

Synthesis and Fluorescence Properties of Novel Pyrazine–Boron Complexes Bearing a β -Iminoketone Ligand

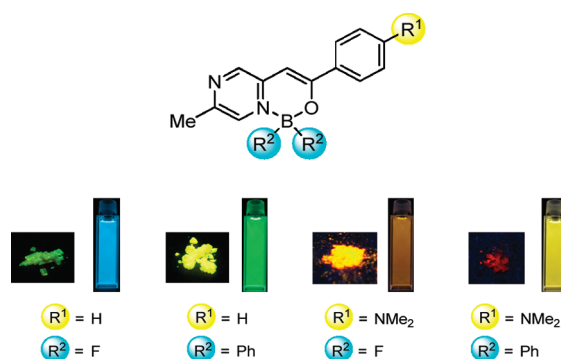
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Received October 21, 2011

ABSTRACT



A novel fluorescence dye based on pyrazine–boron complexes bearing a β -iminoketone ligand has been synthesized by using a simple two-step reaction. Synthesized complexes exhibited fluorescence in solution (F_{max} : 472–604 nm) and in the solid state (F_{max} : 496–624 nm). These complexes showed a larger Stokes shift (3690–4900 cm^{-1}) than well-known boron dipyrromethene dyes (400–600 cm^{-1} , in most cases).

Organoboron complexes are one of the most important fluorescent dyes. Fluorescent organoboron complexes such as pyrrromethene,¹ diketone,² pyridomethene,³ subphthalocyanine,⁴ subporphyrin,⁵ azobenzene,⁶ and others⁷

have been reported. In particular, boron dipyrromethene (BODIPY) is known to show excellent optical properties

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such as high fluorescence quantum yield, sharp absorption and fluorescence emission spectra, and high photo- and chemical stability. Therefore, BODIPY dyes have played increasingly important roles in many fields involving molecular probes,⁸ photodynamic therapy,⁹ laser dyes,¹⁰ and solar cells.¹¹ However, most BODIPY dyes have a very small Stokes shift (400–600 cm⁻¹, in most cases) because they have a rigid molecular structure with minimal differences between the ground- and excited-state structures.¹² Such a small Stokes shift makes it difficult for optical filters to cut the excitation light, making it difficult to read the fluorescence signal over the noise in a bioassay.^{12a} A small Stokes shift also induces the reabsorption of its own fluorescence, which causes a reduction in fluorescence intensity. Also, most BODIPY dyes have high planarity, which increases intermolecular interactions, causing concentration quenching in the solid state.¹³ Thus, they hardly exhibit fluorescence in the solid state.¹⁴ Recently, we reported on a pyridomethene–BF₂ complex that is an analog of a BODIPY dye.^{3d} Although this complex exhibited fluorescence in the solid state, the Stokes shift was very small in solution (250–400 cm⁻¹). In this paper, we report the synthesis and fluorescence properties of a novel pyrazine–boron complex that exhibits solid-state fluorescence and has a large Stokes shift (3690–4900 cm⁻¹).

The THF solution of 2,5-dimethylpyrazine and ethyl benzoate was refluxed in the presence of sodium hydride to yield a tautomeric mixture of iminoketone **1a** and iminoenol **1b** (Scheme S1, Table S1). The reaction of the tautomeric mixture **1** with trifluoroborane gave pyrazine-containing BF₂ complex **4** (Scheme 1). Furthermore, **1** was easily reacted with triphenylborane in THF at rt to give BPh₂ complex **7**. Although this result is different from the reaction of pyrromethene with triphenylborane, which does not yield the BPh₂ complex, it is consistent with that

of diketone with triphenylborane, which gives the BPh₂ complex.¹⁵ The structures of **4** and **7** were confirmed by X-ray crystallography (Figures 1, S1).

Scheme 1. Synthesis of Pyrazine–Boron Complexes

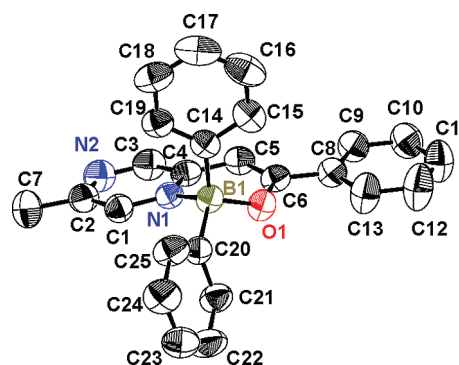
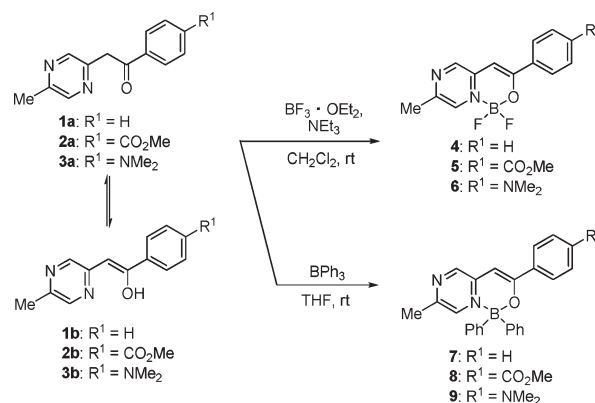


Figure 1. ORTEP view of **7**. Hydrogen atoms have been omitted for clarity.

The absorption and fluorescence spectra of **1**, **4**, and **7** in dichloromethane are shown in Figure 2. Compound **4** exhibited a maximum absorption wavelength (λ_{max}) at 403 nm, which is more bathochromic than **1** (364 nm). Although **1** exhibited no fluorescence, **4** showed blue fluorescence at 480 nm. The λ_{max} of **7** (427 nm) was red-shifted compared to that of **4** (402 nm), and the molar absorption coefficient (ϵ) of **7** (14 000) was lower than that of **4** (24 000). The maximum fluorescence wavelength (F_{max}) of **7** (520 nm) also exhibited a red shift compared to that of **4** (480 nm). As a result, **7** exhibited yellow-green fluorescence. The absolute fluorescence quantum yields (Φ_f) of **4** and **7** in dichloromethane were 0.57 and 0.70, respectively. Interestingly, **4** (3980 cm⁻¹) and **7** (4190 cm⁻¹) exhibited a larger Stokes shift than a fluorescent boron complex such as a BODIPY dye (400–600 cm⁻¹) and a pyridomethene–BF₂ complex (250–400 cm⁻¹). This large Stokes shift may be due to the flexible structure of the pyrazine–boron complex bearing a β -iminoketone ligand at the excited state.¹²

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The $\lambda_{\max}$ and $F_{\max}$ of **4** and **7** were slightly affected by solvent polarity. In hexane, the spectra of **4** and **7** showed vibrational transitions due to exclusion of solvation relaxation¹⁵ (Figures S2–S5 and Tables S2, S3).

Two crystallographically independent conformers, **4A** and **4B**, are identified in the unit cell of **4** ($Z' = 2$), whereas one conformer is found in that of **7** ($Z' = 1$) (Figure S1). The geometrical structures of **4A** and **4B** are almost same. In the crystal structures of **4A** and **4B**, the six-membered ring consisting of the boron atom (B1 or B2) and the iminoenolate (N1–C4–C5–C6–O1 or N3–C17–C18–C19–O2) is almost planar. Yet, in the case of **7**, the six-membered ring that contains atoms N1, C4, C5, C6, and O1 does not form a plane. B1, C6, and O1 atoms are out of the plane of N1–C4–C5; B1 is 0.23 Å above the plane; and C6 and O1 are 0.24 and 0.39 Å, respectively, below the plane (Figure S6). The B1–N1 (1.64 Å) and B1–O1 (1.48 Å) distances of **7** are greater than those of **4A** and **4B** (B1–N1 and B2–N3 are 1.59 Å; B1–O1 and B2–O2 are 1.43 Å). As a result, the molecule of **7** is slightly bent. The spectral red shift and decrease in the extinction coefficient of **7** may be attributed to this molecular bend.¹⁷ The dihedral angle of **7** between the C5–C6–O1 plane and the phenyl ring is 1.4°. The corresponding dihedral angles of **4A** and **4B** are 6.7° and 13.6°, respectively. Therefore, the phenyl group is considered to contribute to the expansion of π conjugation.

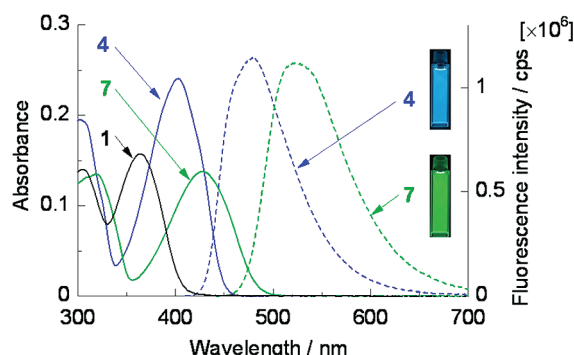


Figure 2. UV–vis absorption and fluorescence spectra of **1**, **4**, and **7** in dichloromethane measured at a concentration of 1×10^{-5} mol dm⁻³ of substrate at 25 °C. Solid and dotted lines represent absorption and fluorescence spectra, respectively.

Compounds **2**, **3**, **5**, **6**, **8**, and **9** were obtained by a similar reaction (Schemes 1 and S1). The absorption and fluorescence spectra of **1**–**3** in dichloromethane are shown in Figure S7. Although **1** and **2** did not show fluorescence, **3** exhibited weak blue fluorescence at 390 nm ($\Phi_f = 0.03$).

The absorption and fluorescence spectra of **4**–**9** in dichloromethane are shown in Figures S8 and S9. As in the case of phenyl derivatives **1** and **4**, the absorptions of

the BPh₂ complexes **8** (429 nm) and **9** (474 nm) are more bathochromic than those of the corresponding BF₂ complexes **5** (402 nm) and **6** (466 nm). The ϵ of the BPh₂ complexes **8** (17 000) and **9** (35 000) are lower than those of the corresponding BF₂ complexes **5** (27 000) and **6** (46 000). Methoxycarbonyl-group-substituted derivatives **5** and **8** exhibited similar absorption and fluorescence properties compared to the corresponding unsubstituted derivatives **4** and **7**. On the other hand, owing to the push–pull effect, dimethylamino derivatives **6** and **9** exhibited a spectral red shift and an increase in the ϵ in the absorption spectra. The Φ_f of **6** and **9** were relatively lower (Table 1).

Table 1. Optical Properties of Pyrazine–Boron Complexes

compd	R ¹	R ²	dichloromethane ^a				solid state	
			$\lambda_{\max}$ (ϵ) (nm)	$F_{\max}$ (nm)	Stokes shift (cm ⁻¹)	ϕ_f^b	$F_{\max}$ (nm)	ϕ_f^b
4	H	F	403 (24,000)	480	3980	0.57	526	0.04
5	CO ₂ Me	F	402 (27,000)	472	3690	0.32	553	0.32
6	NMe ₂	F	466 (46,000)	604	4900	0.07	597	0.11
7	H	Ph	427 (14,000)	520	4190	0.70	553	0.27
8	CO ₂ Me	Ph	429 (17,000)	520	4080	0.71	540	0.18
9	NMe ₂	Ph	474 (35,000)	583	3940	0.28	624	0.03

^a Measured at a concentration of 1.0×10^{-5} mol dm⁻³ at 25 °C.

^b Measured using a FluoroMax-4 spectrofluorometer.

To obtain theoretical results for the absorption properties of **4**–**9**, DFT calculations were performed with the Gaussian 09 package.¹⁸ The geometries of **4**–**9** were optimized at the DFT/B3LYP level using a 6-31G (d,p) basis set. TDDFT calculations were also performed using the B3LYP/6-311++G(d,p) method. The calculated $\lambda_{\max}$, the main orbital transition, and oscillator strength f are listed in Table S4. These calculated $\lambda_{\max}$ values are consistent with the experimental ones. In all the cases, the first and second absorptions are mostly attributed to the transitions from HOMO to LUMO and the transitions from HOMO

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to LUMO+1, respectively. All of the HOMO and LUMO orbitals are delocalized over the entire set of molecules (Figure S10). In the case of dimethylamino derivatives **6** and **9**, calculations indicate that the charge transfer (CT) transition might have occurred from the (dimethylamino)-phenyl group to the pyrazine moiety. The CT transition is considered to cause the red-shifted absorptions of **6** and **9**.

Interestingly, all of the synthesized pyrazine–boron complexes showed fluorescence in the solid state (Figure S11). The fluorescence spectra and Φ_f of **4**–**9** in the solid state are shown in Figure S12 and Table 1, respectively. The kind of substituent groups on the boron atom and the phenyl ring has an effect on the solid-state fluorescence properties. As in the case of the solution, the solid-state fluorescence spectra of **6** and **9** exhibited greater bathochromic shifts and lower Φ_f . To explain the difference in the Φ_f , we conducted X-ray crystallographic studies of **4**, **6**, **7**, and **9**. In the crystal packing of **4**, **4A** and **4B** formed independent stacking columns (Figure S13). In the column of **4A**, gray and orange molecules formed dimers by intermolecular CH/ π interactions (C–C: 3.51 Å) and CH/F interactions (C–F: 3.37 Å). Furthermore, networks of CH/F interactions (C–F: 3.30–3.37 Å) were observed for the dimers. Similarly, networks of CH/F interactions (C–F: 3.23–3.36 Å) were observed in the column of **4B**. It has been known that strong and continuous intermolecular interaction between neighboring fluorophores causes fluorescence quenching in the solid states.¹³ Due to the strong networks of CH/F interactions, **4** exhibited low Φ_f (0.04) in the solid state.

Yet, in the crystal packing of **7**, although dimers were formed between orange and gray molecules by CH/ π (C–C: 3.50 Å) and π/π interactions (C–C: 3.45–3.55 Å), there was no interaction between adjacent dimers (Figures 3 and S14). Because network interactions were avoided by the substitution of fluorines to phenyl groups, **7** exhibited relatively high Φ_f (0.27).

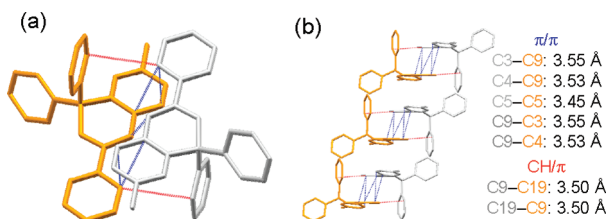


Figure 3. (a) Top view of crystal structure of **7**. (b) Side view of crystal structure of **7**. Hydrogen atoms have been omitted for clarity. The blue and red dotted lines show intermolecular π/π interactions and CH/ π interactions, respectively.

The ORTEP drawing and crystal packing of **9** are shown in Figures 4, S15, and S16. Similar to **7**, in the crystal packing of **9**, orange and gray molecules formed dimers by CH/ π (C–C: 3.53 Å) and π/π interactions (C–C: 3.22–3.57 Å). However, unlike the case of **7**, π/π interactions (C–N: 3.40 Å) were observed between neighboring dimers. As a result, networks of π/π interactions were formed in the crystal packing

of **9**. Thus, networks of strong π – π interactions induced fluorescence quenching in the solid state of **9** (Φ_f = 0.03).

The ORTEP drawing and crystal packing of **6** are shown in Figures S17 and S18, respectively. In the case of **6**, although networks of π/π interactions (C–C: 3.52–3.55 Å) were observed, the interactions were weaker than those of **9** (C–C: 3.22–3.57 Å). Because compound **6** had weak intermolecular interactions, **6** exhibited relatively weak fluorescence in the solid state (Φ_f = 0.11).

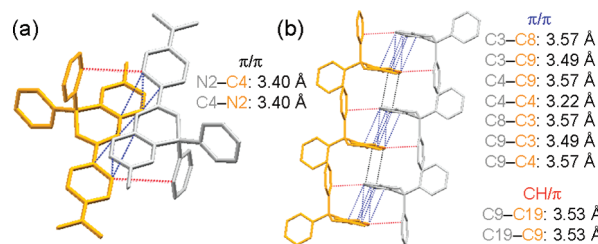


Figure 4. (a) Top view of crystal structure of **9**. (b) Side view of crystal structure of **9**. Hydrogen atoms have been omitted for clarity. The blue, black, and red dotted lines show intermolecular π – π interactions (C–C), π/π interactions (C–N), and CH/ π interactions, respectively.

In conclusion, we have shown that pyrazine–boron complexes bearing a β -iminoketone ligand can be easily synthesized from methylpyrazine and benzoate derivatives. All synthesized complexes exhibited fluorescence in dichloromethane. The $F_{\max}$ (472–604 nm) and Φ_f (0.28–0.71) were affected by the kind of substituents on the boron atom and the phenyl group. Unlike common fluorescent boron complexes such as BODIPY dyes, pyrazine–boron complexes exhibited a large Stokes shift (3690–4900 cm^{-1}). Although BODIPY dyes have a rigid fluorophore, pyrazine–boron complexes have a relatively flexible fluorophore owing to the molecular rotation of the aryl group. Since the flexible fluorophore causes large differences between the ground- and excited-state structures, pyrazine–boron complexes may show large Stokes shifts. Furthermore, these complexes exhibited fluorescence in the solid state (Φ_f : 0.03–0.32). Relationships between the solid-state Φ_f and molecular packing of pyrazine–boron complexes were obtained by X-ray crystallographic analysis. The Φ_f of **4** (0.04) and **9** (0.03) were low owing to networks of CH/F interactions and strong π/π interactions, respectively. The relatively lower Φ_f of **6** (0.11) was caused by networks of weak π/π interactions. Compound **7** exhibited a relatively high Φ_f (0.27) due to the prevention of network interactions.

Acknowledgment. This work was supported by Grant-in-Aid for Young Scientists (B) (23750228).

Supporting Information Available. Details of experimental procedures and copies of ^1H , ^{13}C NMR, and 2D spectra for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.