Sensors

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Charge-Transfer Emission in Nonplanar Three-Coordinate Organoboron Compounds for Fluorescent Sensing of Fluoride**

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Three-coordinate organoboron compounds possess an empty p_π orbital on the boron center and hence have a tendency to display intense intramolecular charge-transfer transitions when an appropriate electron donor is present. Such donor–acceptor charge-transfer properties have enabled a number of important applications of three-coordinate boron compounds in materials chemistry such as nonlinear optical materials,[1] charge-transport materials, and emitters in organic light emitting devices (OLEDs).[2] Recently it has been demonstrated by several research groups that three-coordinate boron compounds can also be used as effective colorimetric, fluorescent, or ratiometric sensors for the detection of fluoride by utilizing the empty p_π orbital on the boron center.[3] Selective detection of fluoride is of current interest because of their importance to human health, their impact on the environment, and their association with nerve agents.[4,5] Previously reported fluorescent sensors based on three-coordinate boron compounds operate on the principle that the binding of fluoride to the boron center disrupts or perturbs the p_π–π conjugation between the boron center and the aromatic chromophore, thus inducing a change in fluorescent signal.[3d] Although the donor–acceptor charge-transfer properties of three-coordinate boron compounds have been exploited extensively for applications in nonlinear optics and OLEDs, surprisingly little investigation has been done on their utility in fluorescent sensor applications. Our preliminary investigation indicates that charge-transfer fluorescence of three-coordinate boron compounds can be very sensitive and selective for fluoride, and that "turn-on" fluorescent sensors for fluoride can be made by manipulating the geometry of the donor and acceptor in the molecule.

All previously reported three-coordinate boron compounds that produce intense charge-transfer fluorescence are planar conjugated systems,[1–3] an example of which is BNPB, reported by us recently.[2k] BNPB has an N(Ph)(1-naphthyl) donor and a B(mesityl)$_2$ acceptor group that are linked by a 4,4′-biphenyl group (see Scheme 2). BNPB produces intense solvent-dependent fluorescent emission (e.g. $\lambda_{em} = 492$ nm, $\Phi_p = 0.67$ in CH_2Cl_2) originating from the charge transfer between the amino and the boron centers.[2k] We have observed that the addition of fluoride to a solution of BNPB causes fluorescent quenching due to the occupation of the boron p_π orbital by electrons from F^-, which effectively blocks intramolecular charge transfer, thus causing decrease in emission intensity. Direct evidence for F^- binding to the boron center in BNPB comes from our ^{19}F NMR study of a $(nBu_4N)F$ solution (TBAF) titrated with BNPB: the spectra revealed distinct ^{19}F chemical shifts for bound and unbound fluoride. We have also established that BNPB binds to fluoride exclusively even in the presence of other halides such as Cl^- or Br^-, which do not cause a significant change in fluorescence when added to the BNPB solution. This high selectivity for F^- by BNPB is consistent with previously reported fluoride sensors based on three-coordinate organoboron compounds in which the boron center is protected by substituent groups at the *ortho* positions.[3] Although BNPB is potentially useful for selective detection of F^-, it is a "turn-off" sensor; that is, fluorescence is quenched in the presence of fluoride. For practical applications, signal detection is more effective in "turn-on" sensors. Even better are "turn-on" sensors that display distinct color changes for fast and efficient sensing.[3f] In our search for "turn-on" organoboron sensors based on intramolecular charge-transfer emission, we synthesized organoboron compound **1** using the procedure shown in Scheme 1. The donor N(Ph)(1-naphthyl) and the acceptor B(mesityl)$_2$ in **1** are linked to two separate biphenyl groups, which are further connected by a naphthalene unit. Thus, the donor and the acceptor groups in **1** have a nonplanar arrangement. Molecule **1** displays solvent-dependent fluorescence ($\lambda_{em} = 504$ nm, $\Phi_p = 0.10$ in CH_2Cl_2), which is characteristic of charge-transfer emission. Molecular orbital calculations (Gaussian 03)[6] confirmed that the HOMO consists indeed of contributions of the aminobiphenyl portion, and the LUMO of the (mesityl)$_2$B(biphenyl) portion. Molecular modeling studies show that the two biphenyl units in **1** are approximately orthogonal to the naphthalene ring, and, as a result, charge transfer from the amine to the boron unit most likely occurs through space rather than through the aromatic linker. In contrast to the behavior of BNPB, whose emission is quenched upon addition of F^-, the emission spectrum of a solution of **1** shifts to a shorter wavelength ($\lambda_{max} = 453$ nm, in CH_2Cl_2) upon addition of TBAF and the emission intensity is drastically enhanced (Figure 1). The color of the emission of **1** changes vividly from green to blue (Figure 1) after addition of F^-. Hence, compound **1** can be described as a "turn-on" sensor for fluoride. A possible explanation for the color change is the presence of dual fluorescent pathways in **1**, that is, charge-transfer emission between the N donor and the B acceptor as well as $\pi^* \rightarrow \pi$ emission localized on the N donor. The binding of F^- to the B center blocks the charge-transfer transition, thus inhibiting the green emission, but the blue emission of the N(Ph)(1-naphthyl)(biphenyl) portion is activated simultaneously (Scheme 2). The closely related molecules 4,4′-bis[(1-naphthyl)(phenyl)amino]biphenyl and 1,8-bis{4-[(1-naphthyl)(phenyl)amino]biphenyl-4′-yl}naphthalene[7] exhibit similar blue emission (see the Supporting

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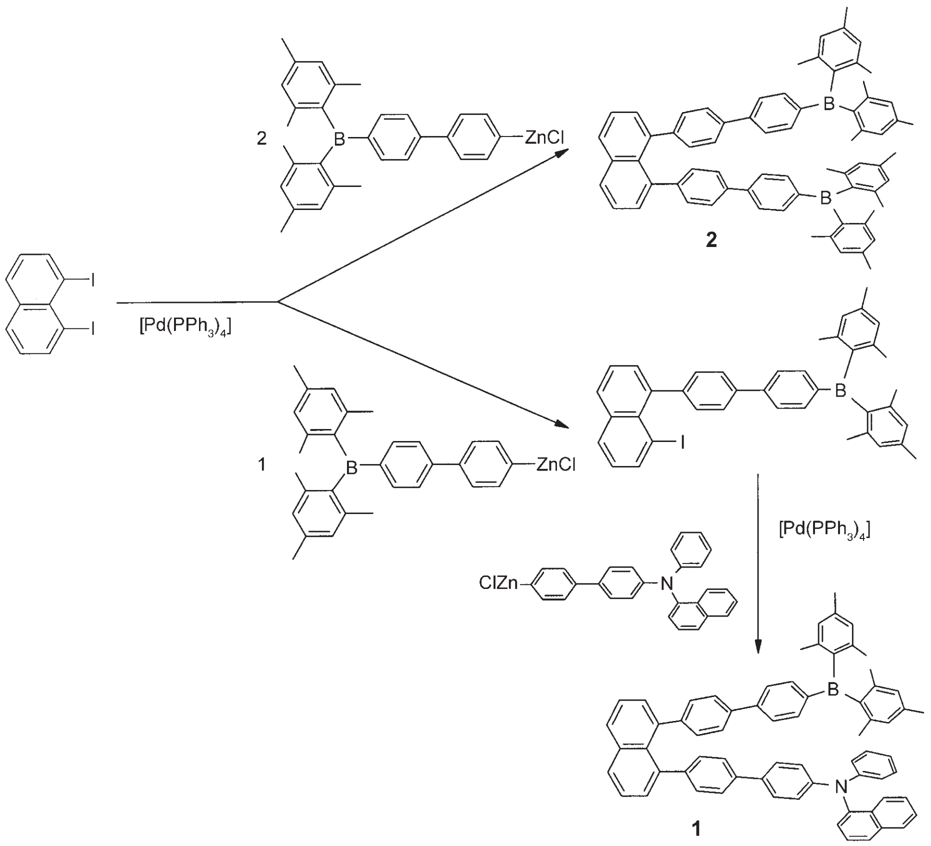


Scheme 1. Synthesis of fluorescent fluoride sensors **1** and **2**.

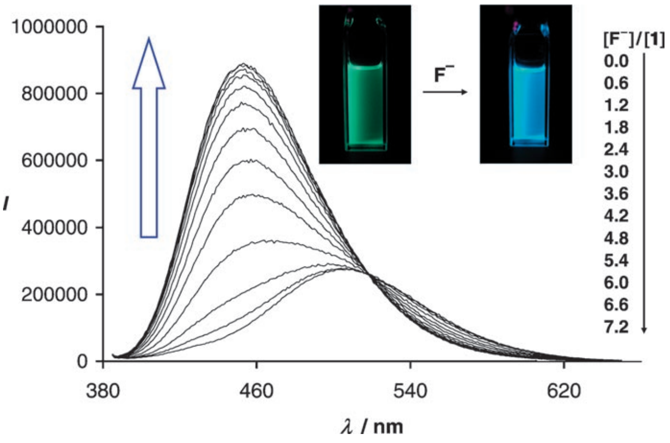
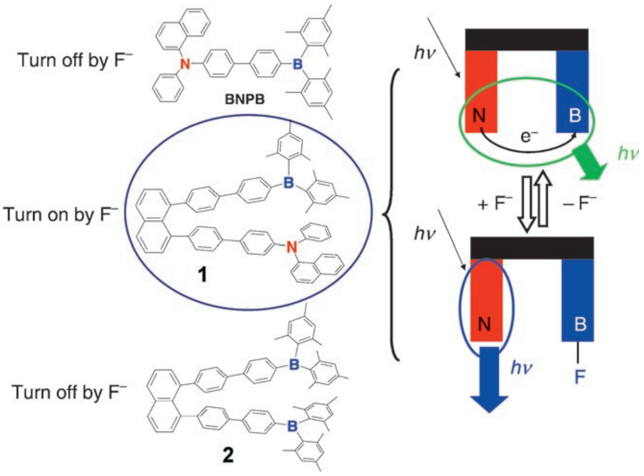


Figure 1. The emission spectra of **1** (7.4×10^{-6} M in CH_2Cl_2) upon addition of TBAF.

Information), which supports the hypothesis that the observed blue emission of F$^-$-bound **1** is indeed from the (phenyl)(1-naphthyl)aminobiphenyl unit. One possible factor that is responsible for the distinct behavior of **1** and BNPB is the difference in their fluorescent quantum efficiencies (0.10 versus 0.67). The emission quantum efficiency of the aminobiphenyl unit in **1** and BNPB is likely between 0.10 and 0.67, and, as a consequence, the quenching of the charge-transfer emission by fluoride leads to an increase in emission intensity for **1**, but a decrease for BNPB. The drastically different emission quantum yields of BNPB and **1** are most likely the consequence of the linker between the donor and the acceptor, namely, a linear aromatic linker versus a nonlinear, nonconjugated linker.

To appreciate the importance of the N(Ph)(1-naphthyl)(biphenyl) group in the "turn-on" sensing of **1**, diboron molecule **2** in which the N(Ph)(1-naphthyl) unit is replaced by B(mesityl)$_2$ was synthesized (Scheme 1). Molecule **2** displays solvent-dependent fluorescence (see the Supporting Information), which is consistent with charge-transfer emission. **2** fluoresces at a much shorter wavelength than **1** and has a much higher quantum efficiency (e.g. $\lambda_{em} = 414$ nm, $\Phi_p = 0.98$ in CH_2Cl_2). Molecular-orbital calculations (Gaussian03) revealed that the HOMO of **2** consists predominantly of the naphthyl ring whereas the LUMO is dominated by the p_π orbitals of the two boron centers and the biphenyl units. The lowest electronic transition in **2** can be therefore attributed to charge transfer between the naphthyl ring and the two boron centers. The response of **2** to fluoride is in sharp contrast to that of **1**: instead of fluorescent enhancement and a color change, the addition of F$^-$ to a solution of **2** quenches the emission from **2** (Figure 2). **2** is therefore a "turn-off" sensor for fluoride. The behavior of **2** in the presence of F$^-$ resembles that of BNPB, which is not surprising since in both molecules the donor and the acceptor are connected through a linear aromatic linker (biphenyl). The fluorescent quenching of **2** by F$^-$ is due to the occupation of the empty p_π orbital of boron by the F$^-$ ligand—the same operating mechanism as in BNPB. The contrasting fluorescent properties of **2** and its response to fluoride establish unequivocally that the aminobiphenyl unit in **1** is indeed



Scheme 2. Operating principle of "turn-on" and "turn-off" sensors for fluoride.

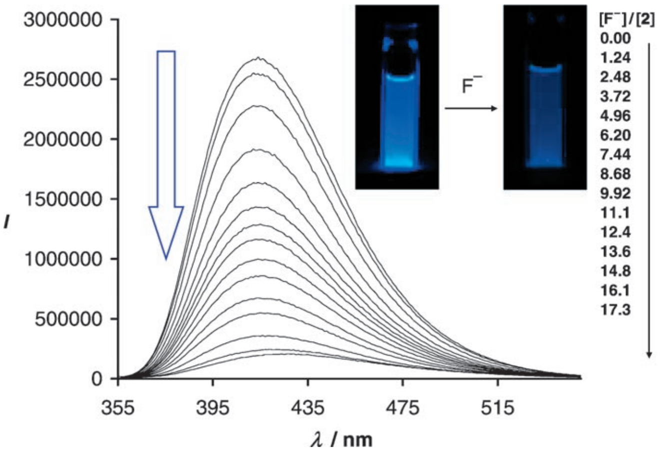


Figure 2. The emission spectra of **2** (9.1×10^{-6} M in CH_2Cl_2) upon the addition of TBAF.

responsible for the fluorescent color change and intensity enhancement of **1** induced by F^-.

The binding of fluoride to **1** and **2** was verified by titration experiments with ^{19}F NMR spectroscopy. The addition of **1** or **2** to a solution containing excess TBAF results in two distinct ^{19}F chemical shifts, which correspond to bound and unbound F^- ions, respectively. Furthermore, the NMR data indicated that **1** forms a 1:1 complex with F^- whereas **2** forms a 1:2 complex. Solé and Gabbai demonstrated that two unsaturated boron groups attached directly to the 1 and 8 positions of naphthalene can capture an F^- ion, which acts as a bridging ligand and results in a complex with an exceptionally large binding constant.[3g] We did not observe any evidence of bridging F^- ligands in the NMR experiments with **2**. Molecular-modeling studies and geometry optimization with the Gaussian 03 program suite showed that the two boron centers in **2** are approximately 10 Å apart, which is too far for an F^- bridge. The binding constants of **1** and **2** with fluoride were determined from the fluorescence titration data (see the Supporting Information for details) to be approximately $4.0\times10^4\,\text{M}^{-1}$ and $9.0\times10^8\,\text{M}^{-2}$, respectively, which are comparable to previously reported three-coordinate monoboron compounds.[3] (The binding constant of **2** is seemingly large because it is the overall binding constant for two fluoride ions.) The fluorescence spectra of **1** and **2** (Figures 1 and 2) change significantly upon addition of around two equivalents of F^- ions. This corresponds to a detection limit for $F^-$of between 0.015 and 0.020 mM under the experimental conditions used; thus, **1** and **2** are very sensitive to F^-. Moreover, they do not respond to chloride, bromide, or iodide ions, they can be recovered fully from the titration solution, and the original color and intensity of their fluorescence can be restored fully by adding water to extract the fluoride ions (for organic solvents such as CH_2Cl_2 that are not miscible with water; see the Supporting Information). The use of water to reverse fluoride binding to three-coordinate boron molecules in organic solvents has been noted by Yamaguchi et al.[3c] A large enhancement in the fluorescence of **1** and a drastic quenching of the fluorescence of **2** upon addition of fluoride are also observed in tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF). The disadvantage of using THF or DMF as the solvent is the difficulty of recovering the sensor molecules by using water, as these solvents are water-miscible. When mixed solvents such as THF and H_2O or DMF and H_2O are used for the fluoride titration experiments, no apparent fluorescence change was observed; this observation can be attributed to the formation of hydrogen bonds between fluoride ions and water molecules, which compete with the binding to the boron center.

In summary, we have demonstrated that a nonplanar linker, such as 1,8-bis(4,4′-biphenyl)naphthalene, can be used effectively to bring either two electron acceptor groups (e.g. diaryl boron groups), or an electron donor and an acceptor (e.g. a diaryl amino group and a diaryl boron group) together to form molecules that are stable in water and display distinct fluorescent responses to fluoride. By linking a nitrogen donor and a boron acceptor group in a nonplanar arrangement (as in **1**), it is possible to produce through-space donor–acceptor charge-transfer emission that can be switched off by the addition of fluoride, which in turn activates the fluorescence from the donor chromophore, thus producing a sensitive and selective "turn-on" fluorescent sensor for fluoride. Energy-transfer systems involving three-coordinate boron compounds that exploit dual signaling pathways for the detection of fluoride ions have been reported previously.[3f] Compound **1** demonstrates that dual signal pathways in nonplanar three-coordinate boron compounds can also be modulated by intramolecular charge transfer and exploited effectively for the detection of anions such as fluoride.

Experimental Section

Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster Model C-60 spectrometer. Fluorescence titrations were carried out by adding stock solutions of TBAF in CH_2Cl_2 to the solutions of **1** or **2** in CH_2Cl_2. Binding constants were obtained by using the fitting methods described by Connors.[8] Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. The Gaussian 03 program suite[6] was used for all molecular-geometry optimization and molecular-orbital calculations. The calculations were carried out at the B3LYP level of theory with 6-311G** as the basis set. 1,8-Diiodonaphthalene[9] and 4-iodo-4′-(1-naphthylphenylamino)biphenyl[10] were synthesized by modified literature methods. The experimental and synthetic details are provided in the Supporting Information.

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