Fluorescent azobenzenes and aromatic aldimines featuring an N–B interaction

Junro Yoshino,a Naokazu Kanob and Takayuki Kawashima*c

Azobenzenes are constituents of the commonly and widely used azo dyes. Many dyes, except for the azo dyes, have been utilized for fluorescent materials. However, there are only a few fluorescent azobenzene derivatives and their fluorescence efficiencies are quite low. The current perspective provides an account of the fluorescent azobenzenes and aromatic aldimines featuring an N–B interaction. Incorporation of the intramolecular N–B interaction by using the bis(pentafluorophenyl)boryl group makes the azobenzenes and aromatic aldimines fluorescent with a range of colours. Some of them fluoresce with extraordinarily high fluorescence quantum yields. Their synthesis, structures, fluorescence properties, and applications are discussed.

1. Introduction

Fluorescent materials have become indispensable tools in the wide field of science and technology. Their applications for various purposes, such as fluorescent probes, fluorescent indicators, fluorescent paint, and light-emitting devices, play important roles in scientific research and our life.1 Fluorescent compounds consisting of organic compounds have the following advantages: fine adjustability of optical properties, ease of synthesis, lightweight, and ease of moulding. Therefore, many types of organic fluorescent compounds have been developed to date.

Construction of organic fluorescent molecules requires a π-conjugated structure and a rational method for the processes of both efficient absorption of light and radiative transition. The nitrogen–boron interaction is one of the rational methods to provide fluorescence properties to organic compounds. Boron dipyromethene (BODIPY) is a well-known example of a fluorescent organic compound featuring the N–B interaction.2 In BODIPY dyes, the N–B interaction fixes the dipyromethene framework in the coplanar conformation to avoid thermal degradation from the photoexcited state upon irradiation. The N–B interaction also perturbs the orbital energy levels, and the S0 and S1 states correspond to the HOMO (π orbital) and LUMO (π* orbital), respectively. As a result, BODIPY dyes emit intense fluorescence via the S1–S0 relaxation process upon photoirradiation. Thus, this intensely fluorescent fluorophore gains its fluorescent nature by forming N–B dative bonds, while the dipyromethene free base itself has poor emission characteristics. The N–B dative bond is also a key feature of the boronic acid sugar sensors, and the N–B dative bond changes the fluorescence quenching efficiency of the amine in the aminomethyl fluorophore.3

Azobenzenes are π-conjugated molecules and constituents of commonly and widely used azo dyes and pigments. One of their important features is ease of adjustment of their properties precisely and facilely. They hold the promise of utilization for attractive fluorescent compounds, considering the π-conjugated structures. However, there were only a few examples of fluorescent azobenzenes when we started a project on fluorescent azobenzenes.4 Furthermore, the fluorescence efficiencies of the previous fluorescent azobenzenes were quite low. The above features are also true for diphenylimines. There are several fluorescent compounds including a C═N double-bond structure utilizing the co-ordination of a nitrogen atom of the heterocyclic ring to the boron atom.5 Fluorescent imines incorporated into a π-conjugated structure are also known to be a part of multi-dentate ligands for metal complexation.6,7 However, there have been only a few fluorescent diphenylimine derivatives with a simple structure.8

Azobenzenes efficiently undergo photoisomerization in the photoexcited state, and this process is surely a reason for their non-fluorescence.9 Photoisomerization accompanies the change in the direction of the lone pair of one nitrogen atom. Restraining the lone pair from changing direction should prevent the photoisomerization. Therefore, suppression of the photoisomerization movement in the azobenzenes was
considered a key to provide them with a fluorescent nature. The authors initially tried to form an N–B dative bond in the azobenzenes during the course of studies on azobenzenes bearing a main-group-element substituent (Fig. 1) and found that 2-[bis(pentafluorophenyl)boryl]azobenzene (1a) fluoresces intensely.\textsuperscript{10,11} In the 2-borylazobenzenes, the lone pair is used to form an intramolecular N–B interaction and the photoisomerization is inhibited. In addition, the N–B interaction restricts the rotation around the nitrogen–carbon bond and the non-radiative deactivation process is depressed.

This perspective aims to provide an overview of the development of fluorescent azobenzenes and aromatic aldimines bearing an N–B interaction as a key interaction and their application to ion sensors.

2. Fluorescent 2-borylazobenzenes and 2,2′-diborylazobenzenes

2.1. Synthesis and structures of fluorescent 2-borylazobenzenes

2-Borylazobenzenes 1a–j were synthesized using the following strategy: first, preparation of 2-idoazobenzences bearing functional groups at the 4- and/or 4′-positions, and then introduction of a bis(pentafluorophenyl)boryl group (Fig. 2, Scheme 1, and Table 1).\textsuperscript{11–14} 2,2′-Diborylazobenzenes 2a–d were also synthesized by a similar method from 2,2′-diiodoazobenzenes (Fig. 2, Scheme 1, and Table 2).\textsuperscript{15} Some of them (1k–o) were obtained by transformation of a functional group on the azobenzene moiety after the introduction of the boryl group.\textsuperscript{13,14}

It is noteworthy that palladium-catalysed cross-coupling reactions, such as the Suzuki–Miyaura cross-coupling reaction, Buchwald–Hartwig amination, and the Sonogashira coupling reaction, are valuable for modifying the brominated 2-borylazobenzenes 1i and 1j, despite the presence of a boryl group in the molecules (Scheme 2).

The molecular structures of all the fluorescent azobenzenes in solution were established by \textsuperscript{1}H, \textsuperscript{11}B, \textsuperscript{13}C, and \textsuperscript{19}F NMR spectroscopy, and the crystal structures of 1a, 1b, 1e, and 2a were determined by X-ray crystallographic analysis. The \textsuperscript{11}B NMR spectra show their chemical shifts in the range of −3.2 to −0.1 ppm, indicating the presence of a tetraco-ordinated boron atom in solution because of the N–B dative bond. According to the crystallographic analysis, the N=N bond lengths [1.270(18)–1.292(3) Å] are in the range of a double bond, despite the existence of the dative bond. The N–B dative bonds, whose lengths are in the range of 1.625(2)–1.638(3) Å, make the N=N double bond coplanar with one of the two benzene rings of the azobenzene (Fig. 3). In 2,2′-diborylazobenzene 2a, which has two N–B dative bonds, the azobenzene moiety is almost coplanar with the two N–B dative bonds.

2.2. Fluorescence properties of 2-borylazobenzenes

2-Bis[pentafluorophenyl]borylazobenzences 1a–n fluoresce in non-polar organic solvents. The fluorescence colours and intensities depend on the substituents on the benzene rings, R and R′. Fluorescence colours of the 2-borylazobenzenes 1a–o are finely tuned by substitution on the azobenzene moiety and the colour variations are green, yellow, orange, and red (Table 1 and Fig. 4). In azobenzenes 1a–g, the stronger electron-donating group at the 4′-position shows a tendency to give the larger red shift of the emission maximum and the
The exceptional fluorescence emission of 2-borylazo- 
benzenes is due to the intramolecular nitrogen– 
boron interaction, which masks the lone pair of the 
boron atom, cannot induce fluorescence emission of the azo- 
benzene. Actually, 2-boryloxyazobenzene (1b) shows almost 1.00 and extraordinarily high compared 
with unsubstituted azobenzene (1a). Its fluorescence quantum yield (\( \Phi_F \)) in dichloromethane (Fig. 6). 11 Other 2-borylazo- 
benzenes 1n and 1o, bearing tetra-alkylammonium and/or 
sulfonate groups, are slightly dispersible in water (1n, 1.15 g 
L\(^{-1}\); 1o, 1.19 g L\(^{-1}\)), and 1n is even more dispersible in water 
than in dichloromethane (Fig. 5). They look transparent, like 
an aqueous solution to the naked eye. They show fluorescence 
emission in water, although the fluorescence quantum yields in 
water are lower than those in methanol (Table 1). Their particle 
 sizes were measured using dynamic light scattering, and 
the results (1n, 212 nm (polydispersity index (PDI) = 1.1) in 
water, 0.76 nm (PDI = 1.1) in methanol; 1o, 424 nm (PDI = 1.1) in 
in water, 0.73 nm (PDI = 1.1) in methanol) suggest that they 
aggregate in water and exist as a monomer in methanol. The aggregation caused by the hydrophobic 2-borylazo- 
benzene moiety is considered to provide the differences in emission 
behaviour between water and organic solvents.

Substituents on the boron atom of the boron-substituted 
azobenzenes affect their fluorescence behaviours. In the 2(di- 
arylboronyl)azobenzenes, replacement of pentafluorophenyl 
groups results in a red shift of the emission maximum; 
however, the fluorescence quantum yields are relatively low in 
comparison with azobenzenes bearing an electron-donating 
group at the 4-position also gives a red shift of the emission maximum; 
the fluorescence quantum yield (\( \Phi_F \)) and fluorescence lifetime (\( \tau_F \)) of the 2,2'- 
diborylazobenzenes in hexane.

The above-mentioned fluorescent azobenzenes are insoluble in water, and we attempted to improve their solubility in 
water by incorporation of ionic functional groups. The dimethylaminoethyl group can be introduced on aromatic 
rings by the Sonogashira coupling reaction and can easily be 
quaternized. The quaternized ionic moiety is expected to 
increase the solubility of the 2-borylazobenzenes in water. 17 
Azobenzenes 1n and 1o, bearing tetra-alkylammonium and/or 
sulfonate groups, are slightly dispersible in water (1n, 1.15 g 
L\(^{-1}\); 1o, 1.19 g L\(^{-1}\)), and 1n is even more dispersible in water 
than in dichloromethane (Fig. 5). They look transparent, like 
an aqueous solution to the naked eye. They show fluorescence 
emission in water, although the fluorescence quantum yields in 
water are lower than those in methanol (Table 1). Their particle 
 sizes were measured using dynamic light scattering, and 
the results (1n, 212 nm (polydispersity index (PDI) = 1.1) in 
water, 0.76 nm (PDI = 1.1) in methanol; 1o, 424 nm (PDI = 1.1) in 
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aggregate in water and exist as a monomer in methanol. The aggregation caused by the hydrophobic 2-borylazo- 
benzene moiety is considered to provide the differences in emission 
behaviour between water and organic solvents.

Table 1: Substituents at the 4- and 4'-positions (R and R', respectively), absorption wavelength (\( \lambda_{\text{abs}} \)), molar absorption coefficient (\( \varepsilon \)), fluorescence wavelength (\( \lambda_{\text{em}} \)), fluorescence quantum yield (\( \Phi_F \)), and fluorescence lifetime (\( \tau_F \)) of the 2-borylazobenzenes.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>( \lambda_{\text{abs}}/\text{nm} )</th>
<th>( \varepsilon/M^{-1} \text{cm}^{-1} )</th>
<th>( \lambda_{\text{em}}/\text{nm} )</th>
<th>( \Phi_F )</th>
<th>( \tau_F/\text{ns} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>386(^{a})</td>
<td>19 000(^{a})</td>
<td>503(^{a})</td>
<td>0.20(^{a})</td>
<td>3.82(4)</td>
</tr>
<tr>
<td>OMe</td>
<td>H</td>
<td>439(^{a})</td>
<td>12 000(^{a})</td>
<td>524(^{a})</td>
<td>0.76(^{a})</td>
<td>6.24(5)</td>
</tr>
<tr>
<td>OMe</td>
<td>H</td>
<td>446(^{a})</td>
<td>14 000(^{a})</td>
<td>536(^{a})</td>
<td>0.98(^{a})</td>
<td>-(^{c})</td>
</tr>
<tr>
<td>NMe(_2)</td>
<td>H</td>
<td>516(^{a})</td>
<td>55 000(^{a})</td>
<td>566(^{a})</td>
<td>0.52(^{a})</td>
<td>6.17(5)</td>
</tr>
<tr>
<td>CF(_3)</td>
<td>H</td>
<td>382(^{a})</td>
<td>22 000(^{a})</td>
<td>511(^{a})</td>
<td>0.039(^{a})</td>
<td>2.67(3)</td>
</tr>
<tr>
<td>F</td>
<td>H</td>
<td>390(^{a})</td>
<td>11 000(^{a})</td>
<td>504(^{a})</td>
<td>0.29(^{a})</td>
<td>-(^{c})</td>
</tr>
<tr>
<td>OTBDMS</td>
<td>H</td>
<td>433(^{a})</td>
<td>16 000(^{a})</td>
<td>524(^{a})</td>
<td>0.90(^{a})</td>
<td>5.50(2)</td>
</tr>
<tr>
<td>Bu</td>
<td>H</td>
<td>402(^{a})</td>
<td>22 000(^{a})</td>
<td>507(^{a})</td>
<td>0.31(^{a})</td>
<td>-(^{c})</td>
</tr>
<tr>
<td>H</td>
<td>OMe</td>
<td>443(^{a})</td>
<td>24 000(^{a})</td>
<td>538(^{a})</td>
<td>0.048(^{a})</td>
<td>&lt;1(^{a})</td>
</tr>
<tr>
<td>H</td>
<td>Br</td>
<td>416(^{a})</td>
<td>23 000(^{a})</td>
<td>509(^{a})</td>
<td>0.045(^{a})</td>
<td>-(^{c})</td>
</tr>
<tr>
<td>H</td>
<td>Ph</td>
<td>445(^{a})</td>
<td>22 000(^{a})</td>
<td>539(^{a})</td>
<td>0.13(^{a})</td>
<td>-(^{c})</td>
</tr>
<tr>
<td>H</td>
<td>NPh(_2)</td>
<td>553(^{a})</td>
<td>28 000(^{a})</td>
<td>634(^{a})</td>
<td>0.37(^{a})</td>
<td>-(^{c})</td>
</tr>
<tr>
<td>O(CH(_2))(_2)N(^{+})Me(_2)(CH(_2))(_3)SO(_3)^-</td>
<td>H</td>
<td>458(^{a})</td>
<td>17 000(^{a})</td>
<td>546(^{a})</td>
<td>0.53(^{a})</td>
<td>-(^{c})</td>
</tr>
<tr>
<td>O(CH(_2))(_2)N(^{+})Me(_2)(CH(_2))(_3)SO(_3)^-</td>
<td>H</td>
<td>456(^{a})</td>
<td>12 000(^{a})</td>
<td>552(^{a})</td>
<td>0.10(^{a})</td>
<td>-(^{c})</td>
</tr>
<tr>
<td>O(CH(_2))(_2)N(^{+})Me(_2)(CH(_2))(_3)SO(_3)^-</td>
<td>H</td>
<td>468(^{a})</td>
<td>12 000(^{a})</td>
<td>555(^{a})</td>
<td>0.14(^{a})</td>
<td>-(^{c})</td>
</tr>
<tr>
<td>O(CH(_2))(_2)N(^{+})Me(_2)(CH(_2))(_3)SO(_3)^-</td>
<td>H</td>
<td>460(^{a})</td>
<td>13 000(^{a})</td>
<td>545(^{a})</td>
<td>0.092(^{a})</td>
<td>-(^{c})</td>
</tr>
</tbody>
</table>

\(^{a}\) In hexane. \(^{b}\) In CH\(_2\)Cl\(_2\). \(^{c}\) In MeOH. \(^{d}\) In water. \(^{e}\) Not available.

Table 2: Substituents at the 4- and 4'-positions (R and R', respectively), absorption wavelength (\( \lambda_{\text{abs}} \)), molar absorption coefficient (\( \varepsilon \)), fluorescence wavelength (\( \lambda_{\text{em}} \)), fluorescence quantum yield (\( \Phi_F \)), and fluorescence lifetime (\( \tau_F \)) of the 2,2'- 
diborylazobenzenes in hexane.

<table>
<thead>
<tr>
<th>R, R'</th>
<th>( \lambda_{\text{abs}}/\text{nm} )</th>
<th>( \varepsilon/M^{-1} \text{cm}^{-1} )</th>
<th>( \lambda_{\text{em}}/\text{nm} )</th>
<th>( \Phi_F )</th>
<th>( \tau_F/\text{ns} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H, H</td>
<td>521, 552</td>
<td>20 000, 16 000</td>
<td>572</td>
<td>0.26</td>
<td>1.7</td>
</tr>
<tr>
<td>Bu, H</td>
<td>547, 582</td>
<td>9500, 9900</td>
<td>597</td>
<td>0.73</td>
<td>6.7</td>
</tr>
<tr>
<td>Br, H</td>
<td>549, 584</td>
<td>52 000, 58 000</td>
<td>602</td>
<td>0.39</td>
<td>3.7</td>
</tr>
<tr>
<td>O(_2)Bu, H</td>
<td>603, 646</td>
<td>55 000, 71 000</td>
<td>663</td>
<td>0.62</td>
<td>2.4</td>
</tr>
</tbody>
</table>
hexane) of the red-shifted fluorescence emission ($\lambda_{\text{max}} = 576$ nm in hexane) is quite low in comparison with 2-borylazo-benzene 1a (Fig. 4 and 6). The intensely fluorescent, weakly fluorescent, and non-fluorescent azobenzenes so far exemplify the significance of both the existence of strong electron-drawing pentafluorophenyl groups on the boron atom and binding of the bis(pentafluorophenyl)boryl group directly to the azobenzene for the intense fluorescence emission from the azobenzene. Using the strong electron-withdrawing bis(pentafluorophenyl)boryl group on the benzene ring in addition to the N–B interaction is important for the intense fluorescence emission from the azobenzene moiety. Replacement of pentafluorophenyl groups with less electron-withdrawing p-fluorophenyl groups changes the HOMO from a $\pi$ orbital of azobenzene to a $\pi$ orbital of one of the p-fluorophenyl groups. The S$_0$–S$_1$ transition after the replacement results in a forbidden $\pi$–$\pi^*$ transition because of spatial separation, which causes the loss of fluorescence.

2.3. Fluorescence properties of 2,2′-diborylazobenzenes

2-Borylazobenzenes 1a–o provide only one of two nitrogen atoms of the azo group for the N–B double bond; however, the other nitrogen atom can be used for an additional dative bond. Furnishing the 2-borylazobenzenes with one more N–B interaction changes their fluorescence properties drastically because of fixation of C–N bond rotation in the azobenzene...
moiety by two strong N–B interactions. Actually, 2,2′-diborylazobenzenes 2a–d fluoresce in orange or red with their emission maxima at 573–663 nm, showing a large red shift from the emission wavelength of the 2-monoborylazobenzenes (Table 2 and Fig. 7). Another notable point of their fluorescence properties is their small Stokes shifts (400 to 630 cm⁻¹). Substituent effects on their fluorescence properties are similar to those of 2-monoborylazobenzenes.

3. Fluorescent boron-substituted aromatic aldimines

Replacement of one nitrogen atom of the azo group (–N≡N–) in azobenzene (3) with a methine gives another dye molecule, N-benzylideneaniline (8), which contains an imine moiety (–CH=N–). The azo and imine compounds differ in thermal stability depending on the substituent on the nitrogen atoms, reactivity towards nucleophiles because of polarization of the C≡N double bond, and absorption wavelength reflecting the HOMO–LUMO energy gap. However, it resembles azobenzene in several respects—molecular structure, availability through easy organic synthetic reactions, adjustability of its π-conjugated system, and virtually non-fluorescent properties. The similarity of the molecular structures of these compounds motivated the authors to synthesize bis(pentafluorophenyl)boryl-substituted aromatic aldimines, in anticipation of fluorescence characteristics (Fig. 1). This molecular design is based on the structure of fluorescent azobenzene 1a. 

3.1. Synthesis and structures of fluorescent boron-substituted aromatic aldimines

Aromatic aldimines 9a–h were synthesized by a simple condensation of 2-borylbenzaldehyde 10 and the corresponding amines (Scheme 3 and Table 3). All of the aldimines 9a–h have an N–B dative bond in their molecular structures in the solution state and the crystalline state, as evidenced by the chemical shifts in ¹¹B NMR spectra (δB: −3.2 to −0.6) and the N–B bond length (1.605(3)–1.646(3) Å), respectively. These aldimines correspond to Lewis-acid activated aldimines, but they are stable in air. In addition, their C≡N double bonds (1.285(3)–1.3003(18) Å) are not elongated severely. Similar to the case of 2-borylazobenzenes 1a, the N–B dative bond in their structures works to make their C≡N double bond coplanar with the benzene ring to which the boron atom binds. In aldimines 9a–d, the aryl group on the nitrogen atom deviates somewhat from coplanarity with the C≡N double-bond plane in the crystal structures (dihedral angle: 14 to 34°). By contrast, in hydrazone-type compounds 9g and 9h, the dihedral angles (62–73°) are much larger because of the
intramolecular π-π stacking between the nitrogen-containing aromatic rings and one of the pentafluorophenyl groups.\textsuperscript{21}

### 3.2. Fluorescence properties of boron-substituted aromatic aldimines

Aldimines 9a-d fluoresce blue or green in hexane solution (Table 3 and Fig. 8). The blue emission is a characteristic of the boron-substituted aromatic aldimines. Blue emission has not been achieved in the fluorescent 2-borylazobenzenes so far, because it is difficult to adjust the emission wavelength of the azobenzenes to be short enough, beyond the region of green light. Compared with the 2-borylazobenzenes, aromatic aldimines 9a-d show shorter wavelengths in both absorption and fluorescence spectra because of the larger HOMO–LUMO energy gap in the C==N double-bond compounds than in the N==N double-bond compounds. The available region of emission wavelengths of the fluorescent azo family has been expanded by adaptation of the azomethine framework.

The fluorescence efficiencies of the boron-substituted aromatic aldimines are much higher than that of non-fluorescent N-benzylideneaniline (8) (Φ\textsubscript{f} < 0.0001).\textsuperscript{22} In particular, aldime 9c, which bears an electron-donating 4-dimethylamino-phenyl group on the nitrogen atom of the imine moiety, shows the highest fluorescence quantum yields (0.73) among 9a-d. It is at least 7000 times higher than that of 8. The high fluorescence efficiencies of 9a-d are provided by the intramolecular N–B interaction. The tight N–B interaction gives high rigidity to the molecular structure to suppress the non-radiative relaxation through internal conversion. Furthermore, the non-radiative relaxation path from the lowest singlet excited state, \( ^1(\pi, \pi^*) \), via the triplet excited state\textsuperscript{23} is blocked by the N–B interaction for the following reasons. Masking the lone pair of the nitrogen atom raises the energy levels of all triplet excited states of \( ^1(\pi, \pi^*) \), which are responsible for the non-radiative relaxation in N-benzylideneaniline, over the energy level of the \( ^1(\pi, \pi^*) \). Therefore, only slow intersystem crossing between \( ^1(\pi, \pi^*) \) and the resulting \( ^3(\pi, \pi^*) \) is available. As a result, relatively fast radiative relaxation from \( ^1(\pi, \pi^*) \) to the ground state occurs in aldimines 9a-d. Thus, the fate of aldimines 9a-d is a radiative relaxation, and they fluoresce. The fluorescence emission mechanism of 9a-d makes a good contrast with that of the 2-borylazobenzenes, in which changing the transition character between the lowest singlet excited state and the ground state is a key for the fluorescent emission.

\( N \)-Alkyl aldime 9e also fluoresces, but its fluorescence is almost invisible because its weak fluorescence emission is mostly in the ultraviolet region. Oxime-type compound 9f does not show fluorescence.

The fluorescence behaviours of hydrazone-type compounds 9g and 9h are interesting. They have two different emission modes: one is based on the transition from the local excited state of the nitrogen-containing aromatic ring moiety to the ground state (HOMO–LUMO + 1 transition), and another is based on the transition from a charge transfer state to the ground state (HOMO–LUMO transition). As a result, they fluoresce with a single emission peak upon excitation at a longer wavelength, while they show dual emission upon excitation at a shorter wavelength, which corresponds to a sufficiently high energy to excite the indole or carbazole moieties (see Table 3).

### 4. Applications of fluorescent azobenzenes and aromatic aldimines

Fluorescence emission is detectable with high sensitivity, and it is used for various purposes, such as labelling for detection of living organisms and chemo-sensors for toxic materials. The fluorescent boron-substituted azobenzenes and aromatic aldimines are sufficiently stable. The boron-substituted fluorescent azobenzene can be used as a vital fluorescent tracer. Microinjection of azobenzene 1b into Xenopus embryos and

<table>
<thead>
<tr>
<th>R</th>
<th>( \lambda_{\text{abs}}/\text{nm} )</th>
<th>( \epsilon/\text{M}^{-1} \text{cm}^{-1} )</th>
<th>( \lambda_{\text{em}}/\text{nm} )</th>
<th>( \Phi_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>324</td>
<td>10 000</td>
<td>460</td>
<td>0.0050</td>
</tr>
<tr>
<td>4-MeOC(_2)H(_4)</td>
<td>366</td>
<td>15 000</td>
<td>466</td>
<td>0.074</td>
</tr>
<tr>
<td>4-Me(_2)NC(_2)H(_4)</td>
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<td>25 000</td>
<td>500, 527</td>
<td>0.73</td>
</tr>
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<td>2-Anthryl</td>
<td>442</td>
<td>9100</td>
<td>497, 531</td>
<td>0.39</td>
</tr>
<tr>
<td>(^6)Bu</td>
<td>290</td>
<td>13 000</td>
<td>398</td>
<td>0.011</td>
</tr>
<tr>
<td>OMe</td>
<td>296</td>
<td>7600</td>
<td>–2</td>
<td>–</td>
</tr>
<tr>
<td>1-Indolyl</td>
<td>398</td>
<td>6800</td>
<td>525 (365, 531)</td>
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</tr>
<tr>
<td>9-Carbazolyl</td>
<td>423</td>
<td>2700</td>
<td>545 (380, 396, 545)</td>
<td>0.0052 (0.020)</td>
</tr>
</tbody>
</table>

* Excited at \( \lambda_{\text{abs}} \) unless otherwise noted. \(^b\) Not detectable. \(^c\) Excited at 290 nm. \(^d\) Not available. \(^e\) Excited at 320 nm.

Fig. 8 Photographs of hexane solution of aromatic aldimines (a) 9a and (b) 9c under irradiation by UV light. The photographs are reproduced from ref. 20 with permission from the American Chemical Society.
observation of the phenotypes revealed its non-toxicity for cells because it did not induce any malformation. Actually, we could observe perceptible fluorescence after the development of the cells. The boron-substituted fluorescent azobenzenes and aromatic aldimines show chemical reactivity towards some reagents. Chemical reactions of the boron-substituted azo derivatives are expected to change the fluorescence emission colours or intensity. The fluorescence changes of the fluorescent azobenzenes and aromatic aldimines in response to chemical stimuli are discussed below.

4.1. Acid sensing

Some fluorescent azobenzenes show switching of fluorescence behaviours upon receiving chemical stimuli. One example is fluorescence switching of 2-borylazobenzene 1c, which bears a dimethylamino group at the 4′-position, by acid-base reactions. The strong orange fluorescence of 1c in hexane was completely quenched by addition of trifluoroacetic acid (TFA), and the colour change can be clearly observed by the naked eye (Fig. 9). The quenched fluorescence was recovered by neutralization of the acidified solution with triethylamine. Therefore, its fluorescence-switching potential by acid-base reactions can be used for a fluorescent pH sensor. The proton-responsive mechanism of 1c is considered to be the same as azo-dye-based pH indicators because the molecular structure of 1c includes that of methyl yellow, 4-(dimethylamino)azobenzene (Scheme 4). Protonation of the azo group of 1c results in a change in the nature of the transition. The allowed π–π* transition on the azobenzene moiety changes to the forbidden transition between the π orbital on a pentafluorophenyl group and the π* orbital on the azobenzene moiety, as confirmed by TD-DFT calculations. This is considered a reason for the fluorescence quenching.

4.2. Fluorescence switching invoked by reduction–oxidation reactions

Another example of reaction-based fluorescence switching is the case of 2,2′-diborylazobenzenes 2a–d. Doubling of the N–B interaction provides 2,2′-diborylazobenzenes 2a–d with high electron affinity. As suggested by cyclic voltammetry and DFT calculations, the energy level of the π* orbital (LUMO) in 2b is much lower than those in azobenzenes 3 and 2-borylazobenzenes 1a because of two N–B dative bonds. Thus, 2b can easily be reduced to the corresponding radical anion. Single-electron reduction of 2b in THF with decamethylcobaltocene afforded its non-fluorescent azobenzene radical anion 11, accompanying the colour change of the solution from red to blue (Scheme 5). Radical anion 11 was readily oxidized by air to give the original fluorescent 2b. Therefore, the fluorescence emission of the 2,2′-diborylazobenzenes is easily quenched and recovered by the redox reactions, and it may be useful for the control of fluorescence emission.

4.3. Cyanide ion sensing

The fluorescent boron-substituted aromatic aldimines can be applied to cyanide ion sensing. Although there are several reports on boron-based cyanide ion sensors in which a cyanide ion co-ordinates to the boron atom, aldmines 9a and 9d function as a unique cyanide sensor from the viewpoint of a sensing mechanism. Initially, a cyanide ion was anticipated to co-ordinate to the boron atom to kick the N–B interaction out in the reaction of the fluorescent aromatic aldmines with a cyanide ion. However, the reaction of aldmine 9a gave its cyanide adduct 12a, in which a cyanide ion binds to the imine carbon atom instead of by co-ordination to the boron atom (Scheme 6). Conversion of the C≡N double bond to a single bond disconnects the π-conjugation and quenches the fluorescence of the aromatic aldimine, performing a turn-off type sensing of cyanide ion.

N-Anthryl aldmine 9d shows a more drastic change upon addition of a cyanide ion. The fluorescence colour of 9d in
interaction have been developed. Many non-fluorescent molecules, which were considered to be non-fluorescent, can be converted into fluorescent molecules by utilizing the co-ordination of its heteroatom to boron or other elements will be useful for converting non-fluorescent or weakly fluorescent molecules to intensely fluorescent molecules. For example, conversion of aromatic thioketone and simple aromatic ketones such as benzophenone, a phosphorescent molecule, into intensely fluorescent molecules by raising the triplet excited state is an interesting subject from the viewpoint of it being the antithesis of common sense.

A popular strategy for molecular design of fluorescent compounds for some applications has been to couple a known fluorescent dye with functional molecules. If we can create new family members of fluorescent dyes by using many π-conjugated structures, we will not need to worry about the difficulty of choosing the correct one among a limited number of fluorescent dyes. We hope that the method of utilizing the intramolecular N–B interaction in this paper is beneficial for people who use fluorescent dyes for practical applications, such as fluorescence chemo-sensors, cell-specific imaging agents, and OLEDs.

5. Conclusions

Incorporation of azobenzene and aromatic aldimines with the intramolecular N–B interaction by using the bis(pentafluorophenyl)boryl group makes these molecules fluorescent. Their fluorescence properties can be easily modified by doubling the N–B interaction or changing the substituents on the benzene rings and the nitrogen atom. Some of them fluoresce with extraordinarily high fluorescence quantum yields. They change their fluorescence properties in response to protons and electrons, and their chemical reactivity shows potential application to fluorescent chemo-sensors. The easily tunable luminescent properties can also be useful for molecular design in applications such as organic light-emitting diodes (OLEDs) and organic light-emitting transistors. This study shows that the π-conjugated molecules, which were considered to be non-fluorescent, can be converted into fluorescent molecules by utilizing the co-ordination of its heteroatom to boron. Actually, some fluorescent aromatic aldimines utilizing an N–B interaction have been developed. Many non-fluorescent

**Scheme 6** Adduct formation of aldimines 9a and 9d with a cyanide ion.

**Fig. 10** Photographs of a benzene solution of aldimine 9d under irradiation by UV light (a) before and (b) after addition of tetrabutylammonium cyanide. The photographs are reproduced from ref. 26 with permission from the Chemical Society of Japan.

benzene changed from yellow to green, with a blue shift of the emission maximum from 547 nm to 500 nm (Fig. 10). This fluorescence colour change can be recognized by the naked eye and has potential for application in the ratiometric detection of cyanide ions. In adduct 12d, the π-conjugated system through the imine moiety is disconnected and the π-conjugation of the anthryl group is delocalized only on the anthryl group and the nitrogen atom, causing 2-aminoanthracene-originated fluorescence.

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**Notes and references**
