Fluorescence Color Change of a Boron-Substituted Diarylazomethine by Reaction with a Cyanide Ion[#]

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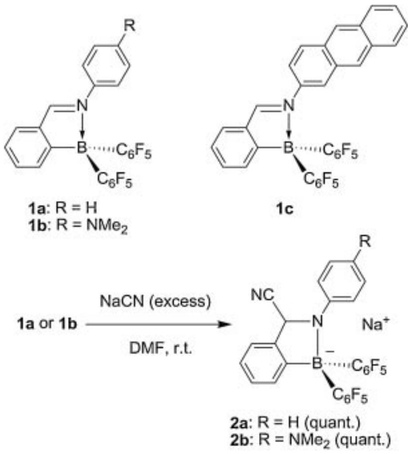
N-(2-Anthryl)-2-[bis(pentafluorophenyl)boryl]benzylideneamine changed its fluorescence color from yellow to green upon addition of an equimolar amount of cyanide ion, in contrast to the *N*-phenyl derivatives, which showed quenching of the emission. Theoretical calculations suggested that switching of the imine-based emission to anthryl-based emission by adduct formation provides the *N*-anthrylimine derivative with the fluorescence color change.



Scheme 1. *N*-Aryl-2-[bis(pentafluorophenyl)boryl]benzylideneamines **1a**–**1c** and reactions of **1a** and **1b** with NaCN.

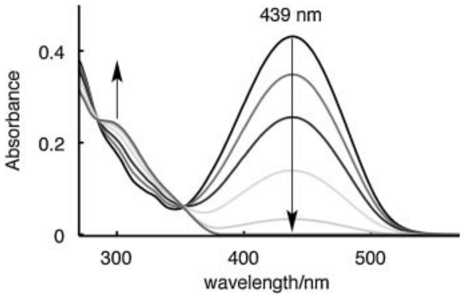


Figure 1. Change in the absorption spectra of **1b** in THF (27 µM) with TBACN. Lines denote spectra of **1b** with 0, 0.2, 0.4, 0.6, 0.8, and 1.0 equiv of TBACN.

Detection and sensing of toxic molecules or ions in the environment have become an important issue. In particular, sensing of the cyanide ion, a highly toxic substance, has attracted much attention. In general, highly sensitive analytical methods are required to detect a trace amount of substances. Analysis using stimuli-responsive fluorescent organic molecules is a promising approach. Several fluorescent cyanide sensors have been reported to date, most of them utilizing reactions of carbonyl groups[1] or boryl groups[2] with a cyanide ion. In contrast, we recently reported fluorescence quenching based on the addition of NaCN to an aldimine group in the study of fluorescent simple *N*-substituted aldimines, *N*-phenyl-2-[bis(pentafluorophenyl)boryl]benzylideneamine derivatives **1a** and **1b**, with a B–N interaction.[3] Although imines are intrinsically nonfluorescent, attachment of a bis(pentafluorophenyl)boryl group and the resulting B–N interaction can provide imines with fluorescence, as in the case of azobenzenes.[4] The binding of the cyanide ion at the aldimine carbon is a key to their fluorescence quenching (Scheme 1). However, excess NaCN was used for the fluorescence quenching in the previous reports because of the low solubility of NaCN in organic solvents, although the amount of required cyanide ion should be as small as possible for a highly sensitive analysis. In this case, the fluorescence quenching, which is a *turn off* mode of sensing of the cyanide ion, has a disadvantage in sensitivity compared with the *turn on* mode of sensing. In the *turn on* mode of sensing, a fluorescence color change, quenching of the original emission signal and simultaneous growth of another emission signal with a different wavelength of emission maximum, is more favorable than simple growth of the emission signal from the nonfluorescent state, because the fluorescence color change permits calculation of a ratio and contributes to the high precision of measurements.[5,6] Here, we report the binding ability toward a cyanide ion and the fluorescence color change of the boron-substituted diarylazomethines upon addition of a cyanide ion.

First, the binding ability of a cyanide ion to the imine moiety of the boron-substituted diarylazomethines was evaluated based on the reaction of **1b** with a soluble cyanide source, tetrabutylammonium cyanide (TBACN). In the absorption spectra in THF, the absorption peak of **1b** at 439 nm decreased upon addition of TBACN. The rate of decrease was proportional to the amount of TBACN, and the band completely disappeared when an equimolar amount of TBACN was added (Figure 1). In the fluorescence spectra, the emission peak of **1b** at 562 nm was also quenched completely at that point (Figure 2). These phenomena showed the strong binding ability of the 2-borylbenzylideneamine to a cyanide ion.

To examine the effects of an extended π-conjugated system in the boron-substituted imines on fluorescence behavior upon cyanide adduct formation, we have investigated *N*-anthryl

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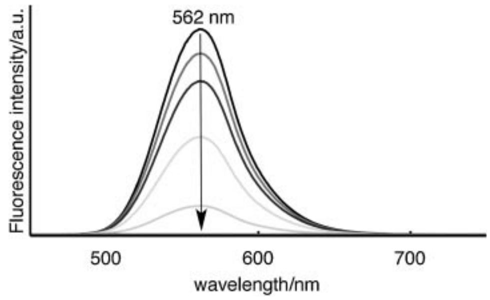
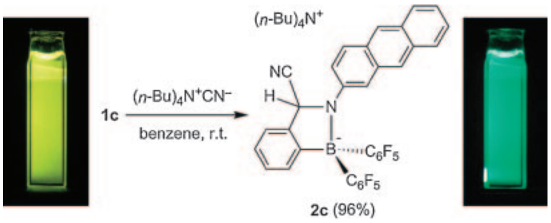


Figure 2. Change in the fluorescence spectra of **1b** in THF (27 µM) excited at 439 nm with TBACN. Lines denote spectra of **1b** with 0, 0.2, 0.4, 0.6, 0.8, and 1.0 equiv of TBACN.



Scheme 2. Reaction of **1c** with TBACN. Inserted photographs show a benzene solution of **1c** under irradiation by UV light before (left) and after (right) addition of TBACN.

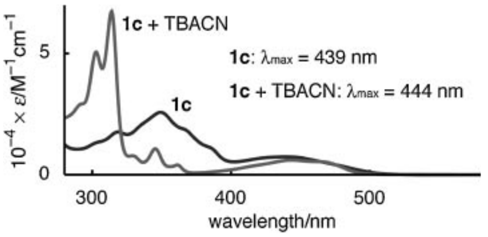


Figure 3. Absorption spectra of **1c** in benzene (20.8 µM) before and after addition of TBACN.

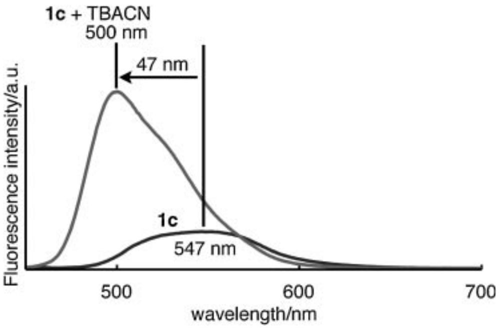


Figure 4. Fluorescence spectra of **1c** in benzene (2.08 µM) excited at 439 nm before and after addition of TBACN.

derivatives, because an aminoanthracene moiety itself is known to be emissive at visible wavelengths.[7] Imine **1c**, bearing a 2-anthryl group, has been chosen rather than other imines bearing 1- and 9-anthryl groups because the 2-anthryl group is less sterically demanding near the C=N double bond and the boryl group than other anthryl groups upon introducing it to boron-substituted imines, and also expected to minimize additional steric effects on fluorescence properties like **1a** and **1b** bearing phenyl and *p*-dimethylaminophenyl groups, respectively.

Imine **1c** reacted with an equimolar amount of TBACN and gave its cyanide adduct **2c** (Scheme 2). Addition of a cyano group at the aldimine carbon of **1c** as well as **1a** and **1b** was confirmed by nonequivalence of two pentafluorophenyl groups of **2c** in ^{19}F NMR induced by generation of the stereocenter. In the absorption and fluorescence spectra of **1c**, upon addition of TBACN (1.0 equiv) to the benzene solution of **1c**, the change in the absorption spectra was complete (Figure 3); however its emission was not quenched: the initial emission peak (547 nm) of **1c** decreased and another blue-shifted emission peak (500 nm) appeared simultaneously (Figure 4). These results showed that **2c** was fluorescent, in contrast to the nonfluorescent cyanide adducts **2a** and **2b** (TBA salts). The fluorescent quantum yield of **2c** was determined as $\Phi_F = 0.85$ in benzene, which is five times higher than that of **1c** ($\Phi_F = 0.17$ in benzene). In benzene, **1c** showed yellow fluorescence upon irradiation by UV light. After addition of TBACN, the fluorescence color immediately changed from yellow to green, as shown in the photographs in Scheme 2, and the change could be clearly observed with the naked eye.

To determine the reason for the difference in the behavior between the *N*-phenyl and *N*-anthryl derivatives upon formation of the cyanide adducts, the frontier orbitals of both of the aldimines and the corresponding cyanide adducts were investigated. Calculations were performed as an approximation by using the ground state geometries to reduce calculation costs. Counter cations of adducts were also omitted for the same reason. Transitions between the ground and the lowest singlet excited state of each species have been considered to be corresponding to the transition between the HOMO and LUMO, based on TD-DFT calculations, which indicated the configuration derived by promoting an electron from the HOMO to the LUMO showed the largest weight in the lowest singlet excited state. Calculated diagrams of frontier orbitals and their energy levels for **1a**, **1a** + CN$^-$, **1c**, and **1c** + CN$^-$ are shown in Figures 5 and 6. In both **1a** and **1c**, their HOMO and LUMO are delocalized on the π-conjugated system of their diarylimine moiety and overlapped with each other. The overlaps give the allowed transitions between the ground and lowest singlet excited states, corresponding to the transition between their HOMO and LUMO. This shows that the fluorescence of both **1a** and **1c** can be attributed to emission of their imine π-conjugated systems. In **1a** + CN$^-$, its HOMO and LUMO arise from those of **1a** and are separated into the borylphenyl and *N*-phenyl moieties, respectively, by the loss of the C=N double bond upon formation of the adduct. As a result, there is very little overlap between the HOMO and LUMO of **1a** + CN$^-$, giving fluorescence quenching of **1a**. In contrast, both the HOMO and LUMO of **1c** + CN$^-$ have *N*-anthryl-localized π-orbitals. The LUMO of **1c** + CN$^-$ principally derives from the LUMO+1 of **1c**. In **1c** + CN$^-$, the transition between the ground and lowest singlet excited states is still allowed. Therefore, despite quenching of the emission from the 2-borylphenylimine by the adduct formation, the emissive characteristics of 2-aminoanthracene moiety (2-aminoanthracene in 2,2,4-trimethylpentane: $\lambda_{abs} = 397$ nm, $\lambda_{em} = 435$ and 461 nm; in aqueous solution: $\lambda_{em} = 503$ nm)[7]

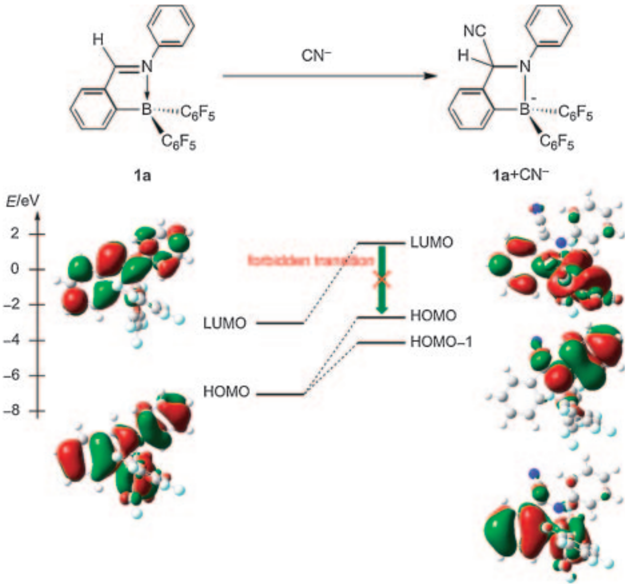


Figure 5. Calculated diagrams of frontier orbitals and the energy levels of **1a** and **1a** + CN^- at the B3PW91/6-31+G(d) level of theory.

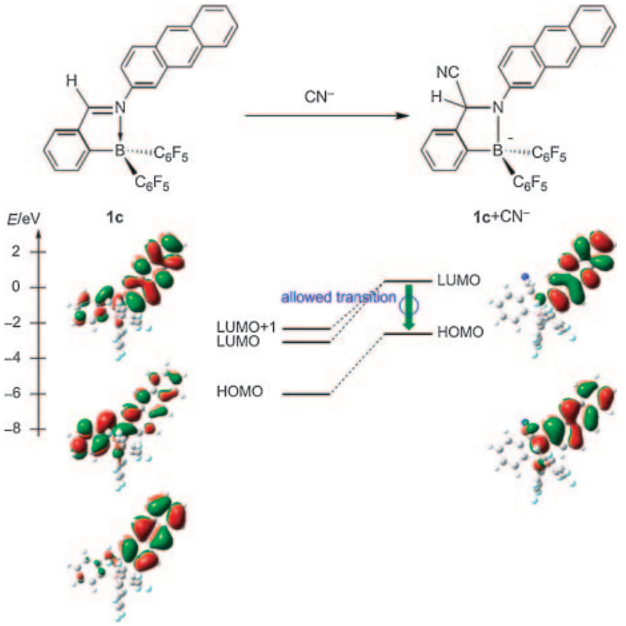


Figure 6. Calculated diagrams of frontier orbitals and the energy levels of **1c** and **1c** + CN^- at the B3PW91/6-31+G(d) level of theory.

appeared instead, resulting in the fluorescence color change of **1c**.

In conclusion, we have shown fluorescence color change behavior of *N*-(2-anthryl)-2-[bis(pentafluorophenyl)boryl]benzylideneamine upon addition of a cyanide ion. Theoretical calculations showed its emissive characteristics both before and after addition of a cyanide ion. Further optimization of fluorescence properties is needed to apply the imine to practical ratiometric measurements, because quenching and increasing regions of emission in the spectra of the imine with a cyanide ion lack proportion. However, the method shown here causing a fluorescence color change response to an equimolar amount of cyanide ion may provide advances in the development of fluorescent sensors.

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Supporting Information

Experimental, spectral data of **1b** and **1c** in some solvents, and Cartesian coordinations of optimized structures by DFT calculations. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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Dedicated to the Late Professor Pascal Le Floch.

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