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# Visual and Colorimetric Detection of Cyanide Anion Based on a "Turn-off" Daylight Fluorescent Molecule

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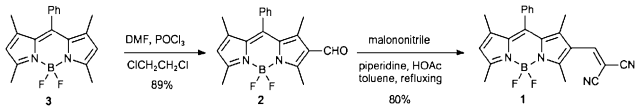
A strong daylight-fluorescent boron dipyrromethene (BODIPY) derivative **1** has been synthesized for the visual and colorimetric detection of cyanide anion in solution. BODIPY **1** shows a glow characteristic of daylight-fluorescent material since emitted fluorescent light has been added to the simple reflection light under daylight illumination. This green daylight fluorescence is diminished upon interaction with cyanide anion, resulting in a highly selective and sensitive naked-eye detection of cyanide anion over other common anions.

The extreme toxicity of cyanide and the environmental concerns from its continued industrial use have lead to the growing interest in the development of facile and sensitive methods for cyanide detection.[1–3] A number of cyanide sensors and indicators have been developed[4–6] based on the coordination ability[4e,5] and nucleophilic reactivity[6] of cyanide anion. Among those, colorimetric chemosensors are of particular interest due to simplicity, allowing naked-eye detection without resorting to any spectroscopic instrumentation.[7] For instance, Sessler[5b,6a,7e] and Akkaya[7f] have developed colorimetric chemosensors for cyanide anion based on the benzil and boradiazaindacene (BODIPY) platform. Kawashima reported a fluorescence color change of boron-substituted diarylazomethine by reaction with cyanide.[7j,7k] However, there remains a need for carefully designed colorimetric chemosensors for the selective, sensitive, and straightforward signaling of the presence of cyanide anion.

BODIPY dyes have excellent photophysical properties, and the recent developments[8] in new synthetic strategies for their functionalizations have lead to wide research interests in a highly diverse fields[9] as fluorescent organic devices,[10] energy-transfer cassettes,[11] light-harvesting systems,[12] potential sensitizers for photodynamic therapy,[13] and ion sensing and signaling reagents.[14,15] Herein, we report a new BODIPY-based optical sensor **1** (Scheme 1) for the naked-eye detection of cyanide anion.

In our sensor design, a dicyanovinyl group, as a putative cyanide-dependent reactive subunit, has been installed onto a BODIPY platform through a simple Knoevenagel condensation on the $\beta$-formyl BODIPY **2**.[8i] The structure of BODIPY **1** was confirmed by $^1$H NMR, $^{13}$C NMR, and MS. It was expected that cyanide, and possibly other nucleophiles, could attack the $\alpha$-position of the dicyanovinyl group to generate stabilized anionic species, resulting in the reduced extent of conjugation and a spectral change. In comparison to the parent $\beta$-unsubstituted BODIPY **3**, the increased conjugation in BODIPY **1** leads to the red shift of both the absorption and emission spectra. Thus, nucleophilic addition of anions to the $\alpha$-position of the vinyl group would be expected to produce a color change or at least in perceived brightness or intensity. BODIPY **1** would act as a cyanide-selective colorimetric sensor in the case that cyanide anion was the only nucleophile capable of inducing such changes.




**Scheme 1.** Synthesis of the optical chemsensor **1**.

The anion sensing property of BODIPY **1** was studied in a 98% $CH_3CN$ ($CH_3CN$/water 98/2 (v/v)) solution. The anions selected for this study were $SCN^-$, $Br^-$, $Cl^-$, $F^-$, $I^-$, $NO_3^-$, $CH_3CO_2^-$, $H_2PO_4^-$, and $CN^-$. When a solution of BODIPY **1** (10 μM) was treated with a fixed amount of selected anions (20 equiv of $CN^-$ and 50 equiv of other anions), only the addition of $CN^-$ caused a significant change in the absorption and emission spectra as shown in Figure 1. The decrease of absorption intensity and a blue shift of absorption band from 508 to 500 nm were observed for BODIPY **1** (Figure 1a). Similarly, the quenching of more than 90% of the fluorescence emission was observed for BODIPY **1** with the addition of $CN^-$, with a blue shift of the emission band from 539 to 514 nm (Figure 1b). Time-dependent UV–vis (Figure S1 in Supporting Information; SI[16]) and fluorescent studies (Figure S2 in SI[16]) indicated the reaction is finished at 20 min at room temperature.

To confirm the good selectivity of BODIPY **1** to $CN^-$ over the other selected anions, competition experiments between $CN^-$ and these anions were performed in a 98% $CH_3CN$ ($CH_3CN$/water 98/2 (v/v)) solution, and the results are summarized in Figure 2 and Figure S3.[16] When 50 equiv of these selected anions was added into solution of BODIPY **1** containing 20

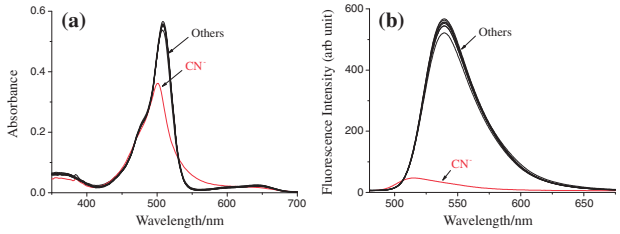



**Figure 1.** (a) UV–vis ($1.0 \times 10^{-5}$ M) and (b) fluorescence ($1.0 \times 10^{-6}$ M, excited at 470 nm) spectra of BODIPY **1** in 98% $CH_3CN$ ($CH_3CN$/water 98/2 (v/v)) in the presence of 20 equiv of NaCN or 50 equiv of other anions (including $SCN^-$, $Br^-$, $Cl^-$, $F^-$, $I^-$, $NO_3^-$, $CH_3CO_2^-$, and $H_2PO_4^-$).

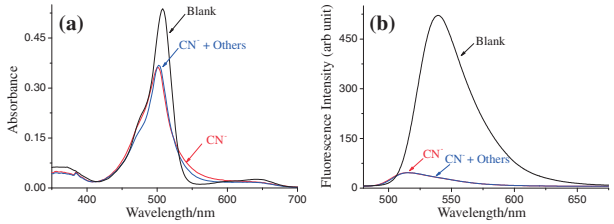



**Figure 2.** (a) UV–vis ($1.0 \times 10^{-5}$ M) and (b) fluorescence ($1.0 \times 10^{-6}$ M, excitation at 470 nm) spectra of BODIPY **1** in 98% $CH_3CN$ ($CH_3CN$/water 98/2 (v/v)). Black line, in the absence of anions (blank); red line, in the presence of 20 equiv of NaCN; blue line, in the presence of 20 equiv of $CN^-$ and 50 equiv of other anions (including $SCN^-$, $Br^-$, $Cl^-$, $F^-$, $I^-$, $NO_3^-$, $CH_3CO_2^-$, and $H_2PO_4^-$).

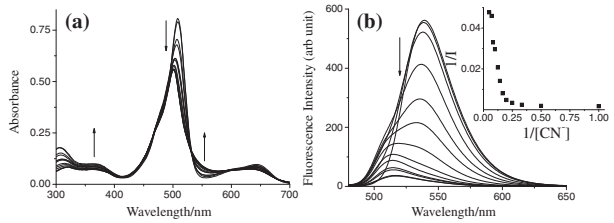



**Figure 3.** (a) UV–vis spectral changes of BODIPY **1** ($1.0 \times 10^{-5}$ M) in 98% $CH_3CN$ ($CH_3CN$/water 98/2 (v/v)) in response to increasing concentration of NaCN (0–$1.4 \times 10^{-4}$ M). The spectra were recorded 20 min after addition of NaCN. (b) Fluorescence spectral changes of BODIPY **1** ($1.0 \times 10^{-6}$ M) in 98% $CH_3CN$ ($CH_3CN$/water 98/2 (v/v)) in response to increasing concentration of NaCN (0–$2.0 \times 10^{-5}$ M). Excitation was set at 470 nm, with slit widths of 5 nm. Insert: Plot of fluorescence intensity at 539 nm vs. number of equiv of $CN^-$.

equiv of $CN^-$, both the absorption and emission spectra displayed similar patterns to those with $CN^-$ alone. Thus, BODIPY **1** showed excellent selectivity for $CN^-$ over the other selected anions.

Once the selectivity of BODIPY **1** for $CN^-$ was established, we further studied its sensitivity toward $CN^-$. Titration of BODIPY **1** in 98% $CH_3CN$ solution ($1.0 \times 10^{-5}$ M; $CH_3CN$/water 98/2 (v/v)) with $CN^-$ showed a progressive blue shift of the absorption band from 508 to 500 nm (Figure 3a), with two isosbestic points at 468 and 530 nm indicating an interconversion into single discrete chemical species during the titration. The corresponding fluorescence spectral changes of BODIPY **1** on addition of increasing concentration of $CN^-$ are shown in Figure 3b. The gradual decrease of fluorescence and a blue shift of the emission band from 539 to 514 nm were observed. It only required 10 μM of $CN^-$ to quench more than 90% of the fluorescence of BODIPY **1**. The detection limit[17] of BODIPY **1** for $CN^-$ is about $3.0 \times 10^{-6}$ M (Figure S4 in SI).[16]

The sensitive sensing ability of BODIPY **1** toward $CN^-$ was also evident by naked-eye inspection as shown in Figure 4: a color change from green to reddish brown (concentrated) or pink (diluted) solution of BODIPY **1** was observed upon addition of $CN^-$ under ambient light. In contrast to ordinary color changes that cyanide anion induced, the dramatic color change observed here is due to the strong green daylight fluorescence of the BODIPY **1** and a dramatic quenching of this daylight fluorescence upon addition of cyanide anion resulting in the formation

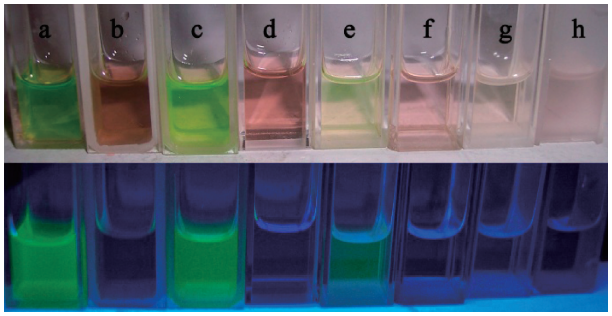



**Figure 4.** Photograph of different concentrations of BODIPY **1** in 98% $CH_3CN$ ($CH_3CN$/water 98/2 (v/v)) solutions in the absence (a, c, e, and g) and presence (b, d, f, and h) of 20 equiv of $CN^-$ under ambient light (top), and a 360 nm hand-held UV light (bottom). Concentrations for BODIPY **1** from left to right: $1 \times 10^{-4}$ (a and b), $5 \times 10^{-5}$ (c and d), $1 \times 10^{-5}$ (e and f), and $5 \times 10^{-6}$ M (g and h).

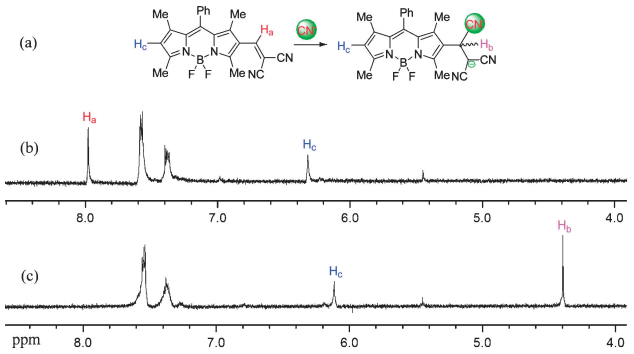



**Figure 5.** The proposed detection mechanism for BODIPY **1** (a) and the $^1$H NMR spectra of BODIPY **1** (4 mM) in the absence (b) and in the presence (c) of cyanide anion (80.0 mM) in $CD_3CN$ at 25 °C. $^1$H NMR spectra of BODIPY **1** was recorded 10 min after the addition of NaCN.

of a reddish-brown nonfluorescent solution. As expected, in 98% $CH_3CN$ solution ($CH_3CN$/water 98/2 (v/v)), quantum yields for BODIPY **1** and the **1**-$CN^-$ complex are calculated to be 0.46 and 0.01, respectively, by using fluorescein as reference (0.95 in 0.1 M NaOH solution). Consistent with the interesting color changes, under 360-nm hand-held UV light excitation, BODIPY **1** showed a strong green fluorescence in the absence of $CN^-$ despite its weak absorption at this wavelength, while a complete shutdown of the fluorescence was observed for **1**-$CN^-$ complex. This naked-eye inspection of $CN^-$ can be performed by using BODIPY **1** at a concentration as low as $5 \times 10^{-6}$ M. Unlike most of the colorimetric sensors that generally rely on a larger shift of the spectra, our naked-eye detection of cyanide anion is based on a "turn-off" daylight-fluorescent molecule to achieve the sensitive and straightforward sensing of cyanide anions, in which a strong daylight-fluorescent molecule and a subsequent dramatic "turn-off" of this daylight fluorescence upon interaction with target anions are required.

The $^1$H NMR spectral changes (Figure 5 and Figure S5 in SI[16]) of BODIPY **1** upon addition of cyanide anion confirmed that it is an irreversible Michael-addition-based response mechanism for cyanide detection as shown in Figure 5a. Upon addition of 20 equiv of cyanide anion to BODIPY **1** in $CD_3CN$

at room temperature, the complete disappearance of vinylic proton ($H_a$) at 7.98 ppm, the appearance of a new peak ($H_b$) at 4.40 ppm, and a slight upfield shift of $\beta$-pyrrolic proton ($H_c$) from 6.32 to 6.11 ppm were observed (Figures 5b and 5c). These observations clearly show that the cyanide anion is added to the vinyl group as expected and leads to the disruption in the extended $\pi$ conjugation of BODIPY **1**. This explains the observed optical spectral changes for the BODIPY **1** solution on contact with cyanide anion. Interestingly, the absence of the signal corresponding to the $\beta$-proton of the malononitrile group in the $^1$H NMR spectrum was observed, which may be attributed to the formation of the stabilized anionic species upon nucleophilic addition of cyanide anion.[4a] The resulting anionic species may be responsible for the dramatic fluorescence quenching through intramolecular photoinduced electron transfer to BODIPY core.[18]

In summary, we have designed a new visible and colorimetric sensor for the selective and sensitive sensing of cyanide ions based on a strong daylight-fluorescent BODIPY dye. The sensing mechanism has been investigated by UV–vis absorption, emission, and NMR spectroscopy. Cyanide anion has been added to the vinyl group of BODIPY **1** to cause the disruption of the extended $\pi$ conjugation and a dramatic quenching of this daylight green fluorescence. The dramatic color change clearly visible to the naked eye may be attributed to the strong green daylight fluorescence of BODIPY **1** and the subsequent formation of a reddish-brown nonfluorescent solution upon addition of cyanide anion because of the dramatic decrease of the fluorescent quantum yield in **1**-$CN^-$ complex.

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