

Short communication

Synthesis of a series of benzazaboroles as selective fluorescent receptors for iodide



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ABSTRACT

In this paper, four benzazaborole type receptors were synthesized by a one-pot reaction of between 2-formylphenylboronic acid and a primary amine in the presence of diethyl phosphite and tested as fluorescent receptors for iodide. All compounds were characterized by IR, ^1H NMR, MS, UV and FL techniques. The crystal structures of three of these compounds were obtained by X-ray crystallographic study. These receptors exhibit strong fluorescence intensity in a phosphate buffer solution and their fluorescence can be quenched with added iodide. Under optimized conditions, the newly synthesized fluorescent sensor can selectively detect iodide ion. A linear response in the Stern-Volmer plot within a total concentration range of 0.02 mM to 0.1 mM was observed, indicating a highly efficient fluorescent quenching as a result of the interaction between iodide and the benzazaborole receptors. Interestingly, when an ozone (O_3) atmosphere was introduced to the solid powder containing the receptor quenched by iodide, the fluorescence intensity of the system could be partially restored. Theoretical calculations based on DFT were carried out for the complex of receptor **2** and iodide in order to understand the effect of the receptor-bound-iodide anion on the emission spectra of the receptor.

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In recent years various methods based on different principles have been proposed for the detection and quantitative determination of iodide ions, such as electrochemical detection, gas chromatography, electrostatic ion chromatography, liquid chromatography, capillary electrophoresis, and optical spectrometry [1–4]. However, in many cases, practical applications of these methods could be limited due to the involvement of sophisticated instrumentation techniques, multi-step and laborious sample preparation and other time-consuming processes. To solve these problems, optical-based nanoprobe have been developed using small molecules or nanomaterials for the sensing of iodide [3,5–7]. Although some of these systems were shown to possess high selectivity and sensitivity for iodide ions, most of them required expensive, complicated, and tedious chemical modification of the molecular beacon probe to complete the detection process [1]. Therefore, the development of a simple technique for the determination of iodide ions in both biological and environmental samples has become highly desirable. Recently, chromogenic and fluorescent recognition of anions has received much attention for the determination of anions because these methods have high sensitivity and efficiency, low cost, and operational simplicity [4,5,8]. Boron-containing compounds have been widely used as receptors for a variety of analytes such as anions,

saccharides and amino acids [9–12]. Most of the receptors are used as sensors for recognizing the fluorine ion. However, sensors for iodine ion sensor are rare [13,14]. We wish to report here a new class of boron-containing compounds, benzazaboroles [15] as efficient and highly selective fluorescent sensors for the rapid detection of iodide.

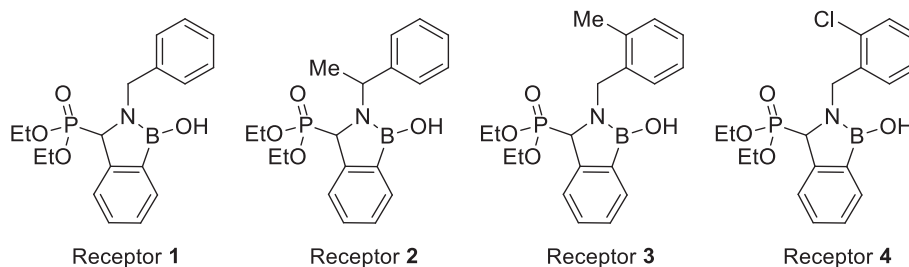
Phosphoryl substituted benzazaboroles were first reported in 2009 [15] during an attempted synthesis of aminobenzylphosphonic acid derivatives bearing a boronic acid group at the orthoposition. However, application of these boron-containing compounds as potential receptors for anions has not been described. Intrigued by their structure uniqueness, we became interested in this new type of fluorophores as fluorescent receptors of anionic analytes such as the iodide. Towards this end, receptors **1–4** were synthesized and their interaction with iodide was systematically investigated by fluorescence spectroscopy (Scheme 1).

Synthetic approach of receptors was by a one-pot reaction between 2-formylphenylboronic acid and a primary amine in the presence of diethyl phosphite. In the first, 2-Formylphenylboronic acid and benzylamine to form schiff base intermediate. Second, diethyl phosphite with the above schiff base intermediate was to form receptor **1–4** [16–19]. The structures of receptor **1**, **2** and **4** were shown in Fig. 1 [20–22].

Each of these receptors exhibits a strong fluorescent emission. Accordingly, the interactions between a series of anions, including F^- ,

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Scheme 1. The structure of benzazaborole receptors **1–4**.

Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} , CH_3COO^- , HSO_3^- , HCO_3^- , $\text{S}_2\text{O}_4^{2-}$, SiO_3^{2-} and CO_3^{2-} , with these receptors are investigated. The fluorescent intensity of the receptors was measured in 10 mM phosphate buffer in the presence of various anions (pH 6.86) (Fig. 2). An efficient quenching of fluorescence upon addition of iodide was observed for all receptors. Under the same conditions, other anions did not cause significant changes in their fluorescence spectra. This demonstrates that these receptors have a high selectivity for iodide in their interaction with anions.

The highly selective recognition of iodide for these receptors prompted us to investigate the interaction between the receptors and the iodide ion. To gain more insight into the use of receptors as a fluorescent sensor for iodide, a titration was performed with increasing amounts of iodide. Fig. 3 shows the fluorescence spectra of the receptors upon addition of iodide in 10 mM phosphate buffer (pH 6.86). The fluorescence quenching interaction between the receptors and the iodide ion was further evaluated using the Stern-Volmer equation, $F_0/F = 1 + K_{\text{SV}}C_{\text{Q}}$, where F_0 is the fluorescence intensity of the receptor, F is the fluorescence intensity of the receptor in the presence of quencher (Q), and K_{SV} is the Stern-Volmer constant derived for a 1:1 complex. The Stern-Volmer plots shown in the insets of Fig. 3 illustrate an excellent fit in the concentration range of 0–10 μL iodide ($n = 1$), indicating that the most abundant complex formed within this concentration range has a 1:1 (host/guest) stoichiometry. Based on the binding constants (Table 1), the degree of interaction of these receptors with the iodide ion follows the order of receptor **2** > receptor **1** > receptor **4** > receptor **3**.

The results obtained in our fluorescence quenching study and the theoretical calculations (vide infra) suggest that electronic interaction between the receptors and the iodide ions may have caused changes in the photophysical properties of ICT fluorophore by effecting the efficiency of charge transfer. The quenching of fluorescence is of two types: (a) static quenching in which an authenticated complex is formed between a receptor (emitter) and an anion (quencher), and (b) dynamic quenching where the quenching is due to the random collisions between a receptor (emitter) and an anion (quencher). In the present investigation, the receptors show static quenching upon addition of iodide due to a strong interaction with the iodide ion.

In the FT-IR spectrum of the best binder, receptor **2**, the B—N stretching band was observed at 1440 cm^{-1} and the B—N stretching band with the scaling factor for B3LYP/6-31G (d, p) is calculated to be at 1420 cm^{-1} with strong intensity. The stretching vibration of B—O was observed at 1338 cm^{-1} and the calculated scaled wavelength for B—O stretching mode is at 1341 and 1328 cm^{-1} . The C—B stretching bands were observed at 1049 , 1012 cm^{-1} and the calculated scaled wavelength for C—B stretching mode is at 1045 cm^{-1} . The calculated results match well with the experimental data.

Absorption spectra reflect the electronic transitions of molecules. The TD-DFT calculation predicts the maximum absorption peak transition to be at 251 nm with the largest oscillator strength 0.1255 corresponding to water solvent, which is in good agreement with the experimental data. The strongest $\text{S}_0 \rightarrow \text{S}_1$ transitions are generally contributed mainly by the HOMO-LUMO excitation. The orbital

composition analysis of receptor **2** in Fig. 4 shows that HOMO is mainly localized over the phenyl ring group and the B—N condensed ring part, while LUMO is contributed by the B—N condensed ring part. Therefore the $\text{S}_0 \rightarrow \text{S}_1$ transition is the charge transfer excitation (CT) and the electrons transfer from the phenyl ring group to the B—N condensed ring part.

The emission spectra of receptor **2** in solvent water and the I^- -receptor **2** complex were simulated at B3LYP/6-31G (d, p) level by using the PCM. The maximum emission wavelengths obtained for the two systems are all in accordance with the above experimental values. The calculated values of the fluorescence emission wavelength for receptor **2** and the I^- -receptor **2** complex are located at 342 nm and 339 nm with the large oscillator strength 0.1096 and 0.0226, respectively. Slight red-shifts (3 nm) of emission wavelengths occur and the oscillator strengths decrease by 80%, which means that the B—N condensed ring part is the electron acceptor in the electronic transition from the ground state to the first excited state. Fig. 5 shows the representation of HOMO and LUMO orbital of the I^- -receptor **2** complex. HOMO is mainly localized over the B—N condensed ring part, while LUMO is contributed by the phenyl ring. The main difference in the frontier molecular orbital between receptor **2** and the I^- -receptor **2** complex is that there is no electronic density at the phenyl ring group in the HOMO orbital in the I^- -receptor **2** complex, and there is also no electronic density at the B—N condensed ring part in the LUMO orbital. Therefore, intramolecular charge transfer is inhibited to some degree once the iodide binds to the receptor **2**.

Receptors **1–4** were also tested in solid-state fluorescent experiments. Fig. 6 shows the fluorescence microscope photographs of these receptors with and without the added anions. These photographs show that the fluorescence intensity of the receptor powders is effectively quenched upon adding iodide, whereas no significant quenching in fluorescence intensity was observed with the addition of other tested anions. Meanwhile, it was also observed that when ozone was introduced into the system, the fluorescent intensity could be recovered to a certain degree (Fig. 7), pointing to the reversibility of iodide binding, probably through oxidation of the bound iodide ion into molecular iodine by ozone ($\text{O}_3 + 2\text{I}^- + \text{H}_2\text{O} = \text{O}_2 + 2\text{OH}^- + \text{I}_2$). This observation points to the possibility of forming an “off-on” switch mechanism for the detection of I^- ions and O_3 .

In conclusion, a series of benzazaboroles receptors were synthesized and characterized. These novel receptors were found to be highly selective binders of iodide based on fluorescence spectroscopic studies. The detection for the iodide ions is based on a strong and specific interaction of I^- ions with receptors. Utilization of these receptors for the detection of iodide has the advantage of being operationally simple, obviating the need for expensive reagents or a complicated instrumentation. Detection of iodide with these receptors was operational over a wide range of iodide concentration. Solid-state experiment shows that ozone can be used to partially recover the fluorescence of the receptors due to the reversibility of these receptors in binding to iodide. The receptors can therefore be potentially used as highly selective fluorescent sensors for the rapid detection of iodide.

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