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Detection of Biologically Important Anions in Aqueous Media by Dicationic Azaborines Bearing Ammonio or Phosphonio Groups

Tomohiro Agou, Masaki Sekine, Junji Kobayashi, and Takayuki Kawashima*[a]

Abstract: New cationic triarylboranes bearing ammonio or phosphonio groups on the periphery were synthesized from a common intermediate, a dibromodibenzoazaborine. These cationic molecules are soluble in highly polar organic solvents as well as water, and they exhibit strong light absorption and photoluminescence emission in water. Complexation of the cationic azaborines with fluoride and cyanide ions in aqueous media proceeded and could be monitored by NMR, UV/Vis, and fluorescence spectroscopy.

Keywords: analytical methods • azaborines • cyanides • fluorides • main group elements • sensors

Introduction

The detection and capture of anions by using organic molecules (molecular sensors) have been investigated extensively, and host molecules have been synthesized that utilize various host–guest interactions.[1] Among guest anions, the sensing of fluoride and cyanide ions in aqueous media has attracted a great deal of attention because of their biological, environmental, and industrial importance.[2,3] Although highly effective molecular sensors for fluoride or cyanide ions have been reported,[1,4,5] aqueous media, which are common in biological systems, often collapse their sensing functions. Because these anions are relatively small and are strongly solvated in protic solvents (water or alcohol), interaction between these anions and anion sensors is hampered.[6] Therefore, much more powerful host–guest interactions are required to develop anion sensors that work in aqueous media.[7]

Tricoordinate organoboron compounds are well known as strong and hard Lewis acids because of vacant 2p orbitals on the boron atoms, and they can capture Lewis bases and hold them quite tightly in the form of Lewis acid–base complexes. This interaction is highly selective to small and hard guests, such as fluoride, cyanide, and hydroxide. Furthermore, complex formation changes the molecular structure of the boron compounds from tricoordinate planar to tetrahedral, which is accompanied by a switch in their electronic and optical properties. These two important features of tricoordinate organoboron compounds make them desirable motifs for optical anion sensors. In fact, the sensing ability of triarylborane-based conjugated molecules has been investigated extensively, and it was revealed by NMR, UV/Vis, and fluorescence spectroscopy that they can detect anions (mostly fluoride ion) very effectively in organic solvents.[8] However, almost all triarylborane-based sensors work only in aprotic organic solvents (THF, CH_2Cl_2, chloroform, etc), and the addition of protic solvents (alcohol or water) prevents the formation of Lewis acid–base complexes through the insufficient Lewis acidity of the hosts compared with the strength of hydrogen bonds between the target anions and solvents.

Very recently, a few triarylborane-based anion sensors useable in aqueous solvent systems were developed. In these compounds, the introduction of cationic functional groups to the host framework greatly improved both the Lewis acidity and the water solubility, and they can form stable complexes with fluoride or cyanide ion under biphasic conditions or in aqueous solutions (dimethyl sulfoxide (DMSO)/H_2O, MeOH/H_2O, or THF/H_2O).[9] On the basis of this strategy, we have developed a cationic triarylborane, phosphonioborin, which contains a combination of a cationic functional group and a triarylborane. The phosphonioborin exhibits quite strong complexation ability against fluoride, chloride, and even bromide ions, unlike ordinary tricoordinate boron compounds.[10] Furthermore, the phosphonioborin-

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[a] Dr. T. Agou, M. Sekine, Dr. J. Kobayashi, Prof. Dr. T. Kawashima
Department of Chemistry, Graduate School of Science
The University of Tokyo
7–3–1 Hongo, Bunkyo-ku, Tokyo 113–0033 (Japan)
Fax: (+81) 5800-6899
E-mail: takayuki@chem.s.u-tokyo.ac.jp

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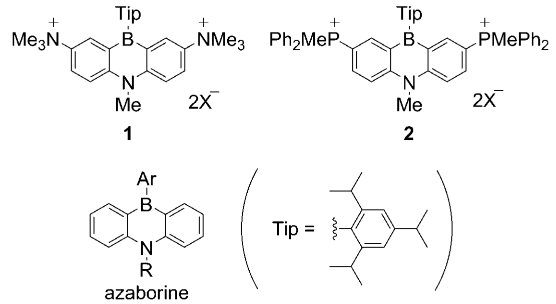
in molecule captured fluoride ions under biphasic conditions and transported them from the aqueous phase to the organic phase efficiently.[11] However, one drawback of this compound is its poor optical properties (weak light absorption and no fluorescence emission), and thus it cannot be applied to optical sensors.

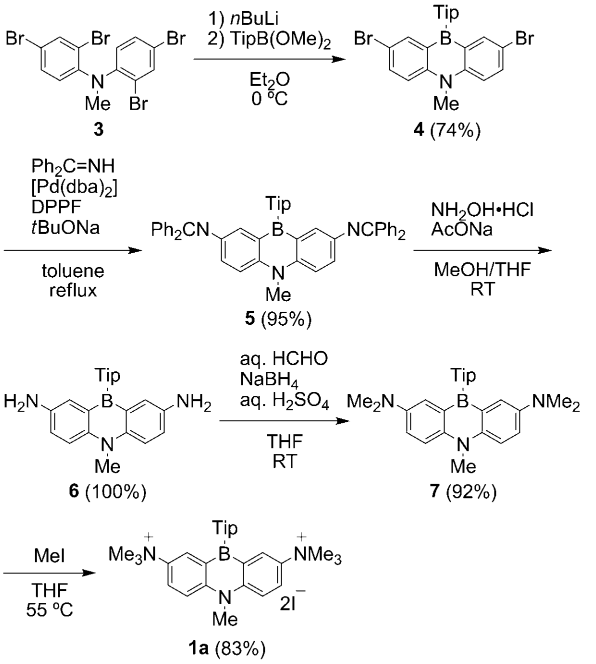
We have also reported the synthesis and optical properties of dibenzoazaborine, a nitrogen analogue of the phosphaborin. Unlike the phosphaborin and its derivatives, the azaborine displays good optical properties, namely strong light absorption as well as intense fluorescence emission in the visible region.[12] On the other hand, a preliminary study on the Lewis acidity of the azaborine indicated that the azaborine itself cannot complex anions. This disadvantage, however, can be solved by the introduction of cationic functional groups that enhance the Lewis acidity and water solubility. Such functionalized azaborines can be easily obtained by taking advantage of a modular synthetic protocol for making periphery-fuctionalized azaborines that we have reported recently.[12c]



Herein we report the syntheses of two dicationic azaborines **1** and **2** bearing ammonio or phosphonio groups at their periphery. These compounds were derived from a common synthetic intermediate, a dibromoazaborine. They retain the optical properties of the azaborine motif not only in organic solvents but also in water and do not aggregate in aqueous media, indicating that the dicationic azaborine can be used for anion sensors in aqueous solvents. The ability of these azaborines to form complexes with biologically important anions, such as fluoride, cyanide, and azide ions, was investigated by NMR and optical spectroscopy, and the phosphonio-functionalized azaborine complexed relatively strongly with fluoride and cyanide ions in aqueous media. Furthermore, the complex formation reaction could be monitored by optical spectroscopy, and thus it could be utilized as an optical sensor of anions in aqueous media.

Results and Discussion

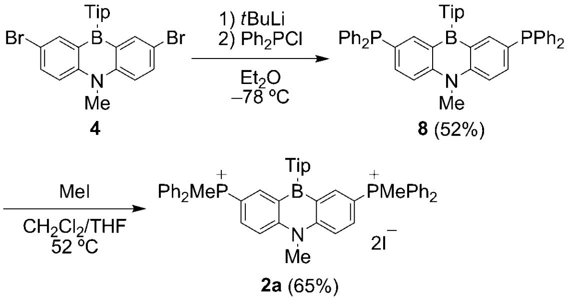
Syntheses of dicationic azaborines: The synthesis of ammonio-fuctionalized dicationic azaborine diiodide **1a** is shown in Scheme 1. Palladium-catalyzed coupling of dibromoazaborine **4**, prepared from tetrabromide **3** by an *ortho*-selective bromine–lithium exchange reaction,[13] with benzophenone imine, a synthetic equivalent of ammonia, gave bis(diphenylimino)azaborine **5** in a good yield.[14] The diphenylmethylene groups of **5** were removed by an imine metathesis reaction with NH_2OH to give diaminoazaborine **6** quantitatively. Because **6** was slightly sensitive to air oxidation, it was subjected to the next step without further purification. First, a direct hexamethylation reaction by using a large excess of MeI under basic conditions was tried, but a complex mixture was obtained. *N*-alkylated azaborines, intermediates in this reaction, seemed to be unstable under basic conditions and decomposed. Alternatively, stepwise alkylation was successful. Reductive methylation with aqueous HCHO and $NaBH_4$ in the presence of H_2SO_4 gave bis(dimethylamino)azaborine **7** in a good yield, and the quarternization of the dimethylamino groups by MeI produced **1a**. Compound **1a** was only sparingly soluble in organic solvents, such as chloroform and THF, but it dissolved in DMSO, MeOH, and water. Although the solubility of **1a** in water is not particularly high (0.83 mg per 1 mL H_2O), the measurement of ^{1}H NMR spectra in D_2O could be carried out. Sharp signals were observed in the ^{1}H NMR spectrum, and, in addition, the spectral shape did not change at all upon changing the concentration, indicating that **1a** does not form aggregates or micelles in water. Compound **1a** does not have a large dipole moment and thus intermolecular interactions seem to be very weak.



Scheme 1. Synthesis of bis(trimethylammonio)azaborine diiodide **1a**. DPPF = 1,1′-bis(diphenylphosphanyl)ferrocene.

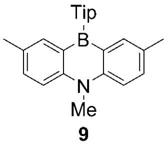
The dicationic azaborine bearing phosphonio groups was also synthesized from dibromoazaborine **4** by a bromine–lithium exchange and the subsequent reaction with Ph_2PCl

as a key step (Scheme 2). The resulting bis(diphenylphosphanyl)azaborine **8** was air stable in the solid state, but it slowly reacted with atmospheric oxygen to give the corresponding monooxide. Treatment of **8** with excess MeI produced the dicationic azaborine diiodide **2a**. Like **1a**, **2a** is only sparingly soluble in hydrophobic organic solvents, but it dissolves easily in DMSO and MeOH. Furthermore, **2a** dissolves in water although the solubility is lower than that of **1a** (0.10 mg per 1 mL H_2O), probably because the bulky methyldiphenylphosphonio groups increase its hydrophobicity.



Scheme 2. Synthesis of bis(methyldiphenylphosphonio)azaborine diiodide **2a**.

Optical properties of dicationic azaborines: UV/Vis and fluorescence spectra of dicationic azaborines **1a** and **2a** were measured in CH_2Cl_2. For comparison, the optical spectra of azaborine **9** were also recorded under the same conditions. These spectra are shown in Figure 1, and the spectral data are summarized in Table 1. The longest absorption maxima of **1a** and **2a** were blue-shifted compared with that of **9**, indicating an increase in the energy gaps between π and π* orbitals on the azaborine rings. To determine its origin, theoretical calculations on model azaborines **1′**, **2′**, and **9′** were performed by using the Gaussian03 program package (Scheme 3 and Table 2).[15]



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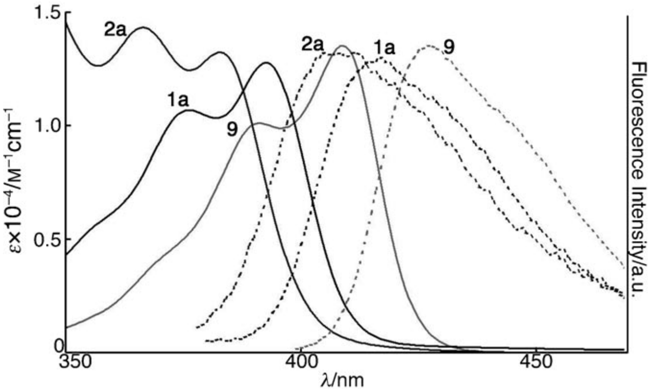
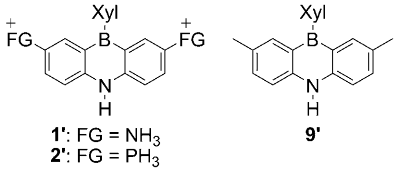


Figure 1. UV/Vis and fluorescence spectra of azaborines **1a**, **2a**, and **9** in CH_2Cl_2 at 298 K (UV/Vis absorption spectra (——), fluorescence spectra (-----)).

Table 1. Optical properties of azaborines **1a**, **2a**, and **9**.

	λ_{max} [nm] (log ε)[a]	λ_{em} [nm] (Φ)[a,c]	λ_{max} [nm] (log ε)[b]	λ_{em} [nm] (Φ)[b,c]
1a	395 (3.90)	420 (0.71)	393 (4.09)	418 (0.10)
2a	383 (3.90)	409 (0.48)	383 (4.12)	407 (0.073)
9	–	–	409 (4.13)	427 (0.64)

[a] In water at 298 K. [b] In CH_2Cl_2 at 298 K. [c] 9,10-Diphenylanthracene in cyclohexane (Φ 1.00) was used as a standard.



Scheme 3. Model azaborines for theoretical calculations. Xyl = 2,6-$Me_2C_6H_3$.

Table 2. Results of theoretical calculations on the model azaborines.

	π Orbital of azaborine [eV]	π* Orbital of azaborine [eV]	ΔE(π–π*) [eV]
1′	−12.1	−7.86	4.2
2′	−12.2	−7.96	4.2
9′	−5.51	−1.67	3.8

From the calculations, the highest-occupied molecular orbital (HOMO) and HOMO−1 orbitals of **1′** and **2′** were shown to be completely localized on Xyl groups and not related to the longest absorption maxima. As a result, we focus on the HOMO−2 orbitals of **1′** and **2′** that are attributed to π orbitals of the azaborine. On the other hand, the lowest-unoccupied molecular orbitals (LUMOs) of **1′** and **2′** were identified as π* orbitals of azaborine, as was seen in **9′**. The π orbitals of the azaborines are mainly constructed from the nitrogen lone pair, and thus, the cationic functionalities at *para* positions to the nitrogen atoms strongly withdraw the electron density from the nitrogen and decrease the energy level of the lone pair, resulting in the decrease in the energy level of the π orbitals and the increase of the π–π* energy gaps. Furthermore, when the absorption wavelengths of the two dicationic azaborines are compared, **2a** showed the more blue-shifted absorption maximum. This is probably due to the stronger electron-withdrawing ability of the phosphonio group.

In CH_2Cl_2, dicationic azaborines **1a** and **2a** emitted photoluminescence with a small Stokes shift (1.5×10^3 cm^{-1}), like the parent azaborine **9**, although the photoluminescence quantum yields were substantially decreased.[16] The emission maxima of **1a**, **2a**, and **9** shifted in accordance with the shift of absorption maxima. These spectral data indicate that the introduction of the cationic functional groups just shifts the energy levels of the molecular orbitals, but does not fundamentally change the nature of the excited states.

UV/Vis absorption and fluorescence spectra of the dicationic azaborines in water are shown in Figure 2. The UV/Vis absorption profiles of the dicationic azaborines in water were almost identical with those in CH_2Cl_2. The absorption maxima were almost the same in both solvents in spite of the substantial difference in the polarity of CH_2Cl_2 (ε: 0.893) and water (ε: 80.2).[17] Therefore, the change of polarity upon photoexcitation should be relatively small in the azaborine systems, despite that the photoexcitation of azaborine systems corresponds to intramolecular charge transfer from nitrogen to boron atoms.[18] Judging from the optical data in water and CH_2Cl_2, the dicationic azaborines can be used in various solvent systems without significant change in the absorption, which is important with respect to their application for colorimetric sensing. Additionally, the UV/Vis absorption profile of **2a** did not show a concentration dependence in water in the range 10^{-4} to 10^{-6} M, which rules out the possibility of aggregate formation.

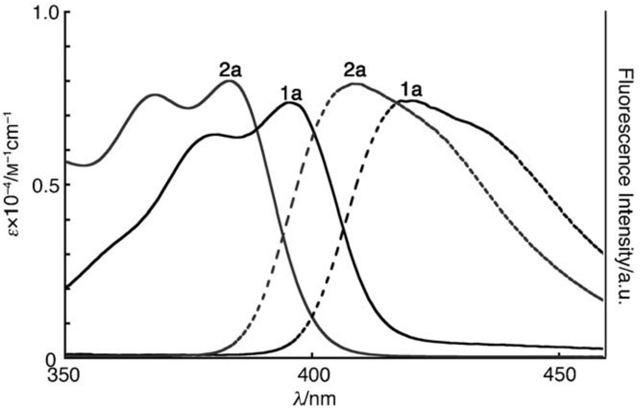
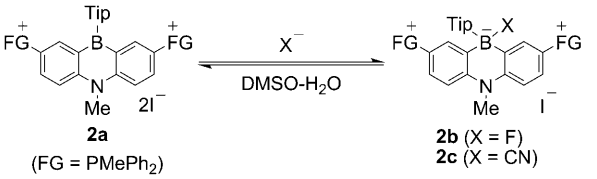


Figure 2. UV/Vis (——) and fluorescence (-----) spectra of dicationic azaborines **1a** and **2a** in water at 298 K.

The dicationic azaborines exhibited strong and sharp photoluminescence in water, unlike the relatively weak photoluminescence emission in CH_2Cl_2. Although highly polar solvents often quench the luminescence through excited-state energy transfer, the fluorescence quantum yields of **1a** and **2a** in water greatly increased compared with those in CH_2Cl_2 (Table 1). As the polarity of the photoexcited states of the azaborines is thought to be very low (see above), the interaction between solvent molecules and the excited azaborines may be weak and thus the quenching of the excited states can be suppressed. Furthermore, linearity of luminescence strength was retained ($<10^{-5}$ M), indicating that intermolecular interactions are negligible at the excited state as in the ground state. From these observations, the dicationic azaborines could be utilized for fluorometric detection in aqueous media as well for colorimetric sensing.

Complex formation of dicationic azaborines with anions: The complexation of various anions by the dicationic azaborines was investigated by UV/Vis absorption and fluorescence spectroscopy. The complexation ability of **1a** was too weak, and no change was observed under the conditions of optical spectroscopy.[19] On the other hand, **2a** showed the absorption change in aqueous media upon adding a fluoride or cyanide ion by formation of Lewis acid–base complexes **2b** or **2c** (Scheme 4).[20] In the DMSO/H_2O mixture (4:6 v/v) buffered by 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES; 0.5 M) and NaOH (pH 7.0), **2a** was mixed with various anions and the absorption change at 368 nm was monitored (Figure 3). Complex **2a** displays a very high affinity for the cyanide ion, but it was almost inactive against other environmentally common anions under these conditions, and thus **2a** can be utilized as a highly selective anion sensor.[20] To obtain quantitative data on the complexation with fluoride and cyanide ions, titration experiments were carried out.[21]



2a
(FG = PMePh$_2$)

2b (X = F)
2c (X = CN)

Scheme 4. Complex formation of dicationic azaborine **2a** with fluoride or cyanide ion.

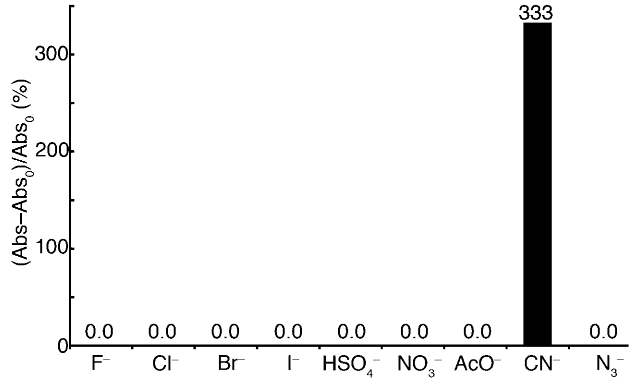


Figure 3. Absorption change of **2a** at 368 nm upon adding various anions (100 equiv) in a DMSO/H_2O mixture (4:6 v/v) containing HEPES (0.5 M) and NaOH (pH 7.0). [**2a**] $= 5.3\times10^{-5}$ M. [anion] $= 5.3\times10^{-3}$ M.

Determination of complex formation constant between 2a and fluoride ion: In the DMSO/H_2O mixture (3:1 v/v), **2a** was titrated with $(n\text{Bu})_4$NF at 298 K, and the reaction was monitored by UV/Vis spectroscopy (Figure 4). By using a least-square fitting method, the complex formation constant between dicationic azaborine **2a** and fluoride ion was deter-

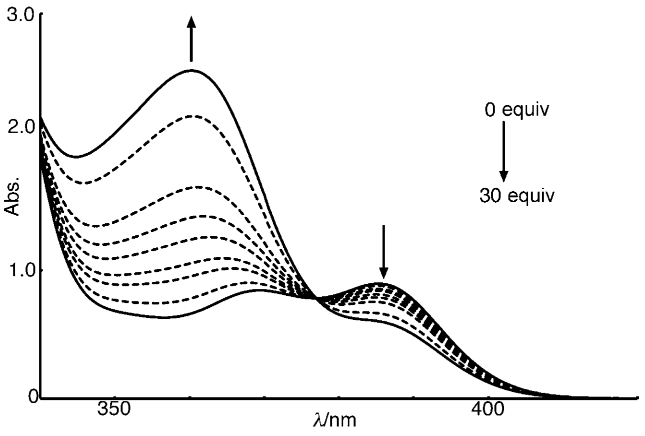


Figure 4. The change of UV/Vis spectra of **2a** upon adding $(n\mathrm{Bu})_4\mathrm{NF}$ in DMSO/H_2O (3:1 v/v) at 298 K ($[\mathbf{2a}]=1.0\times10^{-4}\,\mathrm{M}$).

mined to be $1.9(3)\times10^{2}\,\mathrm{M}^{-1}$ under these conditions. When the amount of H_2O was increased, however, complexation was not detected. This means that **2a** has a higher affinity for the cyanide ion than the fluoride ion in aqueous media (see below).

Complex formation of dicationic azaborine 2a with cyanide ion: Complex formation of **2a** with the cyanide ion could be monitored by UV/Vis spectroscopy as well as fluorescence spectroscopy in the DMSO/H_2O mixture. Upon adding aqueous NaCN to the DMSO/H_2O (4:6 v/v) solution of **2a** buffered by HEPES (0.5 M) and NaOH (pH 7.0) at 298 K, the absorption profile gradually changed, and isosbestic points appeared (Figure 5a). From this spectral change, the complex formation constant between **2a** and the cyanide ion was determined to be $1.2(4)\times10^{5}\,\mathrm{M}^{-1}$. This value is not so high compared with the value reported for a cationic triarylborane-based cyanide receptor under the same conditions, probably because the bulky Tip group prevented the complexation in the case of **2a**.[9d] In contrast, the fluoride ion could not form the complex under the same conditions. That the hydration enthalpy of the cyanide ion is smaller than that of the fluoride ion should be the main reason for the enhanced complex formation ability between **2a** and the cyanide ion in aqueous media. The fluorescence emission of **2a** also changed in accordance with the absorption change, indicating that **2a** can be used as a fluorescence sensor of the cyanide ion (Figure 5b).

Because the complexation ability of **2a** with the cyanide ion was revealed to be very high, its detection in 100% water is expected. Gratifyingly, **2a** reacted smoothly with NaCN in water. As cyanoborate **2c** precipitated under high concentrations ($>10^{-5}\,\mathrm{M}$), a titration experiment was carried out by using a dilute aqueous solution of **2a** ($[\mathbf{2a}]=4.1\times10^{-6}\,\mathrm{M}$). The solution was buffered with HEPES (0.5 M) and NaOH (pH 7.0). UV/Vis and fluorescence spectral changes are shown in Figure 6, and from the UV/Vis spectra, the complex formation constant between **2a** and the cyanide ion in H_2O was determined to be $5.2(5)\times10^{4}\,\mathrm{M}^{-1}$.

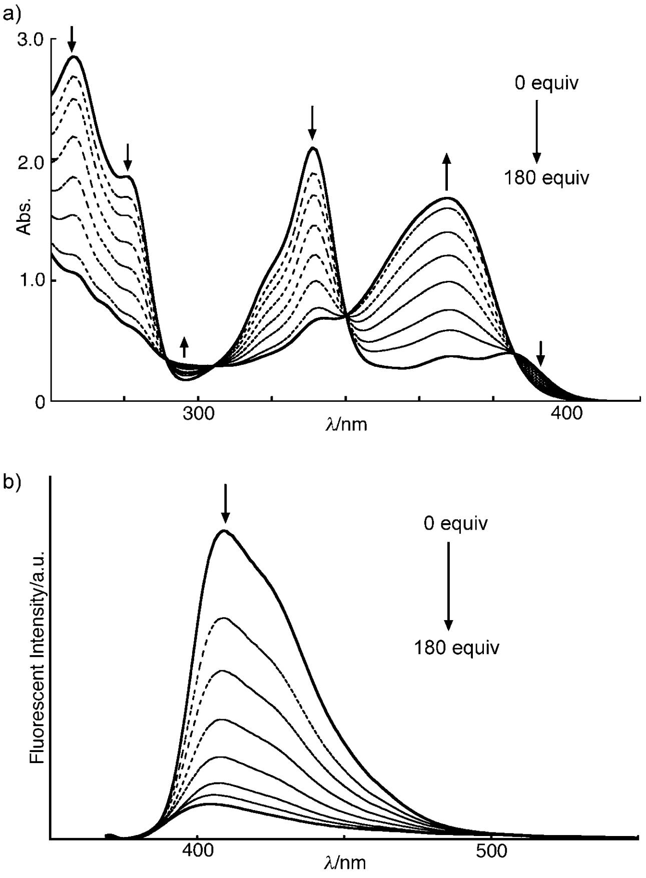


Figure 5. The UV/Vis (a) and fluorescence (b) spectral changes of **2a** upon adding aqueous NaCN in DMSO/H_2O (4:6 v/v) containing HEPES (0.5 M) and NaOH (pH 7.0) at 298 K. $[\mathbf{2a}]=5.3\times10^{-5}\,\mathrm{M}$. $\lambda_{ex}=369$ nm.

The success of the fluorescence detection of cyanide ion in aqueous media by **2a** indicates the possibility of fluorometric detection of these anions with the naked eye. Various anions were added into the solution of **2a** in the DMSO/H_2O mixture (3:1 v/v), and the samples were irradiated with a black light ($\lambda_{max}=370$ nm; Figure 7). Although under these conditions fluoride and iodide ions also caused subtle fluorescence quenching, **2a** was highly selective for the cyanide ion (judging by the photoluminescence intensity) and thus **2a** can be utilized as a convenient fluorometric sensor of cyanide ions in aqueous media.

Conclusion

In conclusion, we have synthesized new dicationic triarylboranes based on the dibenzoazaborine framework by taking advantage of periphery-functionalization methods developed previously by our group. These dicationic azaborines are soluble in common organic solvents, such as CH_2Cl_2, DMSO, and MeOH. In addition, these azaborines are moderately soluble in water, and the optical properties of the azaborine were retained in aqueous solvent systems.

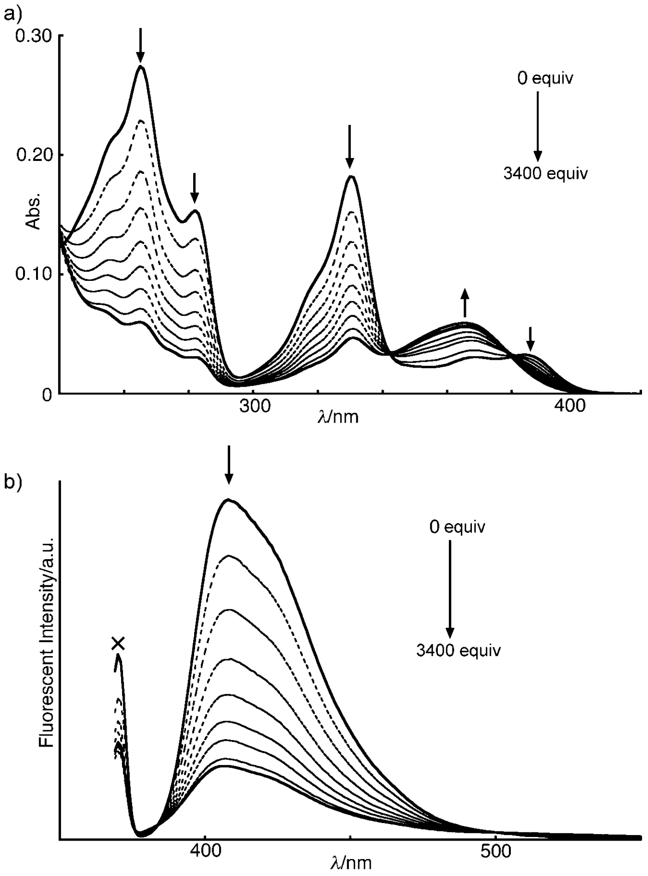


Figure 6. The UV/Vis (a) and fluorescence (b) spectral changes of **2a** upon adding aqueous NaCN in H_2O containing HEPES (0.5 M) and NaOH (pH 7.0) at 298 K. [**2a**] $=4.1\times10^{-6}$ M. $\lambda_{ex}=369$ nm.

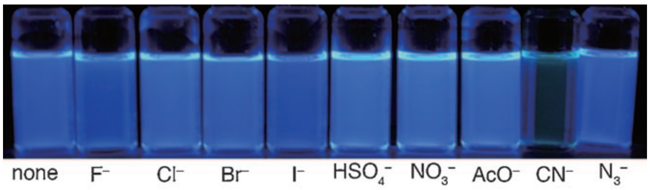


Figure 7. The photograph of the solution of **2a** in DMSO/H_2O solution (3:1 v/v) upon adding various anions (100 equivalents) under 370-nm UV lamp irradiation.

These dicationic azaborines showed enhanced Lewis acidity compared with the parent azaborine owing to the strong electron-withdrawing properties of the cationic functionalities. This was determined from a complex formation study with fluoride and cyanide ions in organic solvents as well as in aqueous solvents. In addition, bisphosphonioazaborine exhibited a higher complex formation ability with the cyanide ion than with the fluoride ion in an aqueous solvent system, and complexation with the cyanide ion could be monitored by optical spectroscopy.

These results indicate that the introduction of cationic functional groups into the azaborine framework is an effective way to develop optical anion sensors for use in aqueous media. The optimization of the molecular structure of the cationic azaborines is now under way in our laboratory with the aim to detect fluoride ions as well as other biologically important anions, such as the azide ion, in 100 % water.

Experimental Section

Bis(trimethylammonio)azaborine diiodide 1a: MeI (1.5 mL, 24 mmol) was added to a solution of azaborine **7** (550 mg, 1.1 mmol) in THF (30 mL), and the mixture was stirred at 55 °C for three days. The resulting precipitate was filtered off, washed with THF, and dried in vacuo to give **1a** as a yellow solid (0.70 g, 83 %). M.p. 117–118 °C (decomp); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=0.96$ (d, $J=6.6$ Hz, 12 H), 1.36 (d, $J=6.8$ Hz, 6 H), 2.18 (sept, $J=6.6$ Hz, 2 H), 3.01 (sept, $J=6.8$ Hz, 1 H), 3.91 (s, 18 H), 4.23 (s, 3 H), 7.15 (s, 2 H), 7.96 (d, $J=3.4$ Hz, 2 H), 8.09 (d, $J=9.6$ Hz, 2 H), 8.74 ppm (dd, $J=9.6$, 3.4 Hz, 2 H); ^{1}H NMR (400 MHz, D_2O): $\delta=0.98$ (d, $J=6.8$ Hz, 12 H), 1.37 (d, $J=7.2$ Hz, 6 H), 2.30 (sept, $J=6.8$ Hz, 2 H), 3.08 (sept, $J=7.2$ Hz, 1 H), 3.62 (s, 18 H), 4.22 (s, 3 H), 7.40 (s, 2 H), 8.14 (d, $J=10.0$ Hz, 2 H), 8.23 (d, $J=3.6$ Hz, 2 H), 8.27 ppm (dd, $J=10.0$, 3.6 Hz, 2 H);^{13}C NMR (126 MHz, CD_3OD): $\delta=24.9$, 25.1, 35.9, 37.1, 37.6, 58.4, 120.5, 121.6, 122.0, 127.1, 128.7, 129.4, 141.3, 147.8, 151.3, 152.7 ppm; ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta=53.7$ ppm; low-resolution (LR)MS (FAB^+): m/z: 638 ($[M-I]^+$); elemental analysis calcd (%) for $C_{34}H_{50}BI_2N_3\cdot1.5H_2O$: C 51.53, H 6.74, N 5.30; found: C 51.73, H 6.77, N 5.08.

Bis(methyldiphenylphosphonio)azaborine diiodide 2a: MeI (1.5 mL, 24 mmol) was added to a CH_2Cl_2/THF (2:3 v/v, 50 mL) solution of azaborine **8** (1.0 g, 1.3 mmol) and the mixture was stirred at 52 °C for 21 h. The solvents were removed under reduced pressure, and the crude material was purified by re-precipitation from CH_2Cl_2 and Et_2O to give azaborine **2a** as a pale yellow solid (0.89 g, 65 %). M.p. 334–335 °C (decomp); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=0.66$ (d, $J=6.8$ Hz, 12 H), 1.28 (d, $J=6.8$ Hz, 6 H), 1.92 (sept, $J=6.8$ Hz, 2 H), 2.87 (sept, $J=6.8$ Hz, 1 H), 3.03 (d, $^1J_{PH}=13.2$ Hz, 6 H), 4.32 (s, 3 H), 6.77 (s, 2 H), 7.48–7.58 (m, 16 H), 7.67–7.75 (m, 6 H), 8.28 (dd, $J=9.2$, 2.4 Hz, 2 H), 8.50 ppm (ddd, $J=11.4$, 9.2, 2.4 Hz, 2 H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): $\delta=10.3$ (d, $J=57.6$ Hz), 23.5 (s), 23.7 (s), 33.9 (s), 34.9 (s), 37.0 (s), 108.7 (d, $J=93.9$ Hz), 118.6 (d, $J=89.7$ Hz), 118.6 (d, $J=12.3$ Hz), 119.4 (s), 128.0 (d, $J=9.8$ Hz), 129.9 (d, $J=13.0$ Hz), 132.5 (d, $J=10.6$ Hz), 134.7 (s), 136.5 (d, $J=12.9$ Hz), 144.8 (d, $J=10.6$ Hz), 148.8 (s), 149.2 (s), 149.5 ppm (s) (one signal corresponding to B–C(Tip) carbon could not be observed); ^{13}C{^{1}H} NMR (126 MHz, CD_3OD): $\delta=9.38$ (d, $J=57.0$ Hz), 25.0 (s), 25.2 (s), 35.8 (s), 36.9 (s), 37.9 (s), 111.5 (d, $J=92.9$ Hz), 120.5 (d, $J=12.0$ Hz), 121.1 (s), 121.3 (d, $J=88.9$ Hz), 129.6 (d, $J=10.5$ Hz), 131.6 (d, $J=12.9$ Hz), 134.5 (d, $J=10.6$ Hz), 135.1 (s), 136.3 (d, $J=2.5$ Hz), 137.9 (d, $J=12.6$ Hz), 146.7 (d, $J=10.5$ Hz), 150.7 (s), 151.1 (d, $J=2.4$ Hz), 151.6 ppm (s); ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta=21.1$ ppm; ^{11}B NMR (128 MHz, CD_2Cl_2): $\delta=56.3$ ppm; LRMS (FAB^+): m/z: 920 ($[M-I]^+$); elemental analysis calcd (%) for $C_{54}H_{58}BI_2NP_2\cdot2H_2O$: C 59.85, H 5.77, N 1.29; found: C 60.00, H 5.79, N 1.32.

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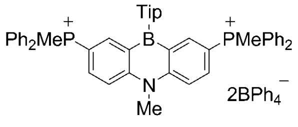
[16] Weak photoluminescence of **1a** and **2a** in CH_2Cl_2 may be due to complexation of the iodide ion to the boron centers in the ground or excited state, because bis(methyldiphenylphosphonio)azaborine bis(tetraphenylborate) **2d** showed a higher photoluminescence quantum yield (Φ 0.19) in CH_2Cl_2 than that of **2a**. In addition, the photoluminescence quantum yields of **2a** in polar solvents increased more than that in the less polar CH_2Cl_2 (in DMSO: $\Phi = 0.57$, in MeOH: $\Phi = 0.78$), indicating that the cation–anion interactions influence the fluorescence property of the dicationic azaborine.



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[18] In general, UV/Vis absorption of azaborine shows only minor solvent dependency as the degree of intramolecular charge transfer between the nitrogen and boron atoms is not so high. T. Agou, J. Kobayashi, T. Kawashima, unpublished results.

[19] Although the complex formation of **1a** with the fluoride ion could not be observed by UV/Vis or fluorescence spectroscopy, at higher concentrations ($[\mathbf{1a}] = 0.04$ M in DMSO/H_2O mixture (3:1 v/v)), the complexation could be monitored by ^{11}B and ^{19}F NMR spectroscopy.

[20] Although **2a** did not react with the fluoride ions in the DMSO/H_2O (4:6) mixture as shown here, the complexation could be observed when the amount of DMSO was increased (DMSO/$H_2O = 3:1$ v/v). See the Supporting Information for details.

[21] Complex **2a** was treated with solid KF and [18]crown-6 or NaCN in CD_2Cl_2 to give **2b** or **2c** in an almost quantitative yield. Fluoroborate **2b** was characterized by ^1H, ^{11}B, and ^{19}F NMR spectroscopy. The formation of cyanoborate **2c** was confirmed by IR spectroscopy ($\nu(CN) = 2163\ cm^{-1}$ in a KBr disk) in addition to ^1H, ^{13}C, ^{11}B, and ^{31}P NMR spectroscopy.

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