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A Highly Selective Bifunctional Luminescence Probe for Potassium and Fluoride Ions

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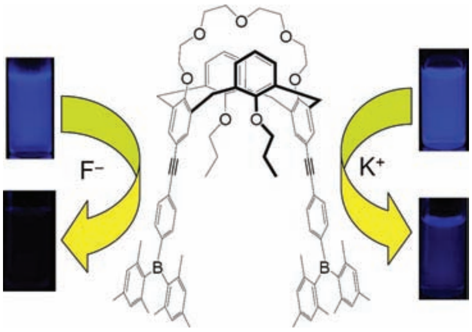
ABSTRACT



A novel bifunctional molecule 1 by a combination of 1,3-alternate calix[4]-crown-5 and triarylborane moieties through alkynyl linkers has been designed and synthesized. Compound 1 shows intense fluorescence with a photoluminescence quantum yield of 0.70 in CH_2Cl_2 solution and can serve as a bifunctional luminescent probe for potassium and fluoride ions with high sensitivity and selectivity.

The sensitive and selective detection of potassium and fluoride ions is essential because of their biological importance. The K^+ ion is crucial for life, and a low potassium ion level has been linked to the risk of stroke, heart disease, arthritis, and infertility.[1] The difficulty in measuring accurately the concentration of potassium ions stems from the presence of a large excess of sodium ions. Therefore, a practical probe must have a great preference for K^+ over Na^+. On the other hand, fluoride plays an important role in preventing dental caries and in the treatment of osteoporosis.[2] High doses of this anion are, however, dangerous and can lead to dental or skeletal fluorosis. Currently, luminescence is widely used as the signal output in the design of chemosensors due to its high sensitivity and the simplicity of its equipment requirement.[3] Although a number of luminescent ion probes have been reported, luminescence probes for potassium[4−6] and fluoride[7−9] ions are still rather rare. In addition, most of the attention has been focused on the design of a monofunctional luminescent anion or cation sensors. To the best of our knowledge, there is no report on the design of bifunctional fluorescent

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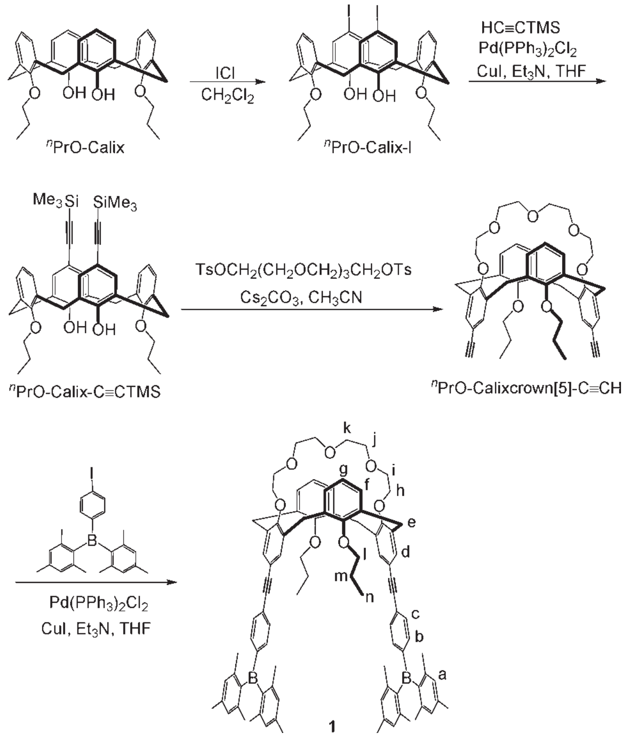
sensors which could selectively detect potassium and fluoride ions.

Herein, we report a novel bifunctional luminescence probe for potassium and fluoride ions with high sensitivity and selectivity, by a combination of 1,3-alternate calix[4]-crown-5 and triarylborane moieties through alkynyl linkers. In previous studies, the 1,3-alternate calix[4]-crown-5 platform has been proven to bind a potassium ion selectively through the complexation of the crown ether ring and additional binding by cation−π interactions between the two phenyl rings.[10,11] A recent study showed that triarylborane compounds containing sterically hindered groups such as dimesityl and triduryl moieties showed enhanced size selectivity toward fluoride ions by utilizing the empty p_π orbital on the boron center.[8] In addition, they have a tendency to display intense intramolecular charge-transfer transitions when an appropriate electron donor is present. The alkynyl group could serve as a very good connector for electron communication which produces intense intramolecular charge transfer from the oxygen to the boron center.

The synthetic procedure of **1** is summarized in Scheme 1. Iodination of dipropoxylcalixarene ^{n}PrO-Calix followed by a Sonagashira cross-coupling reaction gave the bis(trimethylsilylethynyl)-substituted calixarene ^{n}PrO-Calix-C≡CTMS. A subsequent reaction of ^{n}PrO-Calix-C≡CTMS with pentaethylene glycol di-*p*-toluenesulfonate in the presence of Cs_2CO_3 gave 1,3-alternate ^{n}PrO-Calixcrown[5]-C≡CH. A further Sonagashira cross-coupling reaction of ^{n}PrO-Calixcrown[5]-C≡CH and 1-iodo-4-dimesitylborylbenzene afforded the desired compound **1**. The identity of **1** was established by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and satisfactory elemental analysis.

Scheme 1. Synthetic Route of **1**



Compound **1** displays an intense electronic absorption band centered at 342 nm (ε = 77 000) and a bright blue fluorescence (λ_{em} = 430 nm, ϕ_{em} = 0.70) in CH_2Cl_2 solution. The emission is assigned to originate from an excited state derived from the intramolecular charge transfer transition from the phenol O atom to the boron center. In more polar solvents like DMF, a significant red shift in the emission maximum of *ca.* 1830 cm^{-1} was observed, characteristic of charge transfer transitions.

Figure 1 shows the UV−vis and emission spectral changes of **1** in CH_2Cl_2/CH_3OH (1:1, v/v) upon addition of K^+ ions. The addition of K^+ ions to a solution of **1** in CH_2Cl_2/CH_3OH resulted in an increase in the absorbance and a small blue shift in the absorption energy of the low-energy band. Two well-defined isosbestic points at 280 and 348 nm are observed, indicative of a clean conversion of **1** to the ion-bound adduct. In addition, the luminescence response of **1** toward K^+ was found to be more pronounced. Significant emission quenching with a concomitant blue shift of *ca.* 20 nm was observed, which was consistent with the blue shift observed in the UV−vis absorption spectra. The emission quenching and blue shift in emission energies upon K^+ inclusion could be rationalized by the reduced electron-donating ability of the diethynylcalixcrown moiety upon inclusion of the guest metal ion. Although ion-binding may lead to an increase in the rigidity of the calixcrown complex and the inhibition of photoinduced electron transfer and therefore may enhance the emission intensity, the significant changes in the emission intensity may be a result of the high sensitivity of the intramolecular charge transfer emission to the binding event. Moreover, the sensor showed a high sensitivity

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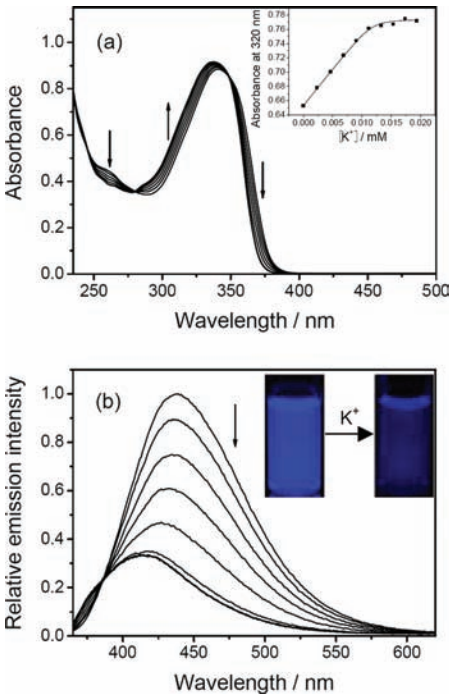

Figure 1. (a) UV−vis and (b) emission spectral changes of compound **1** (1.18×10^{-5} M) in CH_2Cl_2/MeOH (1:1, v/v; 0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of KPF_6. Inset of (a): Plot of absorbance at 320 nm as a function of K^+ concentration and its theoretical fit for the 1:1 binding of complex **1** with K^+. Inset of (b): Emission color change upon addition of KPF_6 to **1** (1.74×10^{-6} M) in CH_2Cl_2/CH_3OH (1:1, v/v; 0.1 M ^{n}Bu$_4$NPF$_6$).

toward K^+ and a pronounced intensity quenching was observed even with a K^+ concentration of 1×10^{-8} M.

Figure 2 shows the ^{1}H NMR spectral changes of **1** upon addition of K^+ in $CDCl_3$/CD_3OD (1:1, v/v). Large downfield shifts of the proton resonances of the crown moiety (H_h−H_k) and the calixarene moiety (H_d, H_g, H_f) were observed upon addition of K^+, confirming the binding mode through the complexation of the crown ether ring and additional binding by cation−π interactions between the two phenyl rings. The downfield shift can be readily rationalized by the electron-withdrawing effect of the cation. In addition, the host−guest complexation equilibrium has a very slow exchange rate compared to that of the NMR time scale. The signals that are assigned to both the complex $[\mathbf{1}\cdot K]^+$ and the free host **1** could be observed in the same NMR spectrum in the presence of 0−1 equiv of K^+. The low exchange rate suggests the very strong binding affinity of **1** for K^+. The ^{1}H NMR spectra reach saturation upon addition of 1 equiv of K^+, suggesting a 1:1 binding stoichiometry with a high binding constant. A very intense ion cluster at m/z 1403, corresponding to the $[\mathbf{1}\cdot K]^+$ complexation upon addition of K^+ ion to **1**, is observed in the positive-ion ESI mass spectrum (Figure S1).

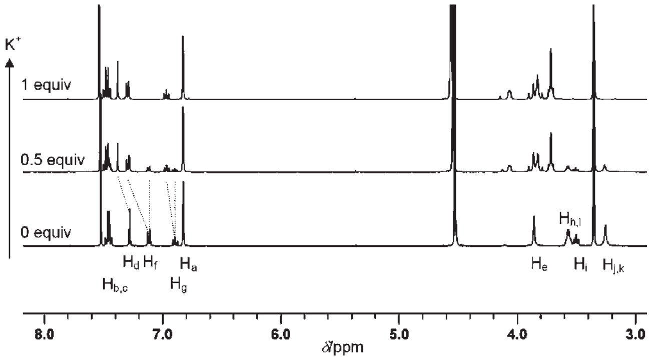

Figure 2. ^{1}H NMR spectral changes of **1** (2.06 mM) upon addition of KPF_6 in $CDCl_3$/CD_3OD (1:1, v/v) at 298 K.

To examine the selectivity of **1** toward various alkali and alkaline earth metal ions, the luminescence response upon the addition of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, and Ba^{2+} has been investigated. As shown in Figure 3, upon addition of 50 equiv of various metal ions, only a drastic spectral change is shown by K^+ ion binding, indicating the high selectivity of **1** toward K^+. In addition, the log K_s values of 7.40 ± 0.14 and 2.38 ± 0.02 of **1** for K^+ and Na^+ ions were obtained from a nonlinear least-squares fit for 1:1 binding. The close agreement of the data to the theoretical fit is further supportive of a 1:1 binding mode. The high K^+/Na^+ selectivity of *ca.* 10^5 is higher than that of the naturally occurring valinomycin, suggesting that **1** would serve as a promising candidate for application as a selective K^+ ion chemosensor.

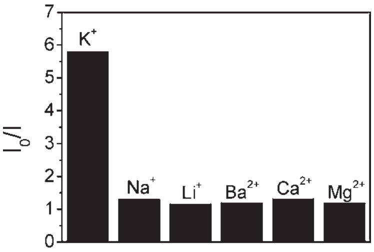

Figure 3. Responses of **1** (1.0×10^{-6} M) in CH_2Cl_2/CH_3OH (1:1 v/v; 0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of 50 equiv of different metal ions as ClO_4^- salts. Excitation was at 350 nm, and the emission was monitored at 450 nm.

The anion-binding properties of **1** were also examined and **1** was found to be highly selective and sensitive to F^-, as revealed by the large UV−vis and emission spectral changes, while the addition of other anions, such as Cl^-, Br^-, I^-, $H_2PO_4^-$, and AcO^- led to negligible changes. Figure 4 shows the electronic absorption and emission spectral changes upon addition of F^- in CH_2Cl_2 solution. Upon complexation with F^-, the characteristic strong absorption band of **1** at 350 nm completely disappeared, and a new band centered at 300 nm gradually appeared. The disappearance of the low-energy band could be ascribed to the interruption of the π-conjugation extended

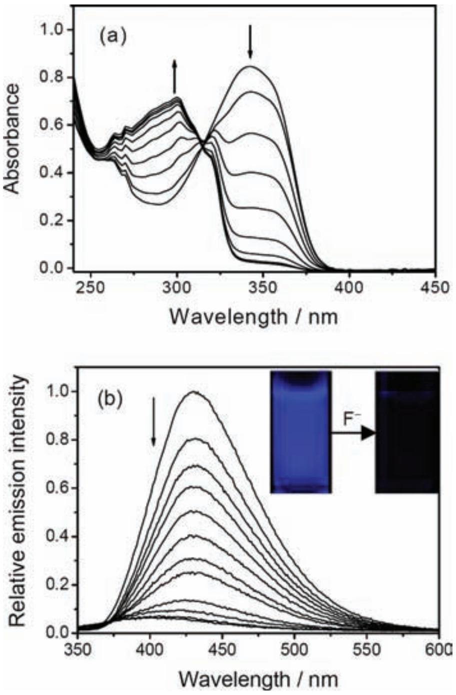

Figure 4. (a) UV–vis and (b) emission spectral changes of compound **1** (1.18×10^{-5} M) in CH_2Cl_2 (0.1 M $^n\text{Bu}_4\text{NPF}_6$) upon addition of $^n\text{Bu}_4\text{NF}$ at 298 K. Inset of (b): Emission color change upon addition of $^n\text{Bu}_4\text{NF}$ to **1** (1.74×10^{-6} M) in CH_2Cl_2 (0.1 M $^n\text{Bu}_4\text{NPF}_6$).

through the boron center upon complexation of F^- to the boron atom. In addition, significant emission quenching was also observed upon addition of F^- to the CH_2Cl_2 solution of **1**, which can be attributed to the destruction of the intramolecular charge transfer. However, in CH_2Cl_2/CH_3OH mixed solvents, no apparent UV–vis and fluorescence changes were observed upon addition of fluoride. This may be attributed to the formation of hydrogen bonds between fluoride ions and methanol, which compete with the binding to the boron center. The binding constant (log K_s) of **1** for a fluoride ion was determined to be 4.46 ± 0.10 in CH_2Cl_2, which is comparable to those of compounds reported previously.[8]

The binding of fluoride ions to **1** was also verified by ^{1}H, ^{19}F, and ^{11}B NMR titration experiments, as shown in Figures 5 and S2. Upon addition of F^-, only the protons of the triarylborane moiety (H_a, H_b, H_c) and the ^{11}B signal underwent an upfield shift, due to the increased electron density as a result of F^--binding to the boron center. The addition of excess F^- ions to **1** in CD_2Cl_2 resulted in two distinct characteristic ^{19}F signals at δ −119.5 and −174.1 ppm, which correspond to the unbound and bound F^- ions, respectively, and the latter is comparable to those observed in other triarylfluoroborate systems.[8d,e]

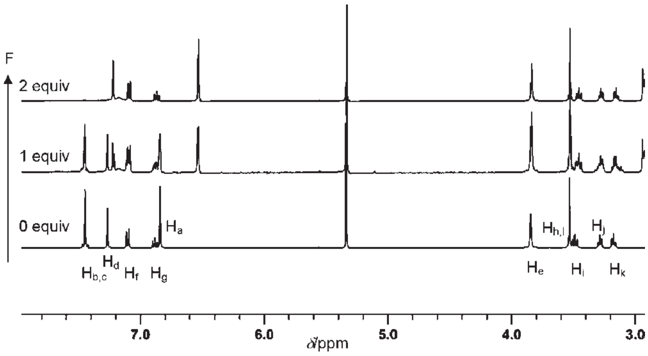

Figure 5. ^{1}H NMR spectral changes of **1** (2.56 mM) upon addition of $^n\text{Bu}_4\text{NF}$ in CD_2Cl_2 at 298 K.

In summary, we have designed and synthesized a bifunctional luminescent receptor **1** by a combination of 1,3-alternate calix[4]-crown-5 and triarylborane moieties through alkynyl linkers. Compound **1** shows high selectivity and sensitivity toward potassium and fluoride ions with large UV–vis and emission changes. In addition, the attachment of the triarylborane moiety to the calix[4]arene provides a novel route to the design of luminescent bifunctional sensors.

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Supporting Information Available. Detailed synthetic procedure and characterization data for **1**; ESI mass spectra for the binding of **1** with K^+; ^{11}B and ^{19}F NMR titration for the binding of **1** with F^-; emission spectra of **1** in different solvents; electronic absorption and emission spectral traces of **1** upon addition of $NaClO_4$; ^{1}H and ^{13}C NMR spectra of **1**; EI mass spectrum of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.