

Dibenzoborole-Containing π -Electron Systems: Remarkable Fluorescence Change Based on the “On/Off” Control of the $p_{\pi}-\pi^*$ Conjugation

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Boron-containing π -electron systems have recently attracted much attention^{1–5} because of their intriguing electronic and photophysical properties due to the $p_{\pi}-\pi^*$ conjugation through the vacant p-orbital of the boron atom. One notable aspect may be the control of this conjugation, which provides an opportunity to modify the properties of these systems.⁶ We recently reported a new fluoride ion sensor using tri(9-anthryl)borane, in which the binding of a fluoride ion onto a boron atom turns off the $p_{\pi}-\pi^*$ conjugation in the LUMO, resulting in a color change from orange to colorless.⁷ We now apply this concept to a new π -electron system consisting of a dibenzoborole skeleton. In this system, the “on/off” control of the $p_{\pi}-\pi^*$ conjugation by the addition of a donor molecule would change the LUMO delocalization mode from “mode A” to “mode B”, as shown in Figure 1. This change would significantly increase the HOMO–LUMO gap and cause a hypsochromic shift in the absorption and fluorescence maxima, but the resulting LUMO in mode B would still be delocalized over the carbon framework as a normal π -conjugated system. Thus, we expect that this change would lead to a photophysical response in the visible region.

To examine this idea, we employed a series of dibenzoborole derivatives, including the parent dibenzoborole **1** and its extended derivatives with (diphenylamino)phenyl (**2**), thienyl (**3**), and bithienyl (**4**) groups at the 3,7-positions (Scheme 1); a bulky 2,4,6-triisopropylphenyl (Tip) group is introduced onto a boron atom for kinetic stabilization.

The parent **1** was prepared by the metalation of dibromobiphenyl **5a**, followed by treatment with TipB(OMe)₂. Similarly, the use of diiodo-dibromobiphenyl **5b** allowed us to synthesize the 3,7-dihalogenated dibenzoboroles **6** and **7**, and the Kosugi–Migita–Stille coupling of the diiodide **7** with appropriate arylstannanes in the presence of Pd₂(dba)₃/P(furyl)₃ catalyst⁸ successfully afforded the extended compounds **2–4**. All the synthesized dibenzoborole derivatives are air- and moisture-stable due to steric protection by the Tip group.

Although the absorption spectra have already been reported for a few dibenzoborole derivatives,⁹ little is known about the fluorescence properties of these compounds. We now find that the parent dibenzoborole **1** has a fluorescence property distinct from those of the carbon and nitrogen analogues, fluorene and carbazole. Thus, in THF, **1** shows a characteristic weak shoulder band at 410 nm (log ϵ = 2.39) in the UV–visible absorption spectrum and exhibits a green fluorescence at 514 nm with a low quantum yield of 0.09. The large Stokes shift (~100 nm) and the considerably longer emission maximum ($\Delta\lambda_{\text{max}}$ = 160–200 nm) compared to those of fluorene (λ_{em} = 314 nm)¹⁰ and carbazole (λ_{em} = 349 nm)¹⁰ suggest the significant contribution of the boron vacant p-orbital

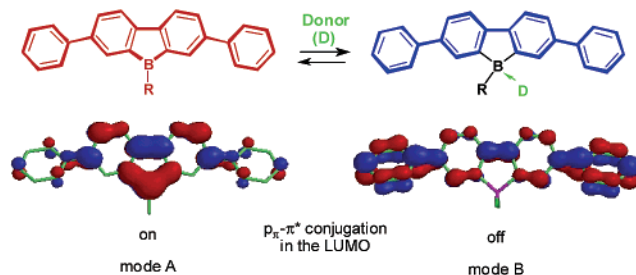
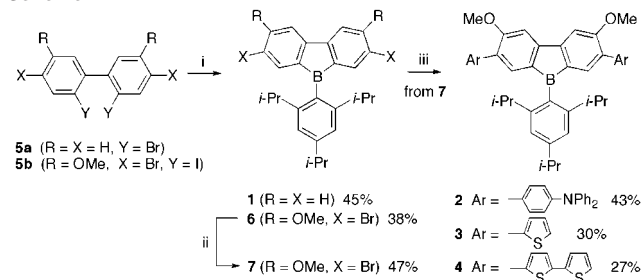


Figure 1. The “on/off” control of the $p_{\pi}-\pi^*$ conjugation in the LUMO of dibenzoborole-containing π -electron systems.

Scheme 1^a



^a Reagents and conditions: (i) (1) Mg (2.1 mol amount), THF, or *n*-BuLi (2.2 mol amount) in THF then MgBr₂ (3.0 mol amount), (2) TipB(OMe)₂ (1.0–1.4 mol amount); (ii) (1) *t*-BuLi (4.4 mol amount) Et₂O, (2) ICH₂CH₂I (4.4 mol amount); (iii) ArSnBu₃ (3.0 mol amount) Pd₂(dba)₃ (0.05 mol amount), P(furyl)₃ (0.2 mol amount), THF.

to the photophysical properties. Actually, the shoulder band of **1** in the absorption spectrum can be ascribed to the transition from the HOMO delocalized over the biphenyl moiety to the LUMO delocalized over the dibenzoborole skeleton through the $p_{\pi}-\pi^*$ conjugation.¹¹

Based on this fundamental feature of the dibenzoborole skeleton, the extended π -conjugated compounds **2–4** also show notable photophysical properties, as summarized in Table 1. In THF, while these compounds have weak absorption bands around 480–504 nm, they show yellow to orange emissions around 550–576 nm, with low quantum yields. The large red shifts in their absorption and emission maxima, by about 70–100 nm and 35–60 nm, respectively, relative to those of **1** suggest that the π -conjugation is substantially extended along with the carbon framework. More importantly, we found that the fluorescence properties of **2–4** are highly dependent on the solvent. Thus, in donor solvents such as DMF,¹² the emission bands observed in THF completely disappear, and new intense blue emission bands appear around 419–478 nm, the quantum yields of which are dramatically increased to about 0.5–0.9. Thus, about 100–140 nm blue shifts and 20–30-fold increments in the quantum yields are observed by changing the

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Table 1. Photophysical Data of Dibenzoborole π -Electron Systems

compd	solvent or additive	absorption $\lambda_{\text{max}}/\text{nm}$ (log ϵ)	fluorescence $\lambda_{\text{max}}/\text{nm}$ (Φ_f) ^a
2	THF	480 (3.08), 361 (4.65)	561 (0.030) ^c
	DMF	479 (2.72), 372 (4.71)	423 (0.89) ^{d,e}
	TBAF/THF ^b	374 (4.78)	419 (0.92) ^d
3	THF	488 (2.95), 394 (4.33)	550 (0.041) ^c
	DMF	389 (4.56)	419 (0.88) ^d
	TBAF/THF ^b	400 (4.65)	417 (0.86) ^d
4	THF	504 (3.51), 405 (4.67)	576 (0.022) ^c
	DMF	498 (3.11), 425 (4.72)	478 (0.55) ^{d,e}
	TBAF/THF ^b	428 (4.82)	478 (0.42) ^d

^a Excited at the longest absorption maximum wavelengths, unless otherwise stated. The Φ_f is the average values of repeated measurements within $\pm 5\%$ errors. ^b n -Bu₄NF in THF. The data for the produced borates are those at the saturated points of the spectral changes upon addition of TBAF. ^c Determined using fluorescein as a standard. ^d Determined using quinine sulfate as a standard. ^e Excited at the second longest absorption maximum wavelength.

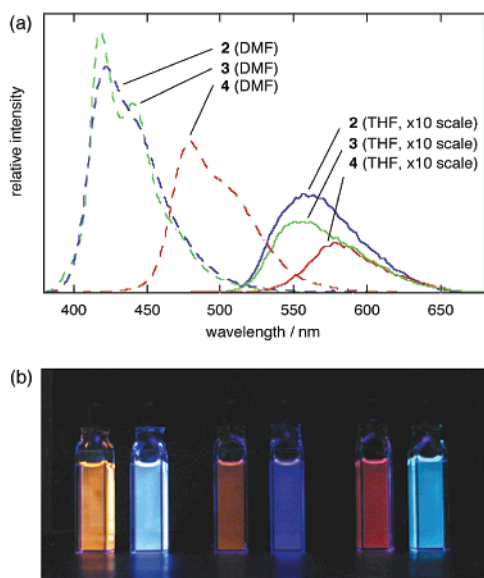
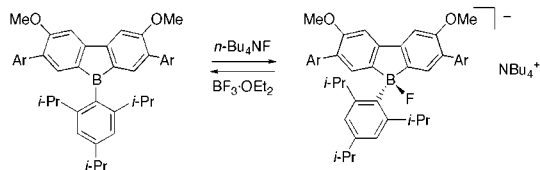


Figure 2. Solvent-dependent fluorescence of **2–4**. (a) Fluorescence spectra. (b) Photograph of their solutions under irradiation by 365 nm light. From left to right: **2** in THF and DMF, **3** in THF and DMF, **4** in THF and DMF (ca. 1 μM).

Scheme 2

solvent from THF to DMF. Figure 2 shows the spectral and visual changes in their fluorescence, which is dependent on the solvents.

We assumed that this solvatochromism is attributable to the coordination of the donor solvent to the boron atom, which prevents the occurrence of the $p_{\pi}-\pi^*$ conjugation in the LUMO. On the basis of this consideration, we next studied the sensing ability of the present boron system toward a fluoride ion. Upon the addition of a THF solution of n -Bu₄NF as a fluoride source to a THF solution of **2** (Scheme 2), the emission band of **2** at 561 nm indeed became weak, and the intensity of the fluorescent band at 419 nm significantly increased (see the Supporting Information). Eventually, the final spectrum was nearly identical with that in DMF. Similar fluorescence changes were observed for the other extended systems

of **3** and **4**. The binding constants toward the fluoride ion determined by these fluorescence titration experiments were $3.5 (\pm 0.4) \times 10^5 \text{ M}^{-1}$ for **2**, $1.1 (\pm 0.5) \times 10^6 \text{ M}^{-1}$ for **3**, and $1.4 (\pm 0.3) \times 10^6 \text{ M}^{-1}$ for **4** at 20 °C. Moreover, the produced borates can be changed back to the starting dibenzoboroles without decomposition by treatment with a stronger fluoride scavenger such as $\text{BF}_3 \cdot \text{OEt}_2$. These results not only support our assumption concerning the origin of the solvatochromism but also demonstrate the significant potential of the present boron system as a new type of fluorescent sensor for the fluoride ion.¹³ It should be noted that the output of the fluoride binding events is the “turn-on” of the fluorescence in terms of the intensity increase along with the dramatic fluorescence color changes in the visible region. Further detailed studies on the photophysics of the dibenzoborole π -electron systems are now in progress.

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Supporting Information Available: Analytical and spectral data for **1–4** and fluorescence spectra for the titration experiments (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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