

A BODIPY–Borane Dyad for the Selective Complexation of Cyanide Ion

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Summary: The coupling of borane as a donor and BODIPY as an acceptor leads to a boron-based receptor (**3**) that shows a 3-fold enhancement in fluorescence response for the selective sensing of cyanide ion by virtue of intramolecular energy-transfer transitions.

Cyanide ion sensing is of great interest because of the high toxicity of cyanide ion in physiological systems,¹ as well as environmental concerns arising from the widespread industrial uses of cyanide.² Among various analytical methods, optical sensors have recently attracted considerable attention, owing to their simple, inexpensive, and fast detection of cyanide by monitoring a change in color and/or fluorescence intensity as the result of a binding event. Although recently reported chemosensors based on organic³ and organometallic⁴ compounds achieve high selectivity and sensitivity for the detection of cyanide, it is still worthwhile to search for a highly selective system that can operate at very low concentrations of cyanide, such as occur in physiologically relevant systems.

Cyanide sensors based on organoboron receptors have rarely been investigated, in spite of the strong B–CN bonding nature. Several organoboron compounds^{5–7} showing high affinity for cyanide are known, but they are often incompatible with the presence of other anions, fluoride in particular, which readily binds to the boron center.^{5,6,8} Very recently, an elegant study demonstrated that cyanide selectivity over fluoride can be

overcome by use of ammonium borane.⁹ Because of the requirement of high sensitivity for cyanide detection, the enhanced signal transduction from the binding event should further be considered for the borane-based receptors that usually utilize a direct change in the absorption and fluorescence intensity at the boron center. An effective method to achieve this would exploit energy-transfer transitions to signal a binding event: for example, using a highly fluorescent donor–acceptor system. Although recent examples have described such energy-transfer transitions for fluoride sensing,¹⁰ little is known for cyanide sensing and the three-coordinate boron center has been regarded as an electron/energy acceptor. The reverse donor–acceptor systems in which the excitation energy from borane activates a well-defined, highly fluorescent acceptor transition are thus quite intriguing and could provide versatile methods to design a novel sensor scheme.

In this report, we combined three-coordinate borane as a donor and highly fluorescent BODIPY as an acceptor to construct a discrete and highly fluorescent borane-based receptor that utilizes intramolecular excitation energy-transfer transitions for the selective detection of cyanide ion.

A Suzuki-type coupling reaction between a BODIPY derivative (**1**)¹¹ and a boronic acid bearing a borane moiety (**2**)¹² afforded the desired Lewis acid **3** as an orange-red solid in 51% yield (Scheme 1). While the ¹H and ¹³C NMR spectra show the expected resonances corresponding to the BODIPY and triarylborane moieties, two ¹¹B NMR signals detected at δ 76.8 and 0.68 ppm confirm the presence of both base-free trigonal-planar and four-coordinate boron centers, respectively, in **3**. The latter ¹¹B nucleus is coupled to the fluorine atoms, giving rise to a sharp triplet ($J_{B-F} = 33.0$ Hz) comparable to those found in the known BODIPY derivatives.^{13,14} These features are

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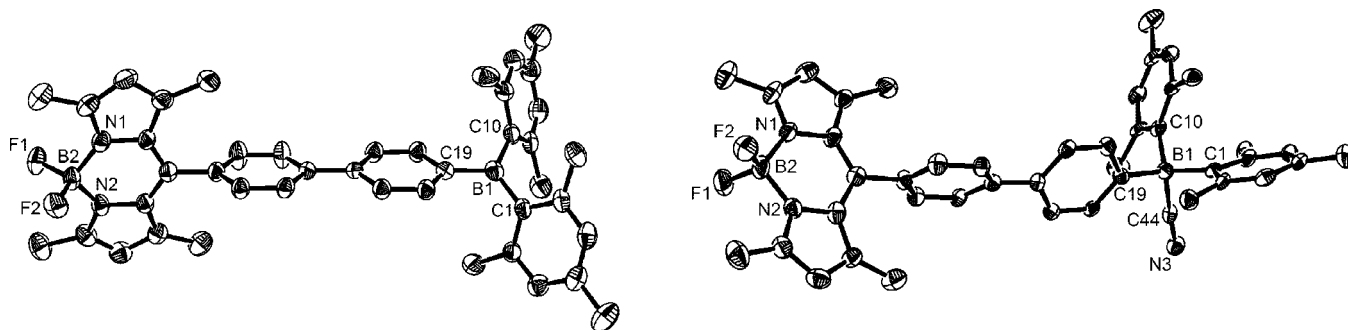
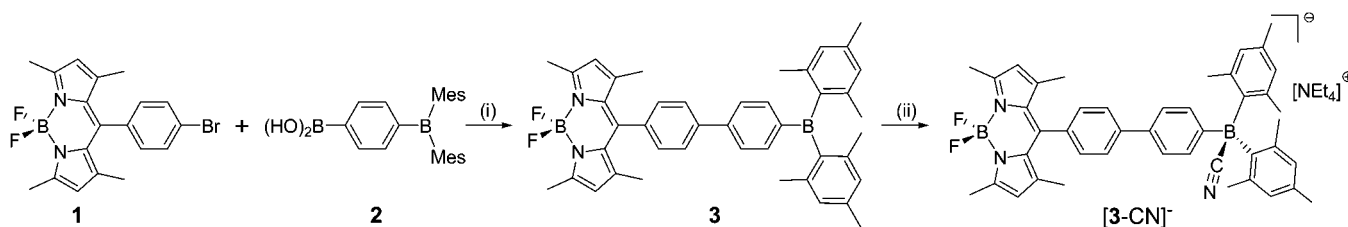


Figure 1. Crystal structures of **3** (left) and $[3\text{-CN}]^-$ in $[\text{NEt}_4][3\text{-CN}]$ (right, molecule **A** only) (50% probability ellipsoids). The $[\text{NEt}_4]^+$, solvent molecules, and H atoms are omitted for clarity.

Scheme 1



(i) $\text{Pd}(\text{PPh}_3)_4$, Na_2CO_3 , EtOH/toluene, 100 °C, 51%. (ii) Et_4NCN , CH_2Cl_2 , 25 °C, 66%.

clearly established from the crystal structure of **3**, which exhibits a trigonal-planar geometry ($\Sigma(\text{C}-\text{B}-\text{C}) = 359.9^\circ$) around the boron atom of the borane moiety and four-coordination of the boron atom by the fluorine and nitrogen atoms in the BODIPY group (Figure 1, left). The dihedral angle of 78.2° between the BODIPY ring fragment and the adjacent phenylene ring reveals a highly twisted conformation between the two rings. In contrast, the biphenylene bridging unit forms a phenylene-phenylene dihedral angle of $4.1(1)^\circ$, showing its considerable planarity, which further extends to the trigonal boron plane.

Compound **3** is readily converted into the cyanide adduct $[3\text{-CN}]^-$ when treated with Et_4NCN in CH_2Cl_2 (Scheme 1). In addition to the triplet ^{11}B NMR signal detected at δ 0.43 ppm ($^1J_{\text{B}-\text{F}} = 33.5$ Hz) which is almost identical with that observed in the neutral **3**, the signal at δ -13.6 ppm confirms the existence of an additional four-coordinate boron center,^{9,15,16} indicating the binding of cyanide to the borane moiety. To elucidate this binding nature, the crystal structure of $[3\text{-CN}]^-$ was determined from an X-ray diffraction study. The asymmetric unit contains two independent molecules, denoted as **A** and **B**, that have very similar structures. As shown in Figure 1 (right), the cyanide group is coordinated to the boron center of the borane moiety through the B-CN linkage. The B(1)-CN bond lengths of 1.622(9) Å (molecule **A**) and 1.620(9) Å (molecule **B**), which are comparable to those observed in triarylcyanoborates^{9,16,17} and slightly shorter than those of B(1)-C_{aryl} bonds (1.64–1.68 Å), indicate the presence of the usual polar covalent B-CN linkage. While the BODIPY ring fragment is almost perpendicular to the adjacent phenylene ring ($\angle_{\text{dihedral}} = 89.9^\circ$

for molecule **A** and 80.3° for molecule **B**), as similarly observed in **3**, the biphenylene bridging unit shows an apparent distortion ($\angle_{\text{dihedral}} = 32.1(3)^\circ$ for molecule **A** and $33.1(3)^\circ$ for molecule **B**), possibly due to the disruption of the extended conjugation after cyanide complexation.

To examine the cyanide binding properties of **3**, UV-vis and PL experiments were carried out. Compound **3** features two major absorption bands at 330 nm ($\log \epsilon = 4.49$) and 501 nm ($\log \epsilon = 4.92$) in THF assignable to the dominant π - $\text{p}\pi(\text{B})$ transition in the borane^{6,9,18} and the π - π^* transition in the BODIPY¹⁹ moiety, respectively (Figure 2).

From a comparison with the absorption spectra of the closely related mononuclear compounds **1** and $\text{Mes}_2\text{B}(p\text{-biphenyl})$ (**4**), one can note that the wavelengths of the absorption maxima (λ_{max}) of the two fluorophores in **3** show almost no change, thus indicating the presence of little electronic communication between the two moieties (Figure S3 in the Supporting Information). The orthogonal arrangement of the BODIPY and the adjacent phenylene ring fragments is probably responsible for this feature.^{13,20,21} Addition of cyanide to a THF solution of **3** leads to a decrease in the intensity of the absorption band of the borane moiety at 330 nm, while the band of the BODIPY fragment at 501 nm remains unaffected throughout the titrations (Figure 2). This result indicates not only the formation of the 1:1 complex $[3\text{-CN}]^-$ with a stability constant that exceeds 10^7

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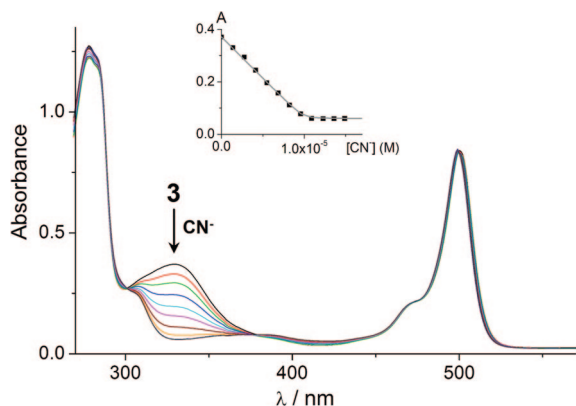


Figure 2. Spectral changes in the UV-vis absorption of a solution of **3** in THF (1.0×10^{-5} M) upon addition of Bu_4NCN (0–15 μM). The inset shows the absorbance at 330 nm as a function of $[\text{CN}^-]$ (■). The line corresponds to the binding isotherm calculated with $K = 5 \times 10^7 \text{ M}^{-1}$.

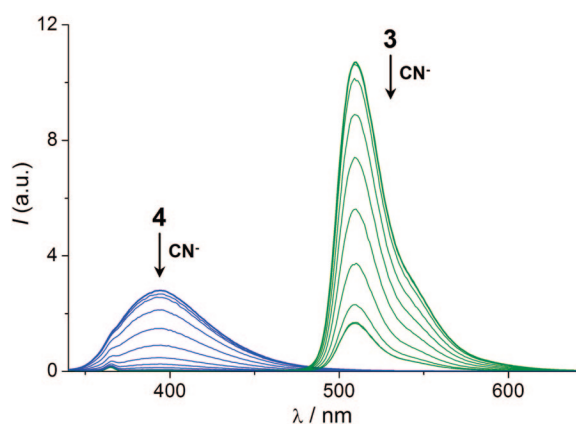


Figure 3. Comparison of the fluorescence response of solutions of **3** (right) and **4** (left) in THF (λ_{ex} 330 nm; 1.0×10^{-6} M) upon addition of Bu_4NCN (0–2 μM).

M^{-1} but also the invariant absorption feature of the BODIPY in **3** and $[\text{3-CN}]^-$ originating from the similar, nonplanar arrangement of the BODIPY moieties in both compounds.

The independent absorption characteristics of the two fluorophores in **3** thus provide a basis for the utilization of **3** as a donor-acceptor pair for intramolecular energy-transfer transitions. The emission spectrum of **3** irradiated at 330 nm exclusively exhibits a very intense green fluorescence (λ_{em} 510 nm; Figure 3, right) while that of **4** at the same excitation gives a blue fluorescence (λ_{em} 394 nm; Figure 3, left).

This result implies an energy transfer from the borane moiety induced by 330 nm irradiation to the BODIPY fragment, where subsequent emission occurs. The observation of the apparent emission bands ascribable to **1** and **4**, respectively, from the solution of an equimolar mixture (λ_{ex} = 330 nm; Figure S7 in the Supporting Information) clarifies such an intramolecular energy-transfer transition phenomenon in **3**.^{13,20,22} A comparison of the quantum yields obtained by irradiation in the borane

moiety ($\Phi = 0.32$, λ_{ex} = 330 nm) and by direct excitation in the BODIPY ($\Phi = 0.56$, λ_{ex} = 480 nm), respectively, indicates that intramolecular energy transfer occurs with 57% efficiency for **3**. This result is also in good agreement with the overlapping feature between the excitation spectrum recorded for the BODIPY emission and the absorption band ascribable to the borane moiety (Figure S9 in the Supporting Information).¹³ Upon addition of cyanide, the emission intensity of **3** at 510 nm gradually decreases and finally reaches the residual emission derived from $[\text{3-CN}]^-$ (Figure 3, right). This result can be correlated to the decrease in energy transfer from the borane moiety to the BODIPY group as cyanide binds to the boron center. Moreover, the quantum yields of **3** ($\Phi = 0.32$) and $[\text{3-CN}]^-$ ($\Phi = 0.30$) measured in THF with 330 nm excitation are very similar and, thus, it can be suggested that the additional quenching effect accompanying the formation of $[\text{3-CN}]^-$ is negligible in the observed emission. A comparison with the same emission quenching experiments using **4** reveals a 3-fold enhancement effect in **3** (Figure 3, left).

The presence of 10 equiv of tetrabutylammonium salts of other anions such as Cl^- , Br^- , I^- , OAc^- , NO_3^- , H_2PO_4^- , SCN^- , HSO_4^- , and ClO_4^- does not significantly affect the UV-vis spectrum and the emission band of **3** in THF (Figure S10 in the Supporting Information), indicating high selectivity for cyanide. These results also reflect the high stability of the BODIPY moiety toward such anions. In sharp contrast, the addition of fluoride gives rise not only to a spectral change of absorption with a slow disappearance of the band at 501 nm but also to a color change from greenish to colorless, indicating decomposition of the BODIPY moiety. The change of a triplet ^{11}B signal into a singlet signal in the presence of excess fluoride is in good agreement with this observation (Figure S12 in the Supporting Information).²³ Furthermore, the emission color of a solution of **3** in the presence of fluoride is more vividly differentiated from that of the cyanide-containing solution (Figure S11 in the Supporting Information). To obtain a more detailed insight into this feature, UV-vis titrations with incremental amounts of fluoride ion were carried out. The results show that **3** also has a strong affinity for fluoride which, however, induces decomposition of the BODIPY moiety over time (Figure S6 in the Supporting Information). Although **3** responds to a small amount of fluoride ion, these results could further provide a distinction for the detection of cyanide over fluoride. Finally, by taking advantage of the high fluorescence and strong binding affinity of **3**, the emission response at a very low concentration of cyanide was investigated using a 0.1 μM solution of **3**. The fluorescence intensity change indicates that **3** remains highly sensitive even at a submicromolar level of cyanide (Figure S13 in the Supporting Information).

In conclusion, the coupling of borane as a donor and BODIPY as an acceptor leads to an unprecedented boron-based cyanide ion receptor (**3**) that exploits discrete intramolecular energy-transfer transitions. In addition to high selectivity for cyanide over physiologically and environmentally relevant anions, the highly sensitive fluorescence response allows the detection of an extremely low

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level of cyanide. Studies on modifying the given system to make it viable in an aqueous medium are in progress.

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Supporting Information Available: Text, tables, figures, and CIF files giving experimental details, X-ray crystallographic data, and UV-vis and PL spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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