

Highly Sensitive Sensory Materials for Fluoride Ions Based on the Dithieno[3,2-*b*:2',3'-*d*]phosphole System

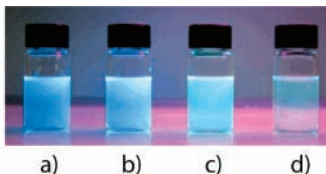
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Received December 1, 2005

ABSTRACT



a) blank ($c=10^{-4}$ M); b) with I^- , Br^- , or Cl^- ($c=10^{-4}$ M);
c) with F^- ($c=10^{-4}$ M); d) with F^- ($c=10^{-5}$ M)

The newly developed functionalization of an unsubstituted dithieno[3,2-*b*:2',3'-*d*]phosphole at the 5,5'-positions gives access to bis(pinacoleboronyl) species that can be utilized as sensory materials for fluoride ions. The fluoride-triggered response of the air- and moisture-stable boronyl-functionalized dithienophosphole oxide manifests itself in the generation of a new fluorescence emission that can be detected at very low analyte concentrations (ppm) or even with the naked eye upon irradiation with UV light (366 nm).

A great deal of attention has recently been focused on the selective sensing of anions by means of synthetic molecular or polymeric sensors.¹ In this context, the detection of fluoride (F^-) is of particular interest as it plays an essential role in a broad range of biological, medical, and chemical processes and applications such as dental care,² treatment of osteoporosis,³ fluorination of water supplies,⁴ or even in chemical and nuclear warfare agents.⁵ As a result of this

diversity, it seems important to develop very sensitive and selective methods to detect the fluoride ion under environmental conditions. Popular approaches to access fluoride-triggered responses involve hydrogen bonding with the fluoride ion or strong Lewis acid–base interactions, such as the strong affinity of electron-deficient boron compounds toward fluoride.^{6–9} Over the past years, a variety of detection methods have been utilized in these sensor materials including electrochemical⁶ or colorimetric responses^{7,8} as well as

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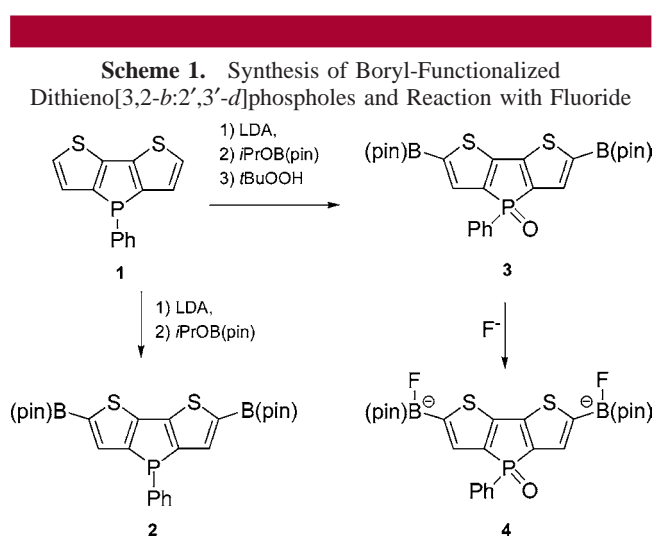
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fluorescence changes.⁹ The latter, very convenient method, is intriguingly attractive for sensing as it exhibits great sensitivity at very low analyte concentrations down to the micromolar scale,^{9b} which is required for detection of physiological fluoride^{3c} as well as fluoride in drinking water.^{4,8c} However, most of the fluorescence-based sensory materials employed rely on changes in the emission intensities that are less reliable than the detection of a new emission at a different wavelength.^{9,10}

An ideal sensory material for the fluoride ion at the parts per million scale could therefore combine the strong affinity of boron centers to fluoride with the generation of a new fluorescence emission upon exposure. With respect to stability under environmental conditions, the use of boronic esters would be particularly favorable. Known fluorescence-based sensor systems that utilize boron–fluoride interactions are sensitive toward oxygen and moisture,^{8a,9d} or they are based on boronic acids, which involve complicated equilibria through the formation of various fluoroborate species.^{10c} Boronic esters such as pinacole borane, on the other hand, provide the necessary stability as well as selectivity toward one fluoride ion only.¹¹ The use of a π -conjugated material with very favorable optoelectronic properties as central fluorophore would also be very helpful for the successful design of an appropriate sensor.⁷ In the context of our work on materials for molecular electronics and optoelectronics, we have established the novel dithieno[3,2-*b*:2',3'-*d*]phosphole moiety that exhibits very promising photophysical properties in terms of wavelength, intensity, and tunability.¹² This system was expected to be an excellent fluorescent relay for a corresponding boron-based sensory material. The desired 5,5'-bis(pinacoleboryl) functionalized system can be accessed by a newly developed general procedure via lithiation of the unsubstituted dithienophosphole **1** with LDA followed by the addition of 2 equiv of isopropoxy(pinacole)-borane (*i*PrOB(pin)) at -78 °C in THF (Scheme 1). The



multinuclear NMR data support the successful functionalization of the dithienophosphole unit showing a ³¹P NMR resonance at $\delta = -24.3$ ppm and a ¹¹B NMR resonance at

$\delta = 29.0$ ppm. The blue luminescent compound **2** exhibits pronounced optoelectronic properties with a maximum wavelength of absorption at 376 nm, an emission at 419 nm, and a very high photoluminescence (PL) quantum yield efficiency of $\phi_{\text{PL}} = 0.61$ ¹³ that is typical for dithienophospholes.¹² Compared to the nonfunctionalized dithienophosphole **1** ($\lambda_{\text{ex}} = 346$ nm; $\lambda_{\text{em}} = 424$ nm),^{12b} the value for absorption experiences a red shift of about 30 nm, supporting the electron-accepting properties of the boryl groups, whereas the emission is almost not affected.

However, to gain the necessary stability at environmental conditions, we targeted an oxidized phosphole species that has been found to fulfill these requirements before.¹² The oxidized bis(boryl)dithienophosphole **3** is accessible in a manner similar to that described for **2** followed by in situ oxidation of the functionalized phosphole intermediate with aqueous *tert*-butylhydroperoxide to give the air- and moisture-stable product **3**. Analysis by ³¹P NMR spectroscopy clearly supports the oxidation of the dithienophosphole moiety with a resonance at $\delta = 16.5$ ppm (δ ¹¹B = 28.5 ppm).

The fluorescence spectrum of the strongly blue luminescing **3** shows a maximum wavelength for absorption at $\lambda_{\text{ex}} = 398$ nm that is red shifted about 20 nm from the one for **2**, whereas the maximum wavelength for emission at $\lambda_{\text{em}} = 452$ nm shows a red shift of about 30 nm supporting the successful oxidation.¹² The oxidized boryl-substituted species **3** also exhibits a very good PL quantum yield efficiency of $\phi_{\text{PL}} = 0.53$.¹³

Treatment of a 1×10^{-4} M or 1×10^{-5} M *undegassed* CH₂Cl₂ solution of **3** with a stoichiometric amount of Bu₄NF results in a significant red shift of the maximum wavelengths for absorption and emission with $\lambda_{\text{ex}} = 415$ nm and $\lambda_{\text{em}} = 485$ nm, now displaying a blue-green emission with a photoluminescence quantum yield of $\phi_{\text{PL}} = 0.55$ ¹³ (Figure 1, top). Owing to the formation of the ionic species **4** (δ ³¹P = 17.9; δ ¹¹B = 5.8; δ ¹⁹F = -132.2 ppm), the intensities for absorption and emission, as observed by fluorescence spectroscopy, drop to some extent but still remain significantly strong. It is important to note that the observed change in the fluorescence emission in a solution of **3** toward the fluoro-substituted borate **4** can even be detected, for the first time for B–F interactions,^{10c} at the micromolar (ppm) scale (see Supporting Information), which is attributed to the extraordinary optoelectronic properties of the dithienophosphole moiety. By contrast, addition of Bu₄NCl, Bu₄NBr, or Bu₄NI does not affect the fluorescence properties of **3** at all, resulting in fluorescence spectra similar to the one observed for genuine **3**, supporting the high selectivity of the boryl-functionalized dithienophosphole toward fluoride ions. Slight differences from the spectrum

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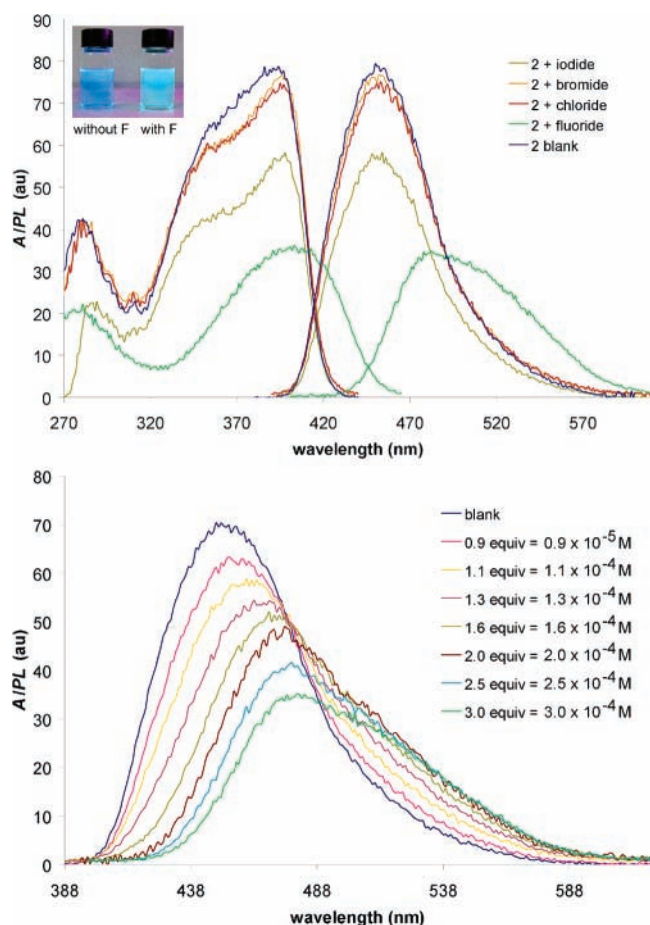


Figure 1. Absorption (left) and emission (right) spectra of **3** ($c \approx 1 \times 10^{-4}$ M) in the presence of various halides (top) and emission spectra with different fluoride concentrations added (bottom).

of **3** can be noticed in some decreased intensities for the mixtures, particularly for Bu_4NI , that can be explained by the *heavy-atom effect* of the iodide.

Furthermore, the addition of fluoride to the CH_2Cl_2 solution of **3** can be monitored ratiometrically by a gradual red shift of the emission from $\lambda_{\text{em}} = 452$ nm (no F^-) to $\lambda_{\text{em}} = 485$ nm (excess F^-), potentially also allowing for a quantitative determination of fluoride in dilute solutions by using the dithienophosphole **3** (Figure 1, bottom). The derivation of two binding constants ($\lg K_1 = 4.02(8)$; $\lg K_2 = 3.79(8)$) obtained from a fluorescence titration indicates a stepwise addition of fluoride. This is further supported by the ^{11}B NMR data of $\mathbf{3} \times \text{F}$ with two resonances at $\delta = 5.8$ and 28.5 ppm indicating one borane and one borate moiety.

Although **3** is not water soluble itself, fluoride ions can nevertheless also be detected in aqueous solutions, as the fluoroborate **4** is soluble in water. Addition of solid **3** to fluoride containing *undegassed* water results in a blue-green emission of the resulting solution with features ($\lambda_{\text{ex}} = 391$ nm; $\lambda_{\text{em}} = 478$ nm) similar to those observed in CH_2Cl_2 (Figure 2). The formation of **4** in water is further supported by multinuclear NMR studies showing values comparable to those in CH_2Cl_2 (see Supporting Information). The dithienophosphole sensor **3** is likely to also have a pH-

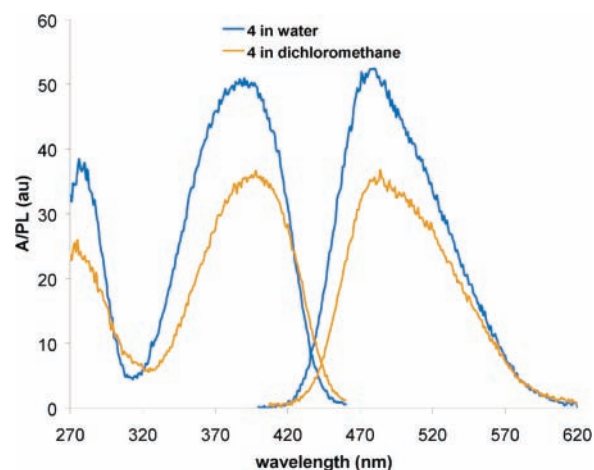


Figure 2. Absorption (left) and emission (right) spectra of **4** in CH_2Cl_2 and water ($c \approx 1 \times 10^{-4}$ M).

dependent response in water, although at neutral pH, such as in drinking water or physiological fluids, the interaction can be assumed to be minimal. In general, environmental and physiological sensing applications do not experience significant pH changes.^{10c}

It should be mentioned in this context that the same selectivity toward the fluoride ion is also observed with the phosphole species **2**. However, the fluorescence emission of the corresponding bis(fluoroborate) still occurs in the blue region of the optical spectrum ($\lambda_{\text{ex}} = 377$ nm; $\lambda_{\text{em}} = 454$ nm) which is inferior to the blue-green emission observed for **4** in terms of signal transduction; the latter even allows for a naked-eye detection of fluoride ions when irradiated with UV light.

In conclusion, we have synthesized the first boryl-substituted dithieno[3,2-*b*:2',3'-*d*]phosphole derivatives. The corresponding phosphole oxide **3** displays a highly sensitive, selective sensory material for the fluoride ion. The novel, phosphoorganic sensor combines the strong affinity of boron centers toward fluoride with the generation of a new emission that can be detected unambiguously in solution at room temperature, even at very low concentrations (ppm) under environmental conditions. Further investigations will include the potential of dithienophosphole-based sensors, particularly toward water soluble systems, and the utility of **2** and **3** as building blocks for extended π -conjugated materials in molecular electronics.

Acknowledgment. We thank Prof. Dr. J. Okuda for his generous support of this work. Financial support from the *Fonds der Chemischen Industrie* (FCI), the *Deutsche Forschungsgemeinschaft* (DFG), and the *Bundesministerium für Bildung und Forschung* (BMBF) is gratefully acknowledged.

Supporting Information Available: Experimental procedures for the preparation of **2** and **3**; NMR data of **2**, **3**, $\mathbf{3} \times \text{F}$, and **4**; and fluorescence data of **4** under varying conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL052911P