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A simple complex: ‘on–off–on’ colorimetric and ratiometric fluorescence response towards fluoride ions and its solid state optical properties

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ABSTRACT

A simple 1,1'-bi-2-naphthol (1,1'-BINOL) boron complex has been rationally designed and synthesized, the structure of which was confirmed by single crystal X-ray diffraction analysis. Furthermore, the complex exhibited turn-on fluorescence for fluoride ions with high selectivity and sensitivity. The recognition mechanism for promoting was determined by ¹H, ¹⁹F and ¹¹B NMR titrations, which indicated that both the photo-induced electron-transfer (PET) and the intramolecular charge transfer (ICT) effects were functionalized. In addition, the complex showed strong solid-state fluorescence, and the emission spectrum and quantum efficiency (ΦF) of the solid powders were also measured.

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Introduction

To date, fluorophores such as BODIPY, incorporating a four-coordinate boron bound to a π -conjugated chelate^{1–5} have been applied widely ranging from biological sensing and imaging to the search for new electroluminescent devices.^{6–8} Although many BODIPY dyes exhibit high fluorescence quantum yields in dilute solutions ($\Phi F > 0.5$), they are scarcely emitted in the solid state as a result of emission quenching upon aggregation. Therefore, the usage of BODIPY dyes in a practical level still remains a major challenge.^{9–11} Of the many exceptional optical molecules, fluorine–boron complexes, *Boranils*, as the analogues of BODIPY, have been reported to have achieved a high solid state fluorescence¹² or as the receptor for various cations¹³, anions¹⁴, and also as a fluorescent label for various bioactive molecules.¹⁵ To improve the molecular diversity within the boron-based dye family, N^{^O}¹⁶ π -conjugated chelating fragments coordinated to boron-containing entities for examples, BF₂, B(Ar)₂, B(OAr)₂, and B(ArF₅)₂, have been investigated (Fig. 1).¹⁷ However, most of these N^{^O} bidentate π -conjugated *Boranil* complexes are based on 2-(2-hydroxyphenyl)benzoxazole (HBO) scaffold or its analogues.¹⁸ Consequently, there has been an increasing interest in the development of novel boron complexes with well-designed

structures furnishing both the good optical properties and the high selectivities for anions¹⁹.

1,1'-bi-2-Naphthol (BINOL) is a commercially available material that can be synthesized and functionalized in a large quantity. The outstanding C₂ chiral properties make BINOL an excellent ligand for asymmetric catalysis²⁰ as well as a chiral induction core for probes.²¹ Although many probes based on BINOL framework have been developed in the form of small molecules²¹ or cations²², examples about the use of BINOL for sensing anions are rare.²³ In addition, the large dihedral angle and twisted conformation of the binaphthyl unit yields a stable amorphous phase that can increase the luminescence intensity.²⁴ To the best of our knowledge, rare studies of *Boranil* complexes based on BINOL framework²⁵ as sensors have been reported.

As fluoride anion is a strong hydrogen bond receptor and has a high affinity for silicon atom and boron atom, these unique

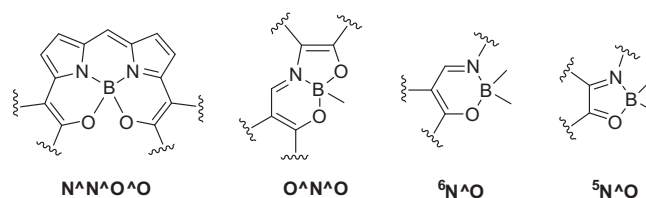


Figure 1. Various chelating modes of B(III) complexes.

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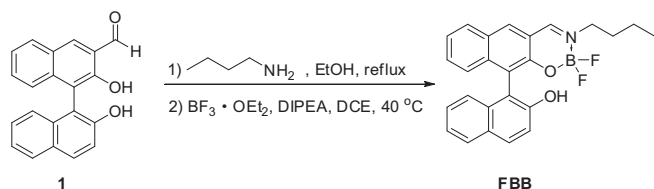
chemical properties have been employed in the design and development of many fluorescent sensors of fluoride anions.²⁶ However, many fluorescent probes of fluoride ions are based on fluorescence measurement at a single wavelength, which may be influenced by variations in the sample environment. To increase the selectivity and sensitivity, ratiometric fluorescent sensors were observed to be undergoing some changes in the ratio of the intensities of the absorption or the emission at two wavelengths.

Thus, ratiometric fluorescent sensors can provide a built-in correction for environmental effects.²⁷ We envisioned that a molecule possessing both hydrogen bond and boron core centre emitting dual peaks could be used as a colorimetric and ratiometric fluoride ions probe. Herein, we synthesized a new BINOL-boron complex (Scheme 1), which can be used for fluoride ions probe, the complex showed a colorimetric and ratiometric fluorescence response for F⁻. It exhibited a high selectivity for F⁻ over other anions in THF. The detection limit was calculated to be 0.12 μM. Meanwhile, it also excited strong solid-state fluorescence, and the emission spectrum and quantum efficiency (ΦF) of the solid powders were measured, which indicated that it or its derivative have great potential application prospects in OLEDs.

Results and discussion

Synthesis of 3-butyl-2,2-difluoro-10-(2-hydroxynaphthalen-1-yl)-2H-naphtho[2,3-e][1,3,2]-oxazaborinin-3-ium-2-uide (FBB)

FBB (3-butyl-2,2-difluoro-10-(2-hydroxynaphthalen-1-yl)-2H-naphtho[2,3-e][1,3,2]oxazaborinin-3-ium-2-uide) was synthesized from BINOL in five steps by the procedure depicted in Scheme 1. The aldehyde **1** was prepared according to our previous Letters^{20,22} and the literature procedures.²⁸ The red precipitate imine was obtained by treating **1** with *n*-butylamine in refluxing ethanol. And then the complexation was feasible with BF₃·Et₂O in basic conditions (diisopropylethylamine, DIPEA) to quench the nascent HF under an inert atmosphere of argon. The mixture was purified by



Scheme 1. The synthetic route of probe **FBB**.

silica gel column chromatography, giving the yellow solid with 92% yield.

The X-ray structure of FBB

The molecular structure of **FBB** was confirmed by single crystal X-ray diffraction analysis²⁹ (Fig. 2), and carbon and hydrogen atoms are omitted for clarity. In the structure, a new six-membered heterocyclic ring has been formed, and the N[∧]O fragment appears *quasi*-planar except for the B atom with a slightly out of the planarity [C–O(1)–B(1)–N(1): 12.7(8)] and [C–N(1)–B(1)–O(1): –7.1(9)] (Table S1). Meanwhile, the B atom has a slightly distorted tetrahedral geometry with angles ranging from 105.0(6) to 111.2(6) (Fig. 2b and Table S1). The two fluorine chelate units are distorted from the planarity. The B(1)···N(1) distance (1.584(7) Å) is similar with the sum of the Van der Waals radii (1.580 Å) for the corresponding atoms, which indicates the formation of covalent-like bond between boron and nitrogen resulting in the stability of **FBB**.

Colorimetric and ratiometric fluorescent probe of fluoride ions

Initially, a THF solution of probe **FBB** was treated with various tetrabutyl ammonium salts, such as F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻,

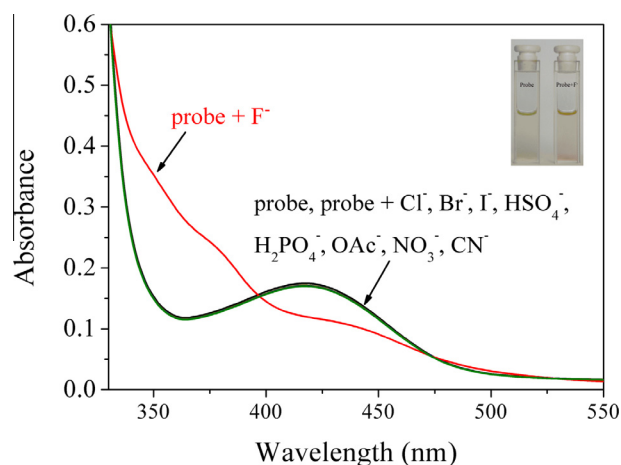


Figure 3. UV-vis absorption spectra of probe **FBB** solution (5×10^{-5} M) in the absence and presence of 5.0 equiv of various anions (F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, H₂PO₄⁻, OAc⁻, NO₃⁻, CN⁻) in THF. Inset: a photograph showing the colour change of **FBB** (1×10^{-4} M) under ambient light in THF without or with addition of 5.0 equiv of TBAF.

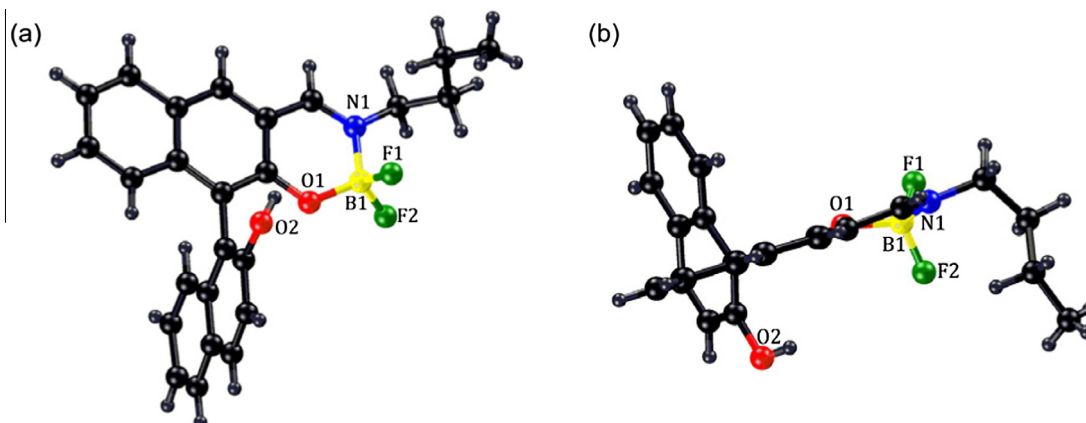


Figure 2. (a) The X-ray crystal structure of **FBB** showing the partial atom-labelling scheme. Carbon and hydrogen atoms are omitted for clarity. (b) Perpendicular view to highlight the slightly distortion at the B atom.

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