single band centered at 435 nm, and the apparent color of the solution changed from yellow-green to yellow in ambient light. In particular, the absorption edge was greatly red-shifted. This shift reversed when TBAF reached about 1.5 equiv of **3**. The presence of two distinct isosbestic points at 385 and 475 nm and molar ratio analysis indicate that the spectral change in this concentration range can be ascribed to 1:1 complexation of **3** with fluoride ion.[13] The binding constant was determined to be 3.2 (±0.3) × 10^5 M^{-1} at 20 °C in THF. Significantly, the further addition of a large excess of TBAF caused subsequent spectral changes with great blue-shift (∼30 nm) and two new isosbestic points, as shown in Figure 4b. These changes can be interpreted as complexation with the second fluoride ion. To our surprise, only the first stage of complexation with F^- was obviously observed from either single or two-photon excited fluorescence properties of **3**, with similar titration curves (see Figure 4c,d and the Supporting Information).

For an excellent chemosensor, high selectivity is a matter of necessity. The experimental results suggest that these compounds show high selectivity in colorimetric and fluorescent sensors for fluoride anion. As depicted in Figure 5, **1** shows scarcely any response with other halide anions and weak complexation with AcO^-, NO_2^-, NO_3^-, $H_2PO_4^-$, and ClO_4^-. Similar selectivities were also confirmed in the corresponding SPEF and TPEF experiments. The highly selective recognition of these organoboron compounds for fluoride anion can be attributed to two factors. On one hand, trivalent B atom and F^- are typical “acid” and “base”, respectively, and the very strong affinity between them is quite natural. On the other hand, the special steric structure of dimesityl group may make some unique contribution.[14] This contribution is also supported by crystal structure data.

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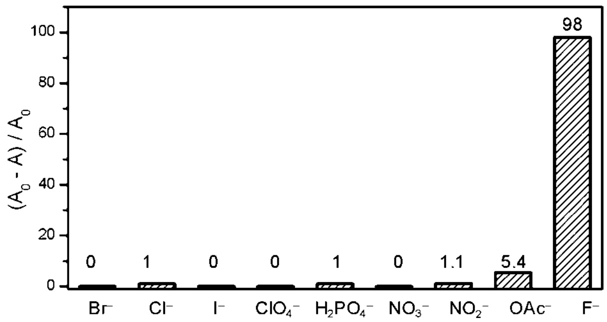

Figure 5. Comparison of the percent decrease of absorbance of **1** in THF (10 μM) at 400 nm in the presence of 10 equiv of anions with a THF solution of their Bu_4N^+ salts.

A single crystal structure (Figure 6) of **3** established the basic geometry of the compound. Solvent disorder precluded obtaining highly accurate parameters, but it can be seen that the boron centers are trigonal planar and well shielded by the ortho-methyl groups of the mesityl moieties, as expected from previous structurally characterized dimesitylboryl.[2c,3a,3b,8,14] From this point, we can explain that only a small "base" such as fluoride anion has the possibility to break through the sterically congested surroundings around the central boron atom. In addition, this steric effect has also been noted by other researchers in their previous work about other boranes.[2c,3a]

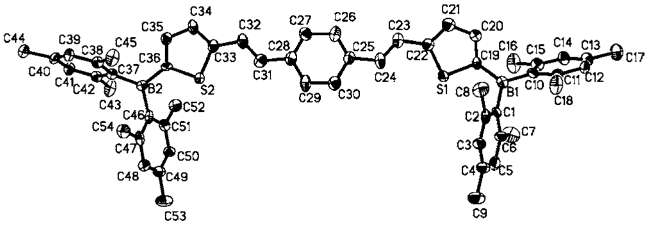

Figure 6. ORTEP drawing of **3**.

In summary, we have demonstrated the effectiveness of three borane-derivatives as single and two-photon excited fluorescent sensors for fluoride ion with high sensitivity and selectivity. The structural features of the dimesityl boryl groups in these sensors are believed to play very important roles for these unique responses. The results provide a useful design strategy for the synthesis of new two-photon sensors for further applications.

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Supporting Information Available: Crystallographic data of compound **3**, the single and two-photon related optical spectroscopy, and the titration curves for **1**−**3** in details. This material is available free of charge via the Internet at http://pubs.acs.org.

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