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Turn-On Fluorescence Sensing of Cyanide Ions in Aqueous Solution at Parts-per-Billion Concentrations

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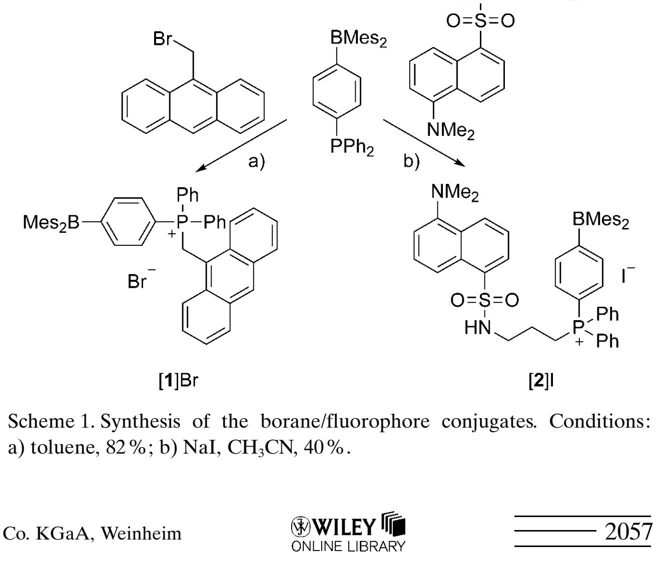
Cyanide is a highly toxic anion[1] that has become a key component of many industrial processes. It is also produced naturally by a number of higher plants, which use it as a protection against predators.[2] Release of this anion in the environment[3] and an increase in the farming and consumption of cyanogenic plants such as cassava[4] have served to spark a renewed interest in methods that can be used to sense the presence of this anion, especially in aqueous media.[5]

One of the current strategies adopted for the design of cyanide sensors is based on the use of electrophilic organic derivatives, which interact with the cyanide anion through formation of a new covalent bond.[6] Although advantageous properties have been discovered, only a limited number of receptors function in water.[6b,c,f,m,7] Some of these receptors necessitate basic pH and high cyanide concentrations. Because of these limitations, strategies that rely on the use of Lewis acidic derivatives have been considered. Such derivatives include zinc–porphyrins,[8] iron–hemes,[9] corrins,[10] and transition-metal complexes[11] that interact with the cyanide anion through formation of a strong coordination bond. This approach, which is typically characterized by elevated binding constants, has been successfully applied to the detection of cyanide at the ppm level. Some of these receptors have also been shown to be compatible with biological matrices, making the detection of cyanide possible directly in plants.[10b]

As demonstrated by a series of recent contributions, three-coordinate boranes possessing an accessible boron center can also be used as sensors for cyanide anions.[12] Whereas neutral boranes can only be used in mostly organic environments, we and others have demonstrated that the incorporation of peripheral cationic groups in such compounds[13] could be used to enhance their cyanide ion affinity.[14] Although the cyanide affinity displayed by some of these boranes is very high, their practical use remains limited by the nature of the photophysical response observed during the recognition event. Indeed, cyanide coordination leads to population of the empty p orbital of boron, thus quenching the absorbance and fluorescence of the triarylboron chromophore. The turn-off rather than turn-on response observed in these complexes is not ideal from an analytical point of view and constitutes one of the major limitations affecting the practical use of cationic boranes as cyanide sensors. In order to overcome this limitation, we have now synthesized *para*-phenylene phosphonium borane/fluorophore conjugates, which behave as highly sensitive fluorescence turn-on sensors for the cyanide anion in aqueous solutions.

Reaction of p-Ph_2P-C_6H_4-$BMes_2$ (Mes = mesityl) with 9-bromomethyl anthracene in toluene, which was heated to reflux, afforded [**1**]Br in 82 % yield (Scheme 1). A similar reaction involving p-Ph_2P-C_6H_4-$BMes_2$ and *N*-(3-bromo-



Scheme 1. Synthesis of the borane/fluorophore conjugates. Conditions: a) toluene, 82 %; b) NaI, CH_3CN, 40 %.

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propyl) dansylamide[15] in acetonitrile afforded [**2**]I in 40% yield (Scheme 1). These phosphonium salts have been fully characterized. The presence of a phosphonium center gives rise to a characteristic ^{31}P NMR resonance detected at $\delta = 19.7$ and 25.2 ppm for [**1**]Br and [**2**]I, respectively. The absorption spectra of these new phopshonium boranes are shown in Figure 1. The low energy part of the absorption spectrum of [**1**]Br in methanol is dominated by anthracene-based absorptions, which can be identified based on the characteristic vibronic progression. The broad absorption band centered at $\lambda = 340$ nm is close to that observed for simple phosphonium boranes such as $[p\text{-}(MePh_2P)C_6H_4\text{-}(BMes_2)]^+$ and can be assigned to the triarylboron chromophore.[16] In the case of [**2**]I, a single broad absorption band bearing contributions from both the triarylboron and dansyl fluorophores is observed at $\lambda_{max} = 335$ nm in methanol. It is important to note the absence of charge-transfer bands in the absorption spectra of these compounds. In turn, excitation of these conjugates does not appear to result in the formation of charge-transfer states.[17]

These two compounds are weakly fluorescent with emission bands centered at $\lambda_{fluo} = 427$ nm for $[\mathbf{1}]^+$ ($\Phi = 1.54\,\%$, $\lambda_{excitation} = 347$ nm, MeOH) and $\lambda_{fluo} = 501$ nm for $[\mathbf{2}]^+$ ($\Phi = 3.78\,\%$, $\lambda_{excitation} = 347$ nm, MeOH) (Figure 2). The emission spectrum of $[\mathbf{1}]^+$ shows a weak emission of the anthryl fluorophore (centered at $\lambda = 427$ nm) complemented by a contribution from the boron-centered chromophore at longer wavelengths. In agreement with this proposal, we note that $[p\text{-}(MePh_2P)C_6H_4\text{-}(BMes_2)]^+$ gives rise to a structure-less emission band at

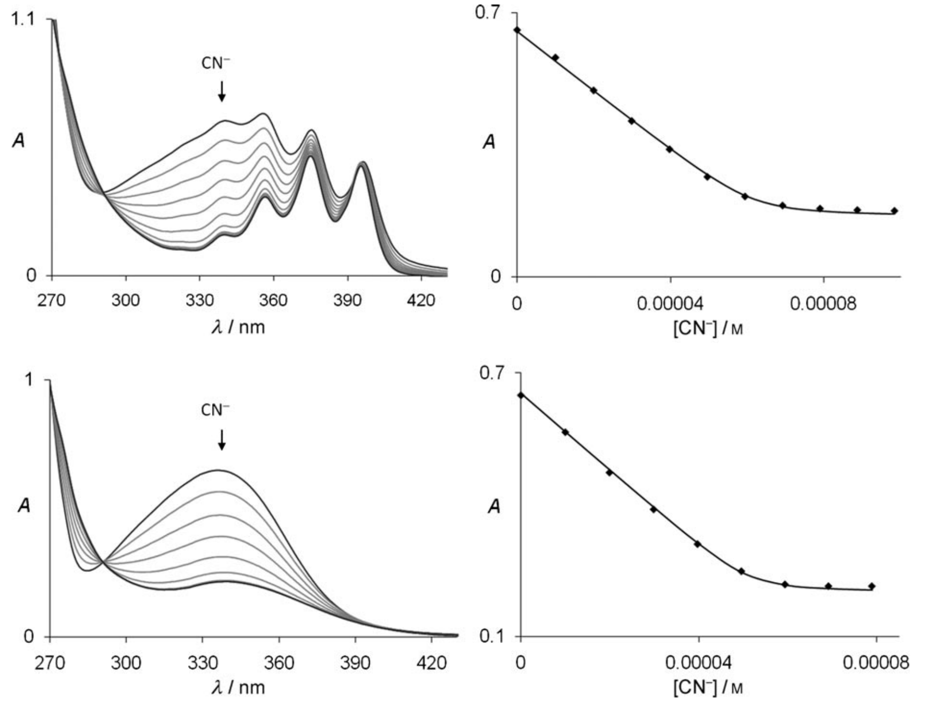

Figure 1. Left) Absorption spectra of $[\mathbf{1}]^+$ (top) and $[\mathbf{2}]^+$ (bottom) in methanol along with changes observed upon formation of [**1**(CN)] and [**2**(CN)], respectively, by addition of cyanide anions. Right) Experimental and calculated 1:1 cyanide binding isotherms for $[\mathbf{1}]^+$ (top) and $[\mathbf{2}]^+$ (bottom). For $[\mathbf{1}]^+$, the data were measured at $\lambda = 340$ nm and fitted with $K = (1.5 \pm 0.5) \times 10^6\,\text{M}^{-1}$ by using $\varepsilon([\mathbf{1}]^+) = 10\,500\,\text{M}^{-1}\text{cm}^{-1}$ and $\varepsilon([\mathbf{1}(\text{CN})]) = 2600\,\text{M}^{-1}\text{cm}^{-1}$. For $[\mathbf{2}]^+$, the data were measured at $\lambda = 335$ nm and fitted with $K = (2.5 \pm 1.0) \times 10^6\,\text{M}^{-1}$ by using $\varepsilon([\mathbf{2}]^+) = 12\,650\,\text{M}^{-1}\text{cm}^{-1}$ and $\varepsilon([\mathbf{2}(\text{CN})]) = 3900\,\text{M}^{-1}\text{cm}^{-1}$.

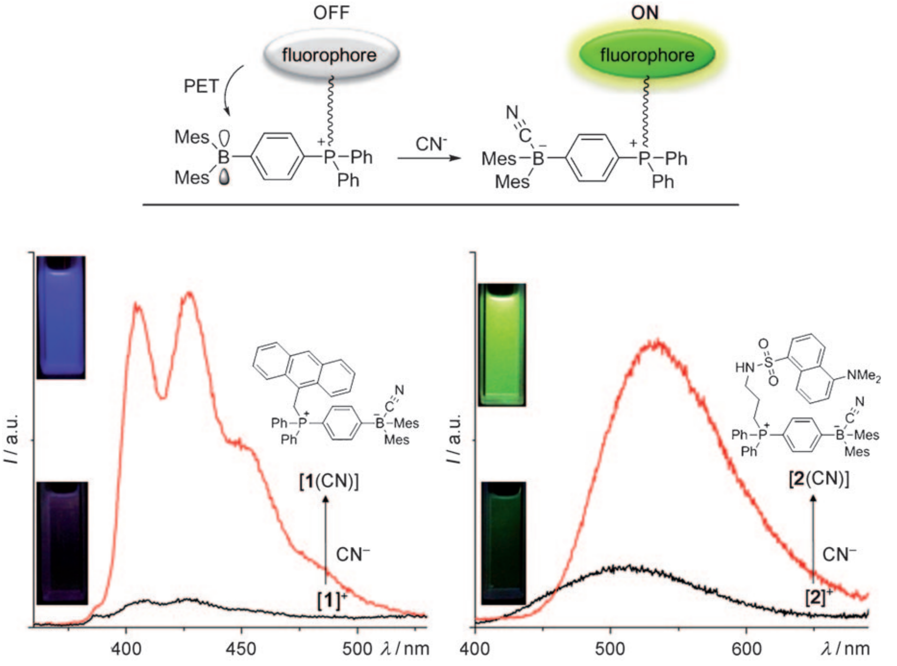

Figure 2. Top) Proposed mechanism of fluorescence quenching and revival in *para*-phenylene phosphonium borane/fluorophore conjugates (PET = photo-induced electron transfer). Bottom) Fluorescence spectrum changes observed upon addition of cyanide ions to $[\mathbf{1}]^+$ (left, 5.96 μM, $\lambda_{excitation} = 347$ nm) and $[\mathbf{2}]^+$ (right, 6.19 μM, $\lambda_{excitation} = 347$ nm) in methanol. The pictures in the inset show the emission observed with the naked eye under a hand-held UV lamp.

$\lambda_{fluo}=476$ nm in methanol (Figure S13 in the Supporting Information). A similar situation can be invoked in the case of $[\mathbf{2}]^+$, whose fluorescence spectrum may be assigned to weak emissions from both the boron-centered and dansyl chromophores. Bearing in mind that the fluorescence quantum yields of the anthracene and dansyl fluorophores are typically elevated, their weak fluorescence in $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ may be assigned to an intramolecular photo-induced electron-transfer process involving the excited fluorophore as the donor and the phosphonium borane as the acceptor (Figure 2). To further test this hypothesis, we decided to monitor the fluorescence intensity of these compounds upon cyanide coordination. Cyanide binding to $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ should result in a neutralization of the electron accepting properties of the phosphonium borane moiety, thereby inhibiting electron transfer from the pendant fluorophore to the cationic borane. In line with these expectations, addition of cyanide to $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ in methanol results in a notable increase of the fluorescence intensity of the pendant fluorophores, a phenomenon assigned to the formation of [**1**(CN)] and [**2**(CN)], respectively (Figure 2). This increase can be quantified by a comparison of the quantum yields of the phosphonium borane conjugates ($\phi=1.54$ and 3.78% for $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$, respectively) and that of their cyanide adducts ($\phi=41.3$ and 44.2% for [**1**(CN)] and [**2**(CN)], respectively) in methanol.

These observations, as well as the absence of charge-transfer bands in the absorption spectrum of these conjugates, suggest that fluorescence quenching of the pendant fluorophore of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ occurs through intramolecular photo-induced electron transfer from the excited state of the fluorophore to the electron-deficient phosphonium borane.[18] In support of this electron-transfer argument, we note that application of the simplified Rehm–Weller equation[19] to donor–acceptor systems consisting of anthracene or *N*-butyldansylamide as donors and $[p\text{-}(MePh_2P)C_6H_4(BMes_2)]^+$ as the acceptor, affords negative Gibbs energies of photo-induced electron-transfer ($\Delta G^{\circ}_{eT}=-55.0$ and -59.8 kJ mol^{-1} for anthracene and *N*-butyl dansylamide, respectively (see the Supporting Information for calculation details).[20] In turn, the proposed mechanism of fluorescence quenching in $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ differs from the charge-transfer mechanism first uncovered by Wang and co-workers for a series of bifunctional triarylamine/triarylborane derivatives.[21]

To confirm the formation of [**1**(CN)] and [**2**(CN)], these two compounds have been isolated and characterized. Both derivatives precipitate spontaneously upon addition of KCN to a methanol solution of the corresponding phosphonium boranes. These zwitterionic cyanoborates are soluble in $CDCl_3$. Their spectroscopic features ($\delta(^{11}B)=-13.5$ and -12.5 ppm for [**1**(CN)] and [**2**(CN)], respectively; $\tilde{\nu}(CN^-)=$ 2163.2 and 2166.8 cm^{-1} for [**1**(CN)] and [**2**(CN)], respectively) confirm the presence of a cyanoborate functionality and are comparable to those of $p\text{-}(Me_3N)C_6H_4(B(CN)Mes_2)$.[14a] Addition of $B(C_6F_5)_3$ to $CDCl_3$ solutions of [**1**(CN)] and [**2**(CN)] leads to regeneration of the free cationic boranes $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$, thus indicating that cyanide binding is reversible. The crystal structure of [**2**(CN)] has also been determined (Figure 3). This compound crystallizes in the *P*1 space group with two independent molecules in the asymmetric unit (Figure 3).[20] The structures of these two molecules slightly differ by the respective orientation of the dansyl and the zwitterionic phosphonium/cyanoborate moieties. Further examination of the structure shows coordination of the cyanide anion to the boron center through an average B−C bond of 1.617 Å. This coordination bond is comparable to those found in other triarylcyanoborate species such as $p\text{-}(Me_3N)C_6H_4(B(CN)Mes_2)$ (1.618(8) Å).[14a] The average of sum of the C_{aryl}-B-C_{aryl} angles (Σ(C-B-C) = 338.6°) indicates that cyanide binding induces a substantial pyramidalization of the boron atom similar to that observed in $p\text{-}(Me_3N)C_6H_4(B(CN)Mes_2)$ (Σ(C-B-C) = 337.5°).[14a]

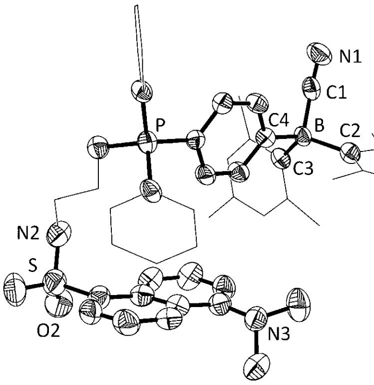

Figure 3. Crystal structure of [**2**(CN)] (only one independent molecule is shown, 40% ellipsoid, hydrogen atoms are omitted for clarity, phenyl and mesityl substituents represented as thin lines); selected bond lengths [Å] and angles [°] (the metrical parameters of the second independent molecule are given in brackets): B−C1 1.595(8) [1.638(9)], B−C2 1.677(8) [1.640(8)], B1−C3 1.667(7) [1.639(9)], B−C4 1.671(7) [1.650(8)]; C1-B-C3 112.2(5) [113.0(4)], C1-B-C2 100.9(5) [101.5(4)], C3-B-C2 116.5(5) [118.1(4)], C1-B-C4 102.7(5) [105.0(4)], C3-B-C4 105.3(5) [103.3(4)], C2-B-C4 118.4(5) [115.5(4)].

Having observed that both $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ can readily be converted into their corresponding cyanide adduct, we decided to determine their cyanide binding constants in a protic solvent such as methanol. To this end, UV/Vis titration experiments were carried out by the addition of increasing amounts of cyanide to a solution of the cationic boranes (Figure 1). Binding of the cyanide to the boron center of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ resulted in a quenching of the absorption band of the triarylboron chromophore leading to a net decrease of the absorbance in the $\lambda=300$–370 nm range. The resulting data was fitted to a 1:1 binding isotherm indicating that the binding constants of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ are at least equal to $10^6\,\text{M}^{-1}$. A complete quenching of the band was not observed because both the anthryl and dansyl fluorophore absorb in the $\lambda=300$–400 nm range. We have previously reported that phopshonium boranes such as $[p\text{-}(MePh_2P)C_6H_4(BMes_2)]^+$ complex fluoride anions in protic media.[16] For this reason, it became important to study the fluoride affinity of **[1]**$^+$ and **[2]**$^+$. Fluoride titration experiments carried out in methanol show that fluoride binding occurs with both **[1]**$^+$ and **[2]**$^+$. The resulting binding constants are, however, very low ($K(\mathrm{F^-}) = (340 \pm 40)\,\mathrm{M^{-1}}$ for **[1]**$^+$ and $K(\mathrm{F^-}) = (500 \pm 50)\,\mathrm{M^{-1}}$ for **[2]**$^+$), thus indicating that **[1]**$^+$ and **[2]**$^+$ are in fact highly selective for cyanide over fluoride anions (Figures S9 and S10 in the Supporting Information). Cations **[1]**$^+$ and **[2]**$^+$ show no detectable affinity for other anions including $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{NO_3^-}$, $\mathrm{H_2PO_4^-}$, $\mathrm{SO_4^{2-}}$, and $\mathrm{CH_3CO_2^-}$, thus pointing to the selectivity of these receptors (Figure S11 in the Supporting Information).

Encouraged by the elevated cyanide binding constants displayed by **[1]**$^+$ and **[2]**$^+$, we decided to test if these cationic boranes could be used in aqueous solutions. Whereas **[1]**$^+$ was found to irreversibly decompose in $\mathrm{H_2O}$/MeOH (6:4, v/v), the fluorescence spectrum of a solution of **[2]**$^+$ at pH 7 in $\mathrm{H_2O}$/MeOH (6:4, v/v) remained unchanged for over an hour. Further information into the stability of **[2]**$^+$ was obtained by monitoring its UV/Vis spectrum as a function of pH. At pH 5.6, the characteristic absorption band of **[2]**$^+$ at $\lambda = 333$ nm is readily observed, indicating that the boron center remains trigonal planar. At pH 6.8, an initial decrease of the band is observed signaling the onset of hydroxide binding (Figure S8 in the Supporting Information). This phenomenon is quickly followed by the formation of a precipitate assigned to the hydroxide adduct. Such adducts are not unprecedented and have been previously obtained with other phosphonium boranes such as $[p\text{-}(\mathrm{MePh_2P})\mathrm{C_6H_4}\text{-}(\mathrm{BMes_2})]^+$.[16b] In agreement with the formation and precipitation of the hydroxide adduct, we found that re-acidification of the solution leads to a 98 % revival of the absorption band of **[2]**$^+$ at $\lambda = 333$ nm. These observations indicate that the $\mathrm{p}K_{\mathrm{R+}}$ of **[2]**$^+$ (i.e., the pH at which 50 % of **[2]**$^+$ is converted into [**2**(OH)]) is in the range of 7–8 . This range is distinctly lower than that measured for $[p\text{-}(\mathrm{MePh_2P})\mathrm{C_6H_4}\text{-}(\mathrm{BMes_2})]^+$ ($\mathrm{p}K_{\mathrm{R+}} = 9.0$) under the same conditions. This observation suggests that **[2]**$^+$ is more Lewis acidic than **[1]**$^+$, possibly because of its greater hydrophobic character.[16b]

Cyanide binding by **[2]**$^+$ also occurs at pH 7 in $\mathrm{H_2O}$/MeOH (6:4, v/v) as indicated by a decrease of the absorbance at $\lambda = 333$ nm upon addition of cyanide ions. Binding is extremely rapid and results in the precipitation of [**2**(CN)], which is observed after addition of only 0.1 equivalent of cyanide when a 51 μM solution of **[2]**$^+$ is employed. This rapid precipitation, which attests to the affinity of **[2]**$^+$ for cyanide in aqueous solutions, also indicates that the cyanide binding constant of **[2]**$^+$ cannot be determined. The apparent high cyanide affinity displayed by **[2]**$^+$ prompted us to investigate even more dilute solutions. Gratifyingly, cyanide anion binding was also observed when a 5.1 μM solution of **[2]**$^+$ ($\mathrm{H_2O}$/MeOH (6:4, v/v), pH 7) was employed as indicated by the fluorescence turn-on response observed upon addition of cyanide. This turn-on response is reproducible even at very low cyanide concentrations. For example, **[2]**$^+$ can be used to detect cyanide concentrations as low as 1 μM or 26 ppb; it is thus one of the most sensitive cyanide sensors known to date (Figure 4).[6f,i,j,9,10,11b–e,12a] It is important to note that the cyanide concentration threshold of 1 μM (26 ppb) at which **[2]**$^+$ becomes competent is well below the drinking water maximum allowable concentrations recommended in the European Union (50 ppb) or in the USA (200 ppb).[22] Determination of the binding constant under these conditions is complicated by the slow kinetics associated with dilution. Nonetheless, the sensing assay is highly reproducible and can be used to reliably detect cyanide at ppb concentrations. In addition to being very sensitive for cyanide, **[2]**$^+$ is also very selective. At these low concentrations, **[2]**$^+$ shows essentially no response to the presence of other anions such as $\mathrm{F^-}$, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{NO_3^-}$, $\mathrm{H_2PO_4^-}$, $\mathrm{SO_4^{2-}}$, and $\mathrm{CH_3CO_2^-}$. For example, the addition of ten equivalents of these anions to a 4.28 μM solution of **[2]**$^+$ causes no apparent changes in the fluorescence spectrum (Figure S12 in the Supporting Information). However, more than a 9-fold fluorescence enhancement was observed upon cyanide addition. This response can even be detected with the naked eye for concentrations of cyanide as low as approximately 50 ppb as shown by the appearance of the characteristic green fluorescence of the dansyl fluorophore after addition of cyanide (Figure 4).

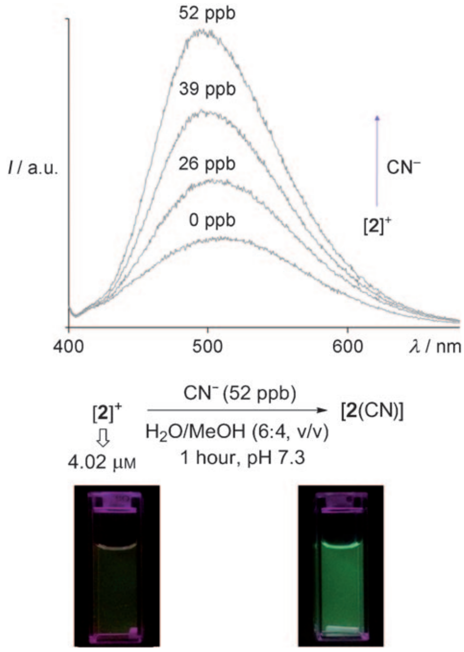

Figure 4. Top) Changes in the fluorescence spectrum of a solution of **[2]**$^+$ (5.1 μM) in $\mathrm{H_2O}$/MeOH (6:4, v/v) upon addition of $\mathrm{CN^-}$ at pH 7 (6 mM HEPES buffer). Bottom) Visible fluorescence turn-on response observed for **[2]**$^+$ (4.02 μM) in the presence of 52 ppb of $\mathrm{CN^-}$ at pH 7.3.

In conclusion, we have demonstrated that cyanide binding to the boron center of the phosphonium boranes **[1]**$^+$ and **[2]**$^+$ results in a turn-on response of the fluorescence of the anthryl and dansyl fluorophores, respectively. This increase can be explained by considering: 1) that the fluorophores of **[1]**$^+$ and **[2]**$^+$ are quenched by intramolecular photo-induced electron transfer from the fluorophore to the electron-deficient phosphonium borane unit and 2) that cyanide coordination to the boron center neutralizes the electron accepting properties of the phosphonium borane unit leading to a revival of the fluorescence of the pendant fluorophore. The success of this approach is illustrated by the use of [**2**]$^+$ for the naked-eye detection of cyanide ions at 50 ppb concentrations in aqueous solutions.

Experimental Section

General considerations: Dimesitylboron fluoride and potassium cyanide were purchased from Aldrich, dansyl chloride from TCI. Solvents were dried by passing through an alumina column (toluene, acetonitrile), heating to reflux under N_2 over Na/K (Et_2O and THF). UV/Vis spectra were recorded on an Ocean Optics USB4000 spectrometer with an Ocean Optics ISS light source. IR spectra were obtained by using an ATI Mattson Genesis Series FT infrared spectrophotometer. Fluorescence measurements were carried out by using a PTI, QuantaMaster spectrofluorometer. Elemental analyses were performed by Atlantic Microlab (Norcross, GA). The pH measurements were carried out with a Radiometer PHM290 pH meter equipped with a VWR SympHony electrode. NMR spectra were recorded on Varian Inova 300 FT NMR (299.96 MHz for ^{1}H, 121.43 MHz for ^{31}P) and Varian Unity Inova 400 FT NMR (399.59 MHz for ^{1}H, 375.99 MHz for ^{19}F, 128.19 MHz for ^{11}B, 161.75 MHz for ^{31}P, 100.45 MHz for ^{13}C) spectrometers at ambient temperature unless otherwise stated. Chemical shifts are given in ppm, and are referenced against external $BF_3{\cdot}Et_2O$ (^{11}B), and 85% H_3PO_4 (^{31}P). Additional experimental and synthetic details can be found in the Supporting Information.[20]

Synthesis of [2]I: A mixture of *N*-(3-bromopropyl)-5-(dimethylamino)-1-naphthalenesulfonamide (0.55 g, 1.48 mmol), sodium iodide (0.54 g, 3.6 mmol), and *p*-Ph_2P-C_6H_4-$BMes_2$ (0.61 g, 1.2 mmol) in acetonitrile (10 mL) was heated to reflux overnight. After cooling to room temperature, the solvent was removed in vacuo to afford a residue which was treated with CH_2Cl_2 (20 mL). The resulting mixture was filtered to afford a CH_2Cl_2 solution which was concentrated in vacuo to a final volume of about 5 mL. This concentrate was purified by flash chromatography over silica gel by using first, ethyl acetate (20 mL) and then methanol (20 mL). The solvents were removed in vacuo and the residue was extracted with CH_2Cl_2 (20 mL) and water (10 mL). The organic layer was separated, dried over $MgSO_4$, filtered and concentrated in vacuo. Further purification was achieved by washing the solid with Et_2O to afford [**2**]I as a yellow solid (0.45 mg, 40%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.90$ (br s, 2H; $CH_2CH_2CH_2$), 1.97 (s, 12H; Mes-CH_3), 2.30 (s, 6H; Mes-CH_3), 2.84 (s, 6H; $N(CH_3)_2$), 3.33 (m, 2H; $NHCH_2CH_2$), 3.83 (m, 2H; CH_2CH_2P), 6.83 (s, 4H; Mes-C*H*), 7.15 (d, $J = 7.5$ Hz, 1H; dansyl-C*H*), 7.43 (t, $J = 8.0$ Hz, 1H; dansyl-C*H*), 7.59–7.83 (m, 15H; Ph/phenylene/dansyl-C*H*), 8.14 (d, $J = 6.6$ Hz, 1H; dansyl-C*H*), 8.40–8.48 ppm (m, 2H; dansyl-C*H*), N*H* not detected; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.68$ (d, $J_{C,P} = 52.4$ Hz), 21.39, 23.70, 23.88, 42.12 (d, $J_{C,P} = 17.5$ Hz), 45.53 (N-CH_3), 115.52, 117.90 (d, $J_{C,P} = 85.8$ Hz), 119.68, 120.45 (d, $J_{C,P} = 84.3$ Hz), 123.10, 128.71, 128.77, 128.96, 129.56, 129.94, 130.24, 130.72 (d, $J_{C,P} = 12.1$ Hz), 132.77 (d, $J_{C,P} = 9.1$ Hz), 133.67 (d, $J_{C,P} = 9.9$ Hz), 135.18, 135.32, 136.62 (d, $J_{C,P} = 12.1$ Hz), 140.10, 140.87, 140.99, 151.71, 153.63 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = +25.20$ ppm; a ^{11}B NMR signal could not be observed despite extended acquisition times; MS (ESI): *m*/*z*: calcd for $C_{51}H_{55}BN_2O_2PS^+$ $[M-I^-]^+$: 801.38; found 801.3569; elemental analysis calcd (%) for $C_{51.45}H_{55.9}BCl_{0.9}IN_2O_2PS$ ([**2**]I·0.45 CH_2Cl_2): C 63.91, H 5.83; found: C 63.88, H 5.80 (^{1}H NMR spectrum shows CH_2Cl_2 residue).

Synthesis of [2(CN)]: [**2**]I (50 mg, 0.054 mmol) was dissolved in methanol (5 mL) and treated with a solution of KCN (33 mg, 0.51 mmol) in methanol (2 mL), which resulted in the formation of a solid. After 30 min, the solid was isolated by filtration, washed with methanol, and dried in vacuo to afford [**2**(CN)] as a pale yellow powder (23 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.56$ (br s, 2H; $CH_2CH_2CH_2$), 1.82 (s, 12H; Mes-CH_3), 2.04 (s, 6H; Mes-CH_3), 2.70 (m, 2H; CH_2CH_2P), 2.77 (m, 2H; $NHCH_2CH_2$), 2.83 (s, 6H; $N(CH_3)_2$), 6.48 (s, 4H; Mes-C*H*), 6.72 (br, 1H; N*H*), 7.11 (d, $J = 7.2$ Hz, 1H; dansyl-C*H*), 7.39–7.60 (m, 13H; Ph/dansyl-C*H*), 7.71–7.74 (m, 2H; phenylene-C*H*), 8.08 (d, $J = 7.6$ Hz, 1H; phenylene/dansyl-C*H*), 8.31 (d, $J = 8.4$ Hz, 1H; phenylene/dansyl-C*H*), 8.45 (d, $J = 8.4$ Hz, 1H; phenylene/dansyl-C*H*), 8.50 ppm (m, 1H; phenylene/dansyl-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.40$ (d, $J_{C,P} = 54.7$ Hz), 20.81, 23.92, 25.67, 42.10 (d, $J_{C,P} = 16.7$ Hz), 45.51, 109.89 (d, $J_{C,P} = 88.9$ Hz), 115.53, 118.64, 119.07 (d, $J_{C,P} = 85.5$ Hz), 119.30, 123.07, 128.72 (d, $J_{C,P} = 12.9$ Hz), 128.92, 129.57, 129.92, 130.20, 130.30 (d, $J_{C,P} = 12.2$ Hz), 131.12, 132.85, 133.54 (d, $J_{C,P} = 9.8$ Hz), 134.77, 135.31, 137.89 (m), 141.86, 145.98, 149.14, 151.76, 170.82 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): $\delta = -12.45$ ppm; ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 23.90$ ppm; IR (film on KBr plate): $\tilde{\nu} = 2166.8\ \mathrm{cm}^{-1}$ (CN^-); elemental analysis calcd (%) for $C_{53.2}H_{59.8}BN_3O_{3.2}PS$ ([**2**(CN)]·1.2 CH_3OH): C 73.76, H 6.96; found: C 73.28, H 6.76 (^{1}H NMR spectrum shows the presence of residual methanol).

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[20] Further experimental and computational details are presented in the Supporting Information. CCDC-792208 ([**2**(CN)]) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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