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Di-(2-picolyl)-*N*-(2-quinolinylmethyl)amine Functionalized Triarylboron: Lewis Acidity Enhancement and Fluorogenic Discrimination Between Fluoride and Cyanide in Aqueous Solution

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Abstract: Triarylboron-based Lewis acids as fluoride sensors face a stimulating academic challenge because of the high hydration enthalpy of fluoride, and are usually influenced by a competing response for cyanide ion. Herein, we present a new triarylborane functionalized by a metal-ion ligand, di-(2-picolyl)-*N*-(2-quinolinylmethyl)amine, with subsequent metallation. In aqueous solution, this triarylborane (**QB**) can capture fluoride and cyanide anions via chelation induced by the synergy of boron and metal ions. Moreover, this triarylborane moiety acts as a fluorescent reporter of the binding, allowing for discrimination between fluoride and cyanide anions through dual-channel fluorescence changes. The different chelation models and fluorogenic responses of this sensor toward F⁻ and CN⁻ were verified by the single-crystal structures of 2-to-2 adduct for KCN and 1-to-1 for KF.

Aryl organoboron compounds are increasingly exploited as a class of promising materials because of their intriguing optical and electronic properties, which arise from the interactions between the empty p orbital of boron and attached π -conjugated systems.^[1-7] Furthermore, the inherent Lewis acidic nature derived from the coordinated unsaturation of trivalent organoboron can be utilized for the complexation of certain nucleophilic anions.[8-13] In particular, triarylboranes containing the $-BMes_2$ unit (Mes = 2,4,6-Me₃C₆H₂) have been widely studied in molecular sensors for the fluoride anion,[14-17] due to their moisture-stability and the large steric encumberance, which prevents the coordination of larger anions to boron. In the past decade, many studies have been executed to enhance the Lewis acidity and electron-accepting ability of ArB(Mes₂) to overcome the hydration enthalpy of fluoride ions for applications in aqueous solution as sensors.^[18,19] In fact, a strategy by which electron-withdrawing substituents are attach to the boroncontaining conjugated system is well known to reduce the LUMO

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level, which thus significantly increases the electron-accepting ability of the boron center.^[15] A remaining challenge is that this class of triarylboranes is almost water insoluble and fails to work in aqueous solutions. In contrast, successful examples of capturing fluoride in aqueous media are the cationic boranes reported by Gabbaï and other groups, [20,21] which use the synergy of Coulombic effects and onium ion-centered Lewis acidity via the decoration of ArB(Mes₂) with ammonium, phosphonium, sulfonium, stibonium or telluronium groups.^[15,20] The presence of a cationic group not only serves to elevate the Lewis acidity of the receptors, but can also form bidentate chelation with boron atoms, which facilitates the capture of fluoride from aqueous solution. However, because the Coulombic attraction between two oppositely charged species is inversely proportional to the distance separating the species involved, the majority of reported cationic boranes possess a structure with a cationic functionality adjacent to the boron atom in order to obtain the highest fluoride affinity and chelation.^[22,23] One downside of using such cationic boranes as fluorescent probes is that they usually exhibit low luminous efficiency and short-wavelength emission due to the low conjugation extent of the molecular system. Another point to note is that, in some cases, the typical triarylboranes used in practical fluoridesensing applications are influenced by a competing response for cyanide ion.^[20] Examples demonstrating that triarylborane-based sensors can discriminate between fluoride and cyanide in aqueous solution remain exceedingly rare.^[24,25]



Figure 1. Left: molecular structures of **QB** and **[QB-Zn]**²⁺, and crystal structure of **QB**. Right: cyclic voltammetry diagrams of tris(2,6-dimethylphenyl)borane, **QB** and **[QB-Zn][OTf]**₂ in THF/0.1 M *n*-Bu₄N[PF₆] (1.0×10^3 M; vs. Fc^{0/+}; scan rate 100 mV·s⁻¹).

Tri-(2-picolyl)amine (TPA) is a ligand that can bind to a variety of metal ions with high affinity, including Ni²⁺, Co²⁺, Cu²⁺, Zn²⁺ and Fe²⁺.^[26,27] Inspired by the success of cationic boranes,^[15] we considered that when combining TPA with ArB(Mes₂), the

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pyridyl group of TPA would be effective in enhancing the Lewis acidity of a triarylborane due to the electronegative pyridine ring compared to a phenyl group. Moreover, after chelating the metal ion, TPA would act cooperatively to enhance the anion binding ability of the boron center. In addition, the tetrahedral shape of the TPA-metal complex should allow for a molecular design whereing π -conjugated linkers connect the boron atom and TPA to achieve this anticipated cooperatively, but also act to extend conjugation to the fluorophore units. Further, the distance from the boron center to the metal ion can be adjusted for corresponding fluoride or cyanide chelation to selectively recognize either of the two competing anions. On the basis of these considerations, we modified the TPA ligand by replacing a single 2-pyridyl group with a 2-quinolinyl group and explored the synthesis of di-(2-picolyl)-N-(8-quinolinylmethyl)amine functionalized PhB(Mes₂) (QB, Figure 1). We examined the Lewis acidity of QB and its metal chelation, and further studied its application as a fluorogenic sensor to discriminate between fluoride and cyanide anions in aqueous solutions.



Figure 2. Changes in the fluorescence spectra of QB (10 μ M) in H₂O/THF (1:9 vol.) upon the addition of KF (a) and KCN (b). Inset: Plot of emission intensity as a function of the concentrations of F or CN; the visual fluorescence color of probe QB (10 μ M) upon addition of F or CN under a 365 nm UV lamp.

The synthetic approach for compound **QB** is outlined in Scheme S1 (Supporting Information (SI)). Mes₂BF was first allow to react with 1 equiv of 1,4-dibromobenzene, followed by borylation of Mes₂BPhBr with bis(pinacolato)diboron to obtain Mes₂BPhB(OR)₂ (2). The reaction of 8-bromo-2-(bromomethyl)quinoline with di-(2-picolyl)amine afforded *N*,*N*-di-(2-picolyl)-*N*-(8-bromo-2-quinolinylmethyl)amine (4). The title

compound **QB** was readily synthesized through a conventional Suzuki reaction by reacting compound **2** with **4**. **QB** is stable in ambient air and H₂O in both solution and the solid state, and was characterized by ¹H, ¹³C, ¹¹B NMR, elemental analysis, and X-ray single-crystallography. As revealed by the crystal structure shown in Figure 1, two mesityl planes and a phenyl plane are arranged in a propeller-like fashion around the central boron, while the boron center is sterically protected by the four orthomethyl groups. And, the B atom and its three-bonded C atoms exhibit perfectly coplane.

To evaluate the influence of this molecular design on the Lewis acidity of the triarylboron, we measured the reduction potential of QB and its Zn²⁺ complex [QB-Zn]²⁺, as well as tris(2,6-dimethylphenyl)borane for comparison by cyclic voltammetry in THF using a glassy carbon electrode and Bu₄N[PF₆] (0.1 M) as a supporting electrolyte. The cyclic voltammogram of tris(2,6-dimethylphenyl)borane displayed a reversible reduction wave $E_{1/2}^{\text{red}}$ at -2.47 V vs. FeCp₂^{+/0}, which is similar to that of Mes₃B. The $E_{1/2}^{\text{red}}$ of **QB** is ~0.21 V (-2.26 V vs FeCp₂^{+/0}) more positive than that of tris(2,6dimethylphenyl)borane, indicative of the presence of guinoline and that enhances the electron-accepting ability of the boron center, Like TPA, N.N-di-(2-picolyl)-N-(2-quinolinylmethyl)amine is a strong chelating ligand for metal ions.^[27] The Zn(II) complex of QB, [QB-Zn][OTf]2, was prepared from the reaction of QB with the equivalent amounts of Zn(OTf)₂ in THF. The complex exhibited a much more positive $E_{1/2}^{red}$ of -1.89 V vs FeCp2^{+/0} than the free ligand QB, thus demonstrating that the Lewis acidity of boron is further enhanced by metal chelation.

In spite of the encouraging results, [QB-Zn]²⁺ is still unable to overcome the hydration enthalpy of fluoride if only depending on the complexation of the boron for fluoride, based on previous studies by Gabbaï and Wang.[12b,18] Whether the designed QB can capture F⁻ from the aqueous solution and distinguish it from competing CN⁻ mainly depends on whether the bidentate chelation for the two anions by boron and the chelated metal ion can form. To examine our design concept and assess the practical application of QB as a chemsensor, we first investigated the responses of QB to F⁻ and CN⁻ through UV-Vis absorption in neutral H₂O/THF (1:9 vol.) solution. The addition of 2.0 equivalents of KF to ${\bf QB}$ resulted in a progressive degradation at 328 nm and a progressive elevation of the absorption bands at 260 and 370 nm (Figure S1 in SI). This suggests the coordination of F to the boron atom and, furthermore, the formation of chelation for F⁻ by the boron and metal ion (K⁺) which was bound by di-(2-picolyl)-N-(8quinolinylmethyl)amine in the aqueous solution. However, the titration of 1.6 equivalents of KCN into QB exhibited a very similar absorption spectral change as KF. It was incomprehensible, because we thought that CN should not be chelated by QB due to the dimensional limitation between the boron atom and the metal ion. Further fluorescent titration was undertaken, which gave promising results. The change in the fluorescence spectra of QB in the H₂O/THF (1:9 vol.) solutions $(c = 1.0 \times 10^{-5} \text{ M})$ upon the addition of KF and KCN is shown in Figure 2. The incremental addition of KF caused a gradual quenching of the fluorescence at 390 nm. However, the addition of KCN resulted in both significant enhancement and redshifted fluorescence peaks at 439 nm. Furthermore, visual fluorescent

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decline or enhancement of the **QB** solution ($c = 1.0 \times 10^{-5}$ M⁻¹) was readily observed by the naked eye upon the addition of KF or KCN, respectively. The vivid fluorescent changes suggest that compound **QB** can be utilized as a convenient colorimetric sensor for F⁻ and CN⁻. The interaction of **QB** with F⁻ and CN⁻ can be verified by ¹¹B NMR, as evidenced by an upfield shift from $\delta_{\rm B}$ 78 to 8 for F⁻ and to -13 ppm for CN⁻ (Figures S15-17).

To expand the detection range of **QB** (not only for the potassium salt of fluoride and cyanide), zinc ion (Zn^{2+}) was used as the assisted metal ion. We firstly reacted **QB** with the equivalent amounts of $Zn(OTf)_2$ in H_2O/THF (1:9 vol.) solutions to form the metal complex [**QB-Zn**][OTf]_2. Tetrabutylammonium fluoride (TBAF) and tetrabutylammonium cyanide (TBACN) were chosen as the anion source to titrate [**QB-Zn**][OTf]_2, in which the cation (tetrabutylammonium) can not be chelated by di-(2-picolyl)-*N*-(8-quinolinylmethyl)amine due to its hydrophobic nature. The titration exhibited very similar spectral changes as **QB** with KF or KCN (Figure S2 in SI). These results indicate that the probe can be used to discriminate between F⁻ and CN⁻ in a complicated solution system.

Binding constant (K) measurements provided useful insights on the relative affinities of the sensor towards both analytes. In H₂O/THF (1:9 vol.) solutions, the binding constants of **QB** with KF and KCN were determined from the absorbance titration data to be approximately 3.4×10^4 M⁻¹ and 5.8×10^4 M⁻¹ (Figures S8 and S9 in SI), respectively. The detection limits of probe **QB** for KF and KCN were 5.43 and 0.21 µM, respectively, based on a signal-to-noise ratio (S/N) of 3 under the test conditions. Finally, fluorescence titration studies of **QB** with other anions (Cl⁻, Br⁻, NO₃⁻, OAc⁻, H₂PO₄⁻, ClO₄⁻ and HSO₄⁻) did not show any affinity toward other anions (Figure S12). In addition, we noticed that the emission intensity of **QB** upon addition of KF decreased on a linear fashion. However, the titration isotherm of **QB** for KCN exhibited a curved shape with little enhancement whthin the low concentration range of CN⁻ (Figure 2b, inset).

To understand the unexpected affinity of QB for CN⁻, the crystal structure of QB-KCN has been dtermined.^[28] The crystal structure demonstrated that clearly the adduct $[K_2]^{2+}[2QB\cdot(CN)_2]^{2-}$ was composed of two QB and two KCN molecules, as shown in Figure 3. The CN⁻ was firmly chelated by boron and potassium centers. Interestingly, the boron and potassium centers are respectively affiliated with two QB molecules. The C-terminal of CN⁻ points toward the boron atom and the C-bound cyanide ligand features an essentially linear B-C-N framework (\angle B-C-N = 173.6(3)°) with B-CN bond length [1.637(2) Å]. The N-terminal of CN⁻ points to K⁺ which is chelated by the di-(2-picolyl)-N-(2-quinolinylmethyl)amine segment of another QB molecule with B-C-N bond angle [168.2(3)°] and CN-K bond length [2.884(3) Å]. The two cyanide anions in this adduct exhibit an identical coordination pattern, but a staggered construction. Furthermore, it is worth noting that, in addition to the di-(2-picolyl)-N-(2-quinolinylmethyl)amine unit, the adjacent phenyl ring is involved in the chelation of K⁺. The multiple complexation and chelation interactions tightly stabilize the molecular framework of the adduct and greatly restrict the intramolecular single-bond rotations and configuration vibrations, which are usually nonradiative decay pathways. We surmise that, when the adduct is excited, the configuration does not undergo any energy-consuming rearrangement. Then, when the excimer

decays back to the ground state, no repulsive interaction is involved. Nonradiative decay pathways are blocked, resulting in strong luminescence. Therefore, probe QB exhibits a turn-on fluorescence response for CN⁻. The hypothesis can be testified by the rate constants of radiation decay $k_{\rm f}$ and nonradiation decay k_{nf} of QB and $[K_2]^{2+}[2QB \cdot (CN)_2]^{2-}$ calculated from the fluorescence quantum yields and lifetimes. [K2]2+[2QB.(CN)2]2exhibited higher $k_{\rm f}$ (1.70 × 10⁸ s⁻¹) than $k_{\rm nf}$ (3.00 × 10⁷ s⁻¹). However, **QB** exhibited higher k_{nf} (1.28 ×10⁹ s⁻¹) than k_f (3.4 × 10⁸ s⁻¹). Based on these results, the curved shape of the titration isotherm of QB for KCN can be easily understood. During the initial additions in the titration, the 2-to-2 adduct [K2]2+[2QB.(CN)2]2- can not form due to the inappropriate stoichiometric ratio of QB and KCN, which can not effectively lock the luminophors to restrict the intramolecular rotations and vibrations, resulting in small fluorescent enhancements, thus generating an inflection in the binding isotherm.



Figure 3. (a) Single-crystal structure of the 2-to-2 adduct of QB and KCN; (b) optimized structure of the complex of QB with KF.

As for the coordination geometry of **QB** with F⁻, on the basis of the result of TOF-MS-EI (Figure S30 in SI), theoretical calculations were performed using TD-DFT methods. As shown in Figure 3b for **[K]⁺[QB-F]**⁻, the coordination mode of F⁻ is not counterintuitive, and the optimized configuration of the complex shows that F⁻ is chelated by the boron atom and metal ion from the same **QB** molecule. On the other hand, we also noted that the K-F bond length (2.99 Å) derived from theoretical calculations in **[K]⁺[QB-F]**⁻ is obviously longer than the normal K-F bond length (2.17 Å) determined from KF crystals. The COMMUNICATION

weak binding interaction is incapable of restricting the intramolecular C-B single-bond rotations and configuration vibrations, resulting in the turn-off fluorescence response of **QB** for F^{-} .

After QB bound CN⁻, QB exhibited bathochromic enhanced fluorescence. Theoretical calculations revealed the reason for this redshift. As shown in Figure 4, the HOMO of QB is mainly composed of binding orbitals localized on the di-(2-picolyl)-N-(2quinolinylmethyl)amine fragment, and the LUMO is mainly composed of anti-bonding orbitals localized on the dimesitylboryl portion. However, CN⁻ (or F⁻) binding results in a switch of the atomic orbitals that the electrons populate in the HOMO and LUMO and a decrease of the HOMO-LUMO energy gaps. We thus postulate that, before binding with the anion, QB has an intramolecular charge-transfer (ICT) absorbance from di-(2picolyl)-N-(2-quinolinylmethyl)amine to dimesitylboryl upon excitation. However, after binding to the anion, the ICT pathway of [K₂]²⁺[2QB·(CN)₂]²⁻ (or [K]⁺[QB·F]⁻) reverses and undergoes dimesitylboryl to di-(2-picolyl)-N-(2-quinolinylmethyl)amine with lower energy, which corresponds to the experimental absorption spectra with an enhanced signal in the region of 360-380 nm of the absorption profiles upon titration of QB with KCN (or KF) (Figure S1), and eventually results in the bathochromic emission.



Figure 4. Molecular orbital diagrams of the HOMOs and LUMOs of QB and $[K_2]^{2+}[2QB\cdot(CN)_2]^2$ with their relative energies from TD-DFT calculations (Isovalue = 0.03).

Having established that **QB** is soluble in pure water (solubility ≈ 8 mM), we investigated the ability of **QB** to capture fluoride and cyanide anions in pure water through UV-Vis absorption and fluorescence spectroscopy (Figure S3 in SI). The addition of 3.2 equivalents of fluoride anions to an aqueous solution of **QB** resulted in moderate quenching of the emission band, which suggests decreased fluoride-ion affinity of **QB** in pure water compared to H₂O/THF (1:9 vol.) solution due to the high hydration of the fluoride anion. The binding constant of **QB** with KF in water was approximately 8.4 × 10³ M⁻¹ (Figure S10), which is an order of magnitude less than that in H₂O/THF (1:9 vol.) solution. However, the titration of **QB** with the cyanide anion in water exhibited very similar spectral changes to that in H₂O/THF (1:9 vol.) solution, with a slightly depressed binding constant of 2.0 × 10⁴ M⁻¹ (Figure S11). These experiments clearly demonstrate that fluoride and cyanide anions can be detected by **QB** in water.



Scheme 1. The Chemical Structures of Compounds NB and m-QB.

To further test our probe design, we additionally synthesized two compounds **NB** and **m-QB** (Scheme 1). The structure of **m-QB** is similar to that of **QB**, but is a meta-position substituted product. Both of the two compounds, as well as the two precursors of **QB** (2 and 4, see SI), exhibited no response to F⁻ and CN⁻ in H₂O/THF (1:9 vol.) solution. The unusual ability of **QB** to bind F⁻ and CN⁻ in the presence of water unequivocally confirms the high Lewis acidity of the boron center and the synergy of Coulombic effect and Lewis acidity.

In conclusion, this paper presents a new triarylborane **QB**, in which the Lewis acidity and electron-accepting ability of boron are enhanced through conjugating a metal ligand to the boron with subsequent metallation. This triarylborane can capture and sense fluoride and cyanide anions via strong chelation induced by the synergy of boron and metal ions in aqueous solutions. More importantly, the sensor **QB**, can effectively discriminate between fluoride and cyanide anions through dual-channel fluorescence changes. The different chelation models and fluorogenic responses of **QB** toward F⁻ and CN⁻ were verified by X-ray single-crystal structure and theoretical calculations.

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Boron and metal ion cooperation: This paper described a chemosensor constructed by conjugating a mental-ion ligand to the triarylborane. In aqueous solution, this conjugate can discriminate between fluoride and cyanide anions via different chelation induced by the synergy of boron and metal ions, which was verified by the single-crystal structures of 2-to-2 adduct for KCN and 1-to-1 for KF.

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