

Fluorescent azobenzenes and aromatic aldimines
featuring an N–B interactionCite this: *Dalton Trans.*, 2013, **42**, 15826Junro Yoshino,^a Naokazu Kano^{*b} and Takayuki Kawashima^{*c}Received 25th June 2013,
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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 dipyrromethene (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 dipyrromethene 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 S_0 and S_1 states correspond to the HOMO (π orbital) and

LUMO (π^* orbital), respectively. As a result, BODIPY dyes emit intense fluorescence *via* the S_1 – S_0 relaxation process upon photoirradiation. Thus, this intensely fluorescent fluorophore gains its fluorescent nature by forming N–B dative bonds, while the dipyrromethene 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 facily. 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

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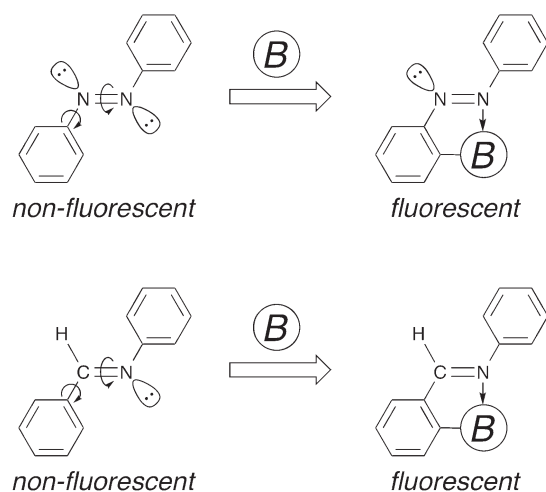


Fig. 1 Concept of the molecular design to make azobenzenes and aromatic aldimines fluorescent upon photoirradiation by formation of an N–B dative bond to restrict both rotation and isomerization.

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.^{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-iodoazobenzenes 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).^{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).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.^{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

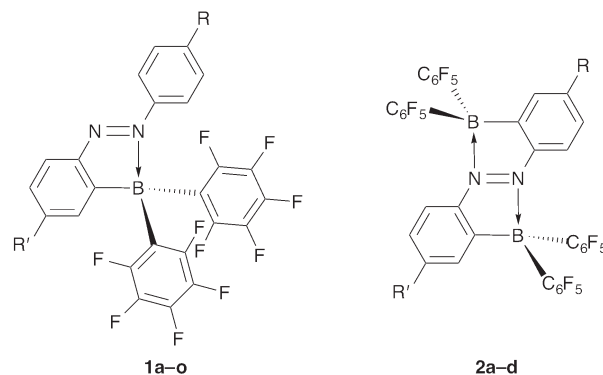
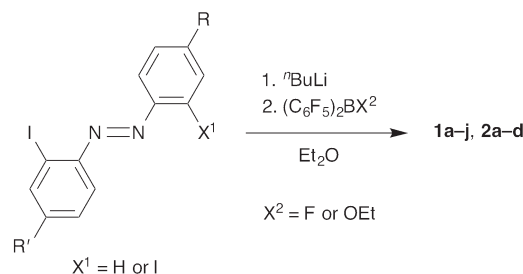


Fig. 2 2-Borylazobenzenes **1a–o** and 2,2'-diborylazobenzenes **2a–d**. Substituents R and R' of **1a–o** and **2a–d** are shown in Tables 1 and 2, respectively.



Scheme 1 Synthesis of 2-borylazobenzenes **1a–j** and 2,2'-diborylazobenzenes **2a–d**.

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 ¹H, ¹¹B, ¹³C, and ¹⁹F NMR spectroscopy, and the crystal structures of **1a**, **1b**, **1e**, and **2a** were determined by X-ray crystallographic analysis. The ¹¹B 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 [1.2704(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)borylazobenzenes **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



Table 1 Substituents at the 4'- and 4-positions (R and R', respectively), absorption wavelength (λ_{abs}), molar absorption coefficient (ϵ), fluorescence wavelength (λ_{em}), fluorescence quantum yield (Φ_{F}), and fluorescence lifetime (τ_{F}) of the 2-borylazobenzenes

	R	R'	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	Φ_{F}	$\tau_{\text{F}}/\text{ns}$
1a	H	H	386 ^a	19 000 ^a	503 ^a	0.20 ^a	3.82(4) ^a
1b	OMe	H	439 ^a	12 000 ^a	524 ^a	0.76 ^a	6.24(5) ^a
1b	OMe	H	446 ^b	14 000 ^b	536 ^b	0.98 ^b	— ^e
1c	NMe ₂	H	516 ^a	55 000 ^a	566 ^a	0.52 ^a	6.17(5) ^a
1d	CF ₃	H	382 ^a	22 000 ^a	511 ^a	0.039 ^a	2.67(3) ^a
1e	F	H	390 ^a	11 000 ^a	504 ^a	0.29 ^a	— ^e
1f	OTBDMS	H	433 ^a	16 000 ^a	524 ^a	0.90 ^a	5.50(2) ^a
1g	ⁿ Bu	H	402 ^a	22 000 ^a	507 ^a	0.31 ^a	— ^e
1h	H	OMe	443 ^a	24 000 ^a	538 ^a	0.048 ^a	<1 ^a
1i	H	Br	416 ^a	23 000 ^a	509 ^a	0.045 ^a	— ^e
1k	H	Ph	445 ^a	22 000 ^a	539 ^a	0.13 ^a	— ^e
1l	H	NPh ₂	553 ^a	28 000 ^a	634 ^a	0.37 ^a	— ^e
1n	O(CH ₂) ₂ N ⁺ Me ₃ I [−]	C≡CCH ₂ N ⁺ Me ₃ I [−]	458 ^c	17 000 ^c	546 ^c	0.53 ^c	— ^e
1n	O(CH ₂) ₂ N ⁺ Me ₃ I [−]	C≡CCH ₂ N ⁺ Me ₃ I [−]	456 ^d	12 000 ^d	552 ^d	0.10 ^d	— ^e
1o	O(CH ₂) ₂ N ⁺ Me ₂ (CH ₂) ₃ SO ₃ [−]	C≡CCH ₂ N ⁺ Me ₂ (CH ₂) ₃ SO ₃ [−]	468 ^c	12 000 ^c	555 ^c	0.14 ^c	— ^e
1o	O(CH ₂) ₂ N ⁺ Me ₂ (CH ₂) ₃ SO ₃ [−]	C≡CCH ₂ N ⁺ Me ₂ (CH ₂) ₃ SO ₃ [−]	460 ^d	13 000 ^d	545 ^d	0.092 ^d	— ^e

^a In hexane. ^b In CH₂Cl₂. ^c In MeOH. ^d In water. ^e Not available.**Table 2** Substituents at the 4- and 4'-positions (R and R', respectively), absorption wavelength (λ_{abs}), molar absorption coefficient (ϵ), fluorescence wavelength (λ_{em}), fluorescence quantum yield (Φ_{F}), and fluorescence lifetime (τ_{F}) of the 2,2'-diborylazobenzenes in hexane

	R, R'	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	Φ_{F}	$\tau_{\text{F}}/\text{ns}$
2a	H	521, 552	20 000, 16 000	572	0.26	1.7
2b	ⁿ Bu	547, 582	9500, 9900	597	0.73	6.7
2c	Br	549, 584	52 000, 58 000	602	0.39	3.7
2d	O ⁿ Bu	603, 646	55 000, 71 000	663	0.62	2.4

higher fluorescence quantum yield. In particular, azobenzene **1b**, which bears an electron-donating methoxy group at the 4'-position, is the most intensely fluorescent azobenzene to date. Its fluorescence quantum yield (Φ_{F} = 0.98 in dichloromethane) is almost 1.00 and extraordinarily high compared with unsubstituted azobenzene (**3**) (Φ_{F} = 2.53×10^{-5}).¹⁶ In azobenzenes **1h**, **1i**, **1k**, and **1l**, the electron-donating group at the 4-position also gives 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.

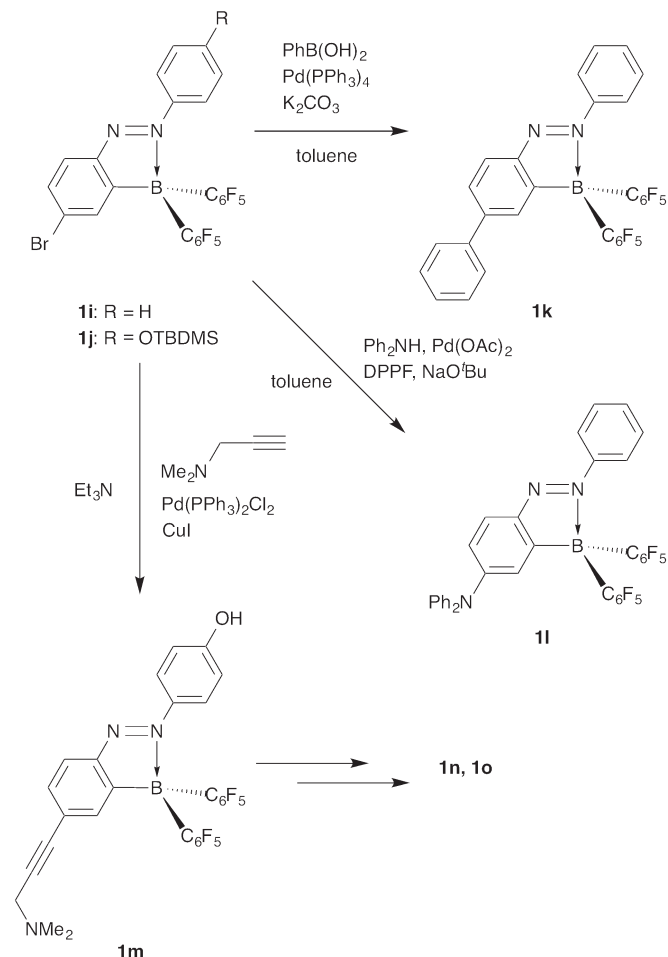
The exceptional fluorescence emission of 2-borylazobenzenes **1a–o** was caused by the blocking of photoisomerization of the azobenzene moiety, enhancement of rigidity of the molecular structure, and the change in nature of the transition between the lowest excited state and the ground state from the optically forbidden $n \rightarrow \pi^*$ transition to the allowed $\pi \rightarrow \pi^*$ transition. The change in the transition was confirmed by TD-DFT calculations.^{11,13} All these factors are provided by the intramolecular N–B interaction, which masks the lone pair of the nitrogen atom of the azo group.

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 dimethylaminoethynyl 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 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-borylazobenzene 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-arylboryl)azobenzenes, replacement of pentafluorophenyl groups on the boron atom with *p*-fluorophenyl groups results in loss of the fluorescent property, and the corresponding azobenzene **4** cannot fluoresce (Fig. 6).¹¹ Other 2-borylazobenzenes **5a–c**,¹⁸ which have a chelate-type diolato ligand on the boron atom, cannot induce fluorescence emission of the azobenzene (Fig. 6). Azobenzenes **6a–c**, which bear two hydroxy groups, a pinacolato group, and an *o*-phenylenediamide group, respectively, no longer hold the N–B dative bond because the Lewis acidity of the boryl groups is weaker than the bis(pentafluorophenyl) group.¹⁹ They do not fluoresce naturally. In contrast, the intramolecular N–B dative bond forms if pentafluorophenyl groups bind to the boron atom, even though the boryl group does not bind directly to the benzene ring of the azobenzene. Actually, 2-boryloxazobenzene **7** fluoresces, but its fluorescence quantum yield (Φ_{F} = 0.033 in





Scheme 2 Palladium-catalysed cross-coupling reactions of **1i** and **1j**.

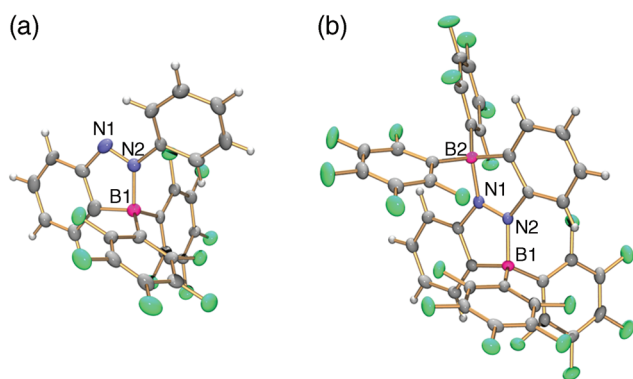


Fig. 3 ORTEP drawings of azobenzenes (a) **1a** and (b) **2a** with a thermal ellipsoid plot (50% probability).

hexane) of the red-shifted fluorescence emission ($\lambda_{\text{max}} = 576$ nm in hexane) is quite low in comparison with 2-borylazobenzene **1a** (Fig. 4 and 6).¹³ The intensely fluorescent, weakly fluorescent, and non-fluorescent azobenzenes so far exemplify the significance of both the existence of strong electron-withdrawing pentafluorophenyl groups on the boron atom and binding of the bis(pentafluorophenyl)boryl group directly to

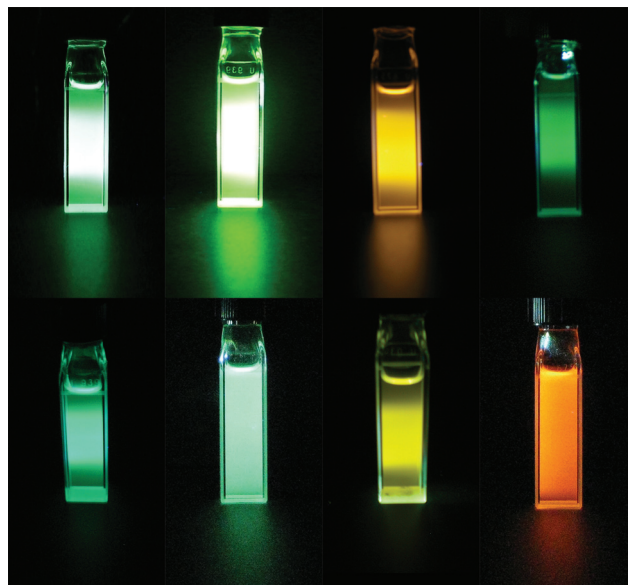


Fig. 4 Photographs of hexane solutions of azobenzenes **1a–e**, **1g**, **1h**, and **7** (from left to right, top to bottom) under irradiation by UV light. The photographs are reproduced from ref. 13 with permission from John Wiley and Sons.

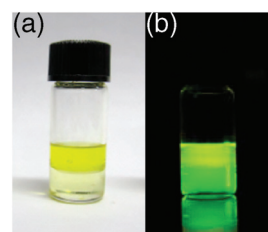


Fig. 5 Photographs of **1n** in water–dichloromethane under irradiation by (a) ambient light and (b) UV light. The upper and lower layers of the sample are water and dichloromethane, respectively. The photographs are reproduced from ref. 14 with permission from Elsevier.

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 π orbital of azobenzene to a π orbital of one of the *p*-fluorophenyl groups. The S_0 – S_1 transition after the replacement results in a forbidden π – π^* transition because of spatial separation, which causes the loss of fluorescence.^{11,13}

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 dative 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

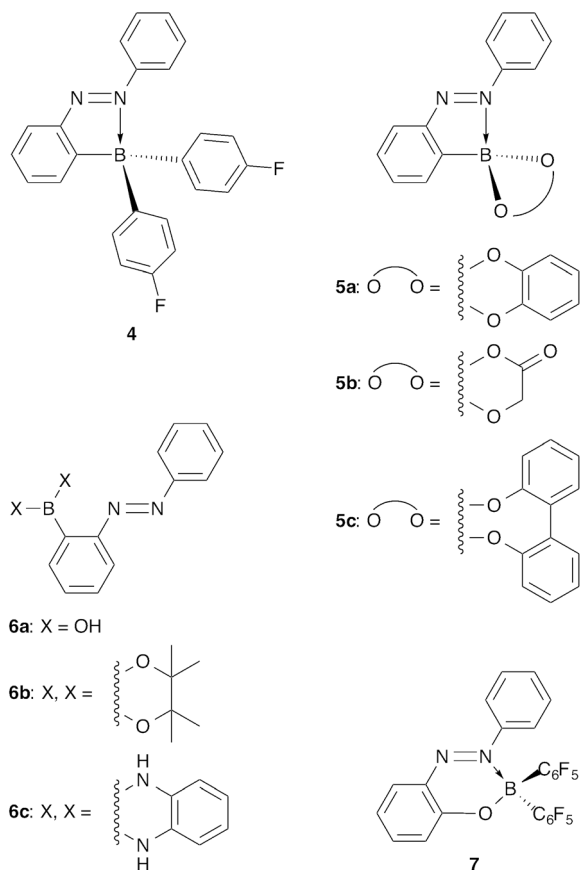


Fig. 6 Non-fluorescent 2-borylazobenzenes **4–6** and fluorescent 2-boryloxyazobenzene **7**.

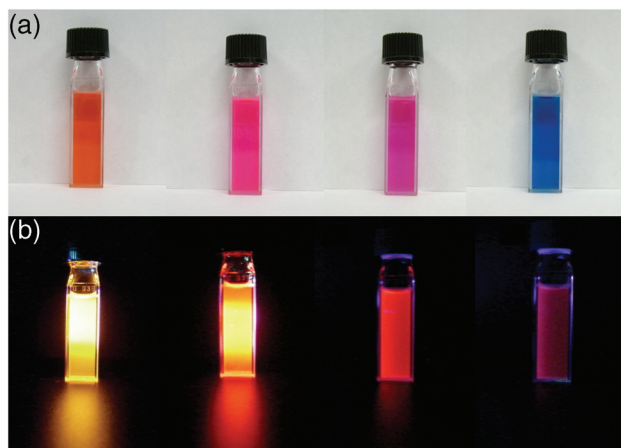


Fig. 7 Photographs of hexane solutions of **2a–d** (from left to right) under irradiation by (a) ambient light and (b) UV light. The photographs are reproduced from ref. 15 with permission from John Wiley and Sons.

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).¹⁵ Another notable point of their

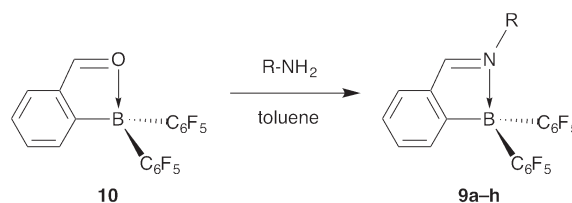
fluorescence properties is their small Stokes shifts (400 to 630 cm^{-1}). Substituent effects on their fluorescence properties are similar to those of 2-monoborylazobenzenes.

3. Fluorescent boron-substituted aromatic aldimines

Replacement of one nitrogen atom of the azo group ($-\text{N}=\text{N}-$) in azobenzene (**3**) with a methine gives another dye molecule, *N*-benzylideneaniline (**8**), which contains an imine moiety ($-\text{CH}=\text{N}-$). 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 $\text{C}=\text{N}$ 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).²⁰ 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 ^{11}B NMR spectra (δ_{B} : -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 $\text{C}=\text{N}$ 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 $\text{C}=\text{N}$ 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 $\text{C}=\text{N}$ 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



Scheme 3 Synthesis of the aromatic aldimines **9a–h**. Substituent R is shown in Table 3.



Table 3 Substituent on the nitrogen atom (R), absorption wavelength (λ_{abs}), molar absorption coefficient (ϵ), fluorescence wavelength (λ_{em}), and fluorescence quantum yield (Φ_{F}) of the boron-substituted aromatic aldimines in hexane

	R	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{em}}^a/\text{nm}$	Φ_{F}
9a	Ph	324	10 000	460	0.0050
9b	4-MeOC ₆ H ₄	366	15 000	466	0.074
9c	4-Me ₂ NC ₆ H ₄	439	25 000	500, 527	0.73
9d	2-Anthryl	442	9100	497, 531	0.39
9e	ⁿ Bu	290	13 000	398	0.011
9f	OMe	296	7600	— ^b	— ^b
9g	1-Indolyl	398	6800	525 (365, 531) ^c	0.0092 (— ^d) ^c
9h	9-Carbazolyl	423	2700	545 (380, 396, 545) ^e	0.0052 (0.020) ^e

^a Excited at λ_{abs} unless otherwise noted. ^b Not detectable. ^c Excited at 290 nm. ^d Not available. ^e Excited at 320 nm.

intramolecular π - π stacking between the nitrogen-containing aromatic rings and one of the pentafluorophenyl groups.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**) ($\Phi_{\text{F}} < 0.0001$).²² In particular, aldimine **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 state²³ 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 $^3(n, \pi^*)$, 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 aldimine **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).

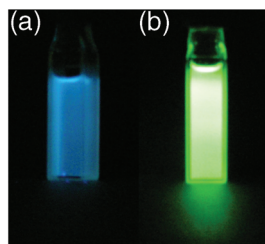


Fig. 8 Photographs of hexane solution of aromatic aldimines (a) **9a** and (b) **9c** under irradiation by UV light. The photographs are reproduced from ref. 20 with permission from the American Chemical Society.

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



observation of the phenotypes revealed its non-toxicity for cells because it did not induce any malformation.¹³ 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).¹² 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-borylazobenzene **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).¹⁵ 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,²⁴ aldimines **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 aldimines with a cyanide ion. However, the reaction of aldimine **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).^{20,25} 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 aldimine **9d** shows a more drastic change upon addition of a cyanide ion. The fluorescence colour of **9d** in

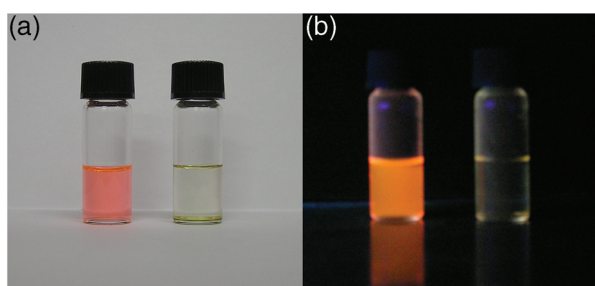
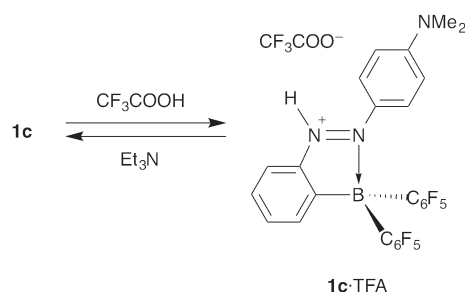
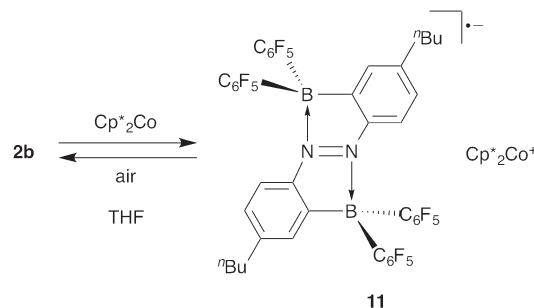


Fig. 9 Photographs of hexane solutions of **1c** under irradiation by (a) ambient light and (b) UV light without (left) and with (right) trifluoroacetic acid. The photographs are reproduced from ref. 12 with permission from the Chemical Society of Japan.

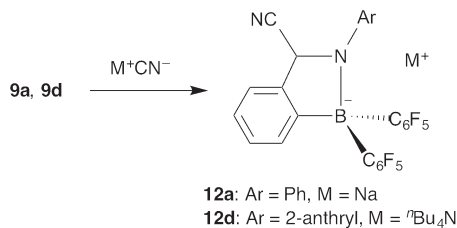


Scheme 4 Acid-base reactions of azobenzene **1c**.



Scheme 5 Reversible reduction of **2b**.





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

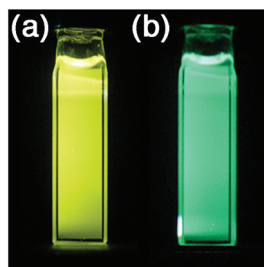


Fig. 10 Photographs of a benzene solution of aldimine **9d** under irradiation by UV light (a) before and (b) after addition of tetrabutylammonium cyanide. The photographs are reproduced from ref. 26 with permission from the Chemical Society of Japan.

benzene changed from yellow to green, with a blue shift of the emission maximum from 547 nm to 500 nm (Fig. 10).²⁶ 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.

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.²⁷ Many non-fluorescent

π -conjugated molecules other than azobenzenes and aromatic aldimines are also anticipated to have fluorescence potential, and they could be applied to some fluorescent materials to provide the fluorescent nature. The method utilizing the intramolecular co-ordination of 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.

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Notes and references

- B. Valeur, *Molecular Fluorescence*, Wiley-VCH, Weinheim, 2002; J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, 3rd edn, 2006.
- A. Treibs and F.-H. Kreuzer, *Liebigs Ann. Chem.*, 1968, **718**, 208; A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891; R. Ziessel, G. Ulrich and A. Harriman, *New J. Chem.*, 2007, **31**, 496; G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184.
- T. D. James, K. Sandanayake and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 1994, 477.
- Y. Wakatsuki, H. Yamazaki, P. A. Grutsch, M. Santhanam and C. Kotal, *J. Am. Chem. Soc.*, 1985, **107**, 8153; M. Shimomura and T. Kunitake, *J. Am. Chem. Soc.*, 1987, **109**, 5175; M. Ghedini, D. Pucci, G. Calogero and F. Barigelletti, *Chem. Phys. Lett.*, 1997, **267**, 341; M. Ghedini, D. Pucci, A. Crispini, I. Aiello, F. Barigelletti, A. Gessi and O. Francescangeli, *Appl. Organomet. Chem.*, 1999, **13**, 565; I. Aiello, M. Ghedini and M. La Deda,



- J. Lumin.*, 2002, **96**, 249; M. Han and M. Hara, *J. Am. Chem. Soc.*, 2005, **127**, 10951; M. R. Han and M. Hara, *New J. Chem.*, 2006, **30**, 223.
- 5 S.-F. Liu, Q. Wu, H. L. Schmider, H. Aziz, N.-X. Hu, Z. Popovic and S. Wang, *J. Am. Chem. Soc.*, 2000, **122**, 3671; C. A. Jask, D. J. H. Emslie, M. J. D. Bosdet, W. Piers, T. S. Sorensen and M. Parvez, *J. Am. Chem. Soc.*, 2006, **128**, 10885; A. Wakamiya, T. Taniguchi and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2006, **45**, 3170; A. Job, A. Wakamiya, G. Kehr, G. Erker and S. Yamaguchi, *Org. Lett.*, 2010, **12**, 5470; Y. Kubota, H. Hara, S. Tanaka, K. Funabiki and M. Matsui, *Org. Lett.*, 2011, **13**, 6544; D. Li, H. Zhang, C. Wang, S. Huang, J. Guo and Y. Wang, *J. Mater. Chem.*, 2012, **22**, 4319; Y. Kubota, S. Tanaka, K. Funabiki and M. Matsui, *Org. Lett.*, 2012, **14**, 4682; S. Shimizu, T. Iino, Y. Araki and N. Kobayashi, *Chem. Commun.*, 2013, **49**, 1621; J.-S. Lu, S.-B. Ko, N. R. Walters, Y. Kang, F. Sauriol and S. Wang, *Angew. Chem., Int. Ed.*, 2013, **52**, 4544.
 - 6 P. Wang, Z. Hong, Z. Xie, S. Tong, O. Wong, C.-S. Lee, N. Wong, L. Hung and S. Lee, *Chem. Commun.*, 2003, 1664.
 - 7 K. Morishige, *J. Inorg. Nucl. Chem.*, 1978, **40**, 843.
 - 8 J. Xie, J. Qiao, L. Wang, J. Xie and Y. Qiu, *Inorg. Chim. Acta*, 2005, **358**, 4451; L. Chen, J. Qiao, J. Xie, L. Duan, D. Zhang, L. Wang and Y. Qiu, *Inorg. Chim. Acta*, 2009, **362**, 2327.
 - 9 H. Rau, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 224; A. Cembran, F. Bernardi, M. Garavelli, L. Gagliardi and G. Orlandi, *J. Am. Chem. Soc.*, 2004, **126**, 3234.
 - 10 N. Kano and T. Kawashima, *TCI Mail*, 2007, **136**, 2.
 - 11 J. Yoshino, N. Kano and T. Kawashima, *Chem. Commun.*, 2007, 559.
 - 12 J. Yoshino, N. Kano and T. Kawashima, *Chem. Lett.*, 2008, 37, 960.
 - 13 J. Yoshino, A. Furuta, T. Kambe, H. Itoi, N. Kano, T. Kawashima, Y. Ito and M. Asashima, *Chem.-Eur. J.*, 2010, **16**, 5026.
 - 14 H. Itoi, T. Kambe, N. Kano and T. Kawashima, *Inorg. Chim. Acta*, 2012, **381**, 117.
 - 15 N. Kano, A. Furuta, T. Kambe, J. Yoshino, Y. Shibata, T. Kawashima, N. Mizorogi and S. Nagase, *Eur. J. Inorg. Chem.*, 2012, 1584.
 - 16 T. Fujino, S. Yu. Arzhantsev and T. Tahara, *J. Phys. Chem. A*, 2001, **105**, 8123.
 - 17 S.-L. Niu, G. Ulrich, P. Retailleau, J. Harrowfield and R. Ziessel, *Tetrahedron Lett.*, 2009, **50**, 3840; S.-L. Niu, G. Ulrich, R. Ziessel, A. Kiss, P.-Y. Renard and A. Romieu, *Org. Lett.*, 2009, **11**, 2049.
 - 18 N. Kano, J. Yoshino and T. Kawashima, *Org. Lett.*, 2005, **7**, 3909; J. Yoshino, N. Kano and T. Kawashima, *Tetrahedron*, 2008, **64**, 7774.
 - 19 K. Ishihara, in *Lewis Acid Reagents: A Practical Approach*, ed. H. Yamamoto, Oxford University Press, New York, 1999, pp. 31–64; J. A. Plumley and J. D. Evanseck, *J. Phys. Chem. A*, 2009, **113**, 5985; B. L. Durfey and T. M. Gilbert, *Inorg. Chem.*, 2011, **50**, 7871.
 - 20 J. Yoshino, N. Kano and T. Kawashima, *J. Org. Chem.*, 2009, **74**, 7496.
 - 21 G. W. Coates, A. R. Dunn, L. M. Henling, J. W. Ziller, E. B. Lobkovsky and R. H. Grubbs, *J. Am. Chem. Soc.*, 1998, **120**, 3641; C. Dai, P. Nguyen, T. B. Marder, A. J. Scott, W. Clegg and C. Viney, *Chem. Commun.*, 1999, 2493; V. R. Vangala, A. Nangia and V. M. Lynch, *Chem. Commun.*, 2002, 1304.
 - 22 M. Belletete and G. Durocher, *Can. J. Chem.*, 1982, **60**, 2332.
 - 23 M. I. Knyazhanskii, M. B. Stryukov and V. I. Minkin, *Opt. Spectrosc.*, 1972, **33**, 484.
 - 24 R. Badugu, J. R. Lakowicz and C. D. Geddes, *J. Am. Chem. Soc.*, 2005, **127**, 3635; C.-W. Chiu, Y. Kim and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2009, **131**, 60.
 - 25 S. Madhu, S. K. Basu, S. Jadhav and M. Ravikanth, *Analyst*, 2013, **138**, 299.
 - 26 J. Yoshino, N. Kano and T. Kawashima, *Bull. Chem. Soc. Jpn.*, 2010, **83**, 1185.
 - 27 Z. García-Hernández and F. P. Gabbaï, *Z. Naturforsch., B: Chem. Sci.*, 2009, **64b**, 1381; B. Neue, R. Frohlich, B. Wibbeling, A. Fukazawa, A. Wakamiya, S. Yamaguchi and E.-U. Wurthwein, *J. Org. Chem.*, 2012, **77**, 2176.

