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Simple and valid strategy for the enhancement of the solid-emissive property of boron dipyrromethenes

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ABSTRACT

This manuscript presents the strategy for obtaining solid-emissive properties from the BODIPY dyes. It is demonstrated that the emission properties can be preserved from the aggregation-caused quenching (ACQ) by introducing the phenyl groups into their boron center. We established the synthetic procedures for the introduction of single or dual phenyl groups into the boron center in BODIPYs. The synthesized BODIPYs having single and dual-phenyl groups showed unimodal photoluminescence spectra both in the solution and solid states with sufficient quantum yields. The pristine and the single-phenyl substituted BODIPYs showed similar optical properties in the solution state. In contrast, the dual-phenyl substituted BODIPY provided broad and red-shifted photoluminescence spectrum. Interestingly, the emission property of the dual-substituted BODIPY was recovered not only in the solid state but also in the viscous solvent. It was revealed that the suppression of the molecular motion should play a crucial role in the enhancement of the emission properties of the dual-substituted BODIPY. Furthermore, it is also presented that the steric hindrance by the phenyl groups can inhibit ACQ in the condensed state.

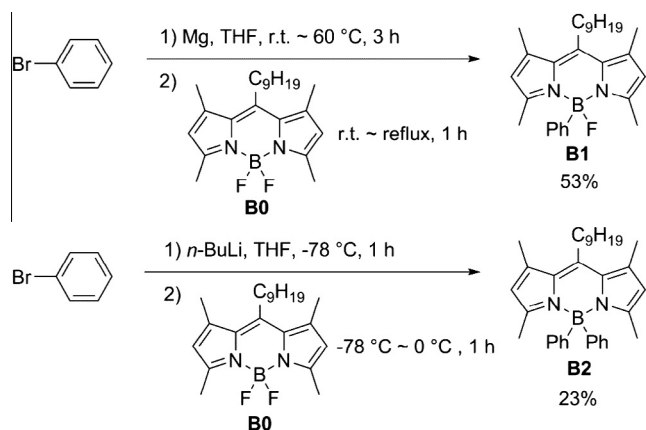
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Boron dipyrromethenes (BODIPYs) are well known as a commodity luminescent dye because of their various advantages such as large absorption and luminescent abilities in the narrow wavelength regions, high photo-stability, and environment-resistant emissive properties.¹ Based on these useful characteristics, we regarded BODIPY derivatives as an attractive element block which is defined as a functional building block including heteroatoms for constructing advanced materials.² Indeed, BODIPYs and their derivatives have been applied not only for emissive materials in an organic optical device³ but also for the molecular probes as a biotechnical tool.⁴ However, optical properties of BODIPYs would be drastically changed in the aggregation state^{5a,b} and sometimes spoiled in the condensed states via the aggregation-induced quenching (ACQ).^{5c,d} The planarity of the dipyrromethene ligand can be greatly enhanced by the complexation with boron. Subsequently, specific or non-specific intermolecular interactions via stacking and adhesion readily occur in the condensed states, resulting in the undesired changes or the loss of the bright green-light emission.^{5c,d} In particular, since materials are used as a thin film in the common organic devices, the crucial changes in the optical properties of BODIPYs in the solid materials should be still the emerging problem to be solved.

One of the most common strategies for avoiding ACQ is to introduce the bulky substituents into the molecules. There are the series of successful examples based on conjugated molecules for realizing solid emissions based on this strategy.⁶ By combining the bulky groups or other units which can hardly influence the electronic state of the conjugation system, the emission properties in the diluted solution were maintained in the condensed state. We recently reported the validity of the cardo structure in polyfluorene for improving the emissive properties in the film state.⁷ The introduction of the dual-phenyl groups into the fluorene moiety played a crucial role in the preservation of the emissions even in the film state. Furthermore, this strategy was also applied for obtaining the solid-emissive BODIPYs.⁸ The modified BODIPYs with the bulky substituents at the ligand moiety showed significant emissions even in the solid state in the previous Letters.⁸ Although the emission quantum efficiencies were apparently maintained in the solid state in these researches, the shapes of the emission spectra were often divergent from that of the general BODIPY dyes. Therefore, the molecular design strategy to preserve the optical properties of BODIPYs is still required for realizing the highly-efficient emissive solid materials.

Most of BODIPYs have two fluorine atoms on their boron atoms. In particular, these fluorine atoms can be replaced by other substituents. Ziessel and co-workers reported the BODIPYs bearing aryl substituents at the boron center.⁹ Matsui and co-workers reported the solid-emissive BODIPY by introducing two phenyl

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Scheme 1. Modifications of the boron atoms for preparing phenyl-substituted BODIPYs.

groups at boron atom.¹⁰ However, to the best of our knowledge, the report on the solid emission of the modified BODIPY with heterogeneous types of the aryl substituents at the boron center was still very few although several synthetic routes have been established.¹¹ Herein, we present syntheses and optical properties of the phenyl-substituted BODIPYs. Initially, the synthetic procedures were established for preparing the BODIPY derivatives having single or dual phenyl groups at the boron center. Next, with the series of optical measurements, the emissive properties of the synthesized BODIPYs were examined. Especially, the influence of the phenyl groups on the emissive properties in the solid state was evaluated. The mechanisms on the solid emissive properties were also mentioned in this manuscript.

The modification of the boron in the BODIPYs is outlined in Scheme 1. We used the difluorinated compound **B0** as a starting material.¹² The bright emission was obtained from the solid state in the Matsui's work.¹⁰ However, the multi-modal emission bands were observed. In this Letter, it was suggested that the local inhomogeneity such as crystal formation could provide the diverse emission bands. To achieve homogeneous amorphous state in the solid sample, the longer alkyl chains were introduced into the *meso* position. The introduction of the single phenyl group required the sensitive control of the reaction condition. In the Ref. 9, the substitution reaction proceeded at 0 °C in the presence of 2 equiv of a Grignard reagent. On the other hand, the reaction hardly occurred at 0 °C in our case. In addition, the dual substitution was observed by increasing reaction time. Thus, we performed the reaction with reflux temperature for 1 h. Finally, the single-substituted BODIPY **B1** was obtained from **B0** with a good yield. To proceed the substitution reaction for obtaining the dual-substituted BODIPY **B2**, the lithiation with *n*-butyllithium was applied. The products showed good solubility in the common organic solvents such as chloroform, THF, and ethanol. The structures of all compounds were

Table 1
Optical properties of the modified BODIPYs in the solutions^a

	λ_{abs} (nm)	ϵ^b ($\text{M}^{-1}\text{cm}^{-1}$)	λ_{em}^c (nm)	Φ_{PL}^d	τ^e (ns)
B0	500	92,000	511	0.81	6.35
B1	500	89,200	511	0.79	6.22
B2	497	88,000	539	0.34	3.36

^a In chloroform (1.0×10^{-5} M).

^b Determined at the peak in the longest wavelength band.

^c Excited at 473 nm (for **B0** and **B1**) and 469 nm (for **B2**).

^d Determined as an absolute value.

^e Excited at 375 nm.

confirmed by ^1H , ^{11}B , ^{13}C NMR spectroscopies and ionization mass measurements (Figs. S1 and S2).

Initially, the UV–vis absorption spectra were compared to evaluate the influence of the modification at the boron center on the electronic states in the ground state (Fig. 1a). The optical properties are listed in Table 1. From the solutions in chloroform (1.0×10^{-5} mol/L), similar absorption spectra were obtained from all three BODIPYs. Typical spectra to the common BODIPYs were observed; large molar extinction coefficients and sharp absorption bands with the peaks at 500 nm attributable to $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transition. These data indicate that the electronic structures in the ground state should be hardly influenced by the substituents.

Figure 1b shows the photoluminescence spectra of the modified BODIPYs in chloroform (1.0×10^{-5} mol/L). Interestingly, the emission spectrum of **B2** was different from those of **B0** and **B1**. **B0** and **B1** showed typical emission properties of BODIPYs. In contrast, **B2** showed a broad and red-shifted emission band. The emission color of **B2** was varied from those of **B0** and **B1**. The quantum yield of **B2** was crucially lower than those of **B0** and **B1**. From the lifetime measurements, it was confirmed that all BODIPYs showed fluorescence emission. Significantly, **B2** presented the shorter lifetime than those of **B0** and **B1** (Table 1). From these data, it can be summarized that the second phenyl substituent in **B2** should perturb the electronic structure of BODIPY only in the excited state.

To receive the information on the electronic states of the synthesized compounds, the computer calculations were performed. We optimized the geometries of the modified BODIPYs by the density functional theory (DFT) and calculated their transitions from S_0 to S_1 by the time-dependent DFT (TD-DFT). The calculation results are shown in Figure 2. It was clearly shown that all highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) delocalized through the whole dipyrromethene ligands in all three BODIPYs. Moreover, the energy level of HOMO or LUMO and energy band gap were very similar in all three compounds. These data corresponded to the experimental results obtained from the similar absorption spectra from all three BODIPYs.

Next, we performed the theoretical calculation using TD-DFT to presume the most stable structure at the excited state (Fig. 3). The phenyl ring at boron of **B1** hardly moves from the original position

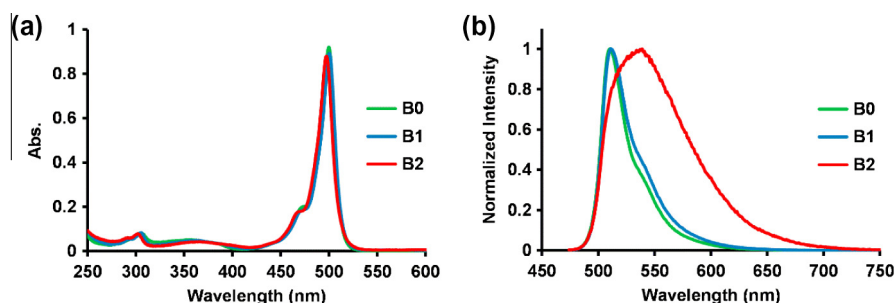


Figure 1. (a) UV–vis absorption and (b) PL spectra of the modified BODIPY in chloroform (1×10^{-5} M).

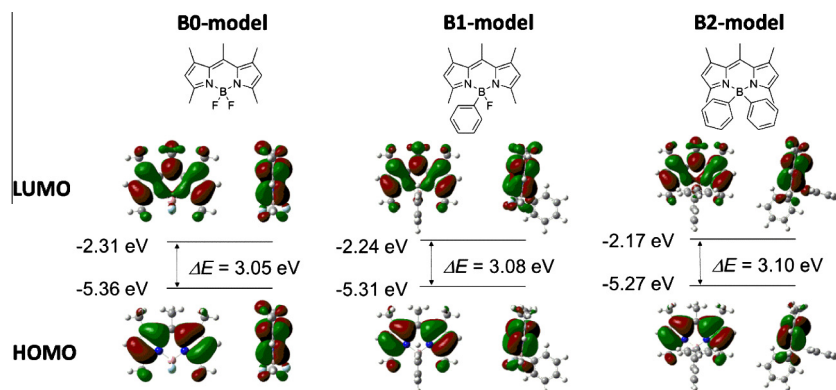


Figure 2. Structures and molecular orbital diagrams for LUMO and HOMO of **B0**-model, **B1**-model, and **B2**-model calculated with DFT (B3LYP/6-31G(d))/B3LYP/6-31G(d)).

before and after the transition. In contrast, it is revealed that the one phenyl ring at boron center in **B2** should rotate at the excited state. This result suggests that the broadening of the emission band and the decrease in quantum yield of **B2** should be derived from molecular motion at the phenyl group induced by the excitation. The electron acceptability of the boron in **B1** could still remain by the strong electron withdrawing from the single fluorine substitution. Therefore, the mobility of the phenyl group on the boron should be suppressed via the tight coordination with the dipyrromethene ligand. The boron atom in **B2** could have slightly longer electron acceptability because of two phenyl substituents. Consequently, it is proposed that the flexibility around boron center could be enhanced. As a result, the perpendicular phenyl group to the dipyrromethene ligand can obtain the mobility in the excited state. To confirm the structural alteration in the excited state, we carried out further experiments.

To understand the mechanism of the differences in the emission properties according to the theoretical investigation, the effect of molecular motion was experimentally examined. Optical measurements by altering the solvent viscosity were performed. Glycerin–ethanol mixture system with various proportions of each component was used for modulating the solvent viscosity. Similarly in chloroform, the absorption spectra were almost same in all proportions (Fig. S3). In addition, the photoluminescence spectra of **B0** and **B1** were also almost same in all proportions

(Fig. 4a and b). In contrast, it was observed that the emission intensity of **B2** increased when the viscosity of solvents increased (Fig. 4c and d). Moreover, the spectrum was similar to those of **B0** and **B1** in relatively-higher viscosity solvent (80 vol % of glycerin content). From these results, it is strongly supported that the broad spectra of **B2** should be caused by the molecular motion of the one phenyl group induced only in the excited state.

Finally, the solid-emissive properties were examined with the powder samples of the modified BODIPYs. Figure 5 shows the photoluminescence spectra of **B0**, **B1**, and **B2** in the solid state, and the optical properties are listed in Table 2. From **B0**, the typical behavior was observed: Very weak emission with quite low quantum yield ($\Phi = 0.09$) was detected. This value was almost 10% of that in solution. The spectrum of **B0** in the solid state shifted much longer wavelength than that in solution. The shape of spectrum of **B0** was broad and multimodal. Because of high planarity of **B0**, stacking and non-specific aggregation should readily occur in the amorphous state, resulting in the peak shifts and ACQ of the emission. On the other hand, **B1** and **B2** showed bright photoluminescence in the solid state. **B1** and **B2** presented narrow emission bands with good quantum yields ($\Phi = 0.25$ and 0.30 , respectively). It should be mentioned that the quantum yield of **B2** in the solid state was similar to that in the solution state ($\Phi = 0.34$). Furthermore, narrow and unimodal emission bands were observed. From these data, the introduction of phenyl groups into the boron center

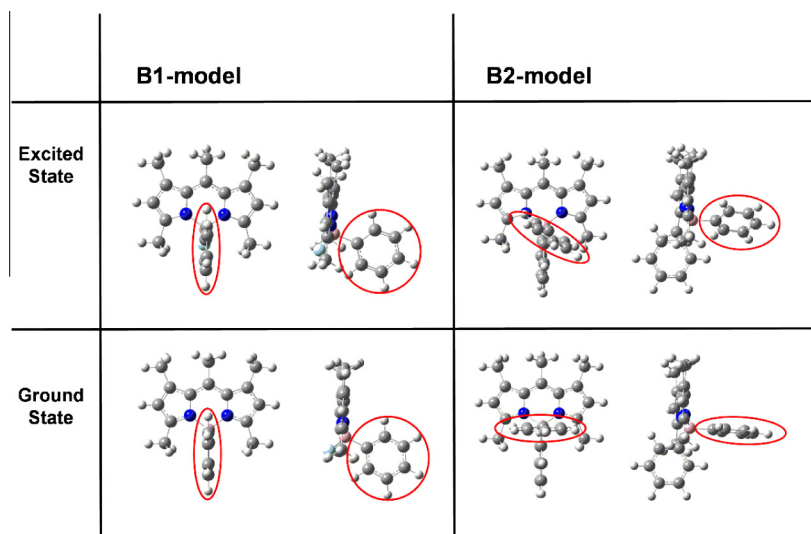


Figure 3. Structural changes of **B1** and **B2** during excitation. Optimized geometries in the excited states were estimated with TD-DFT (B3LYP/6-31+G(d)).

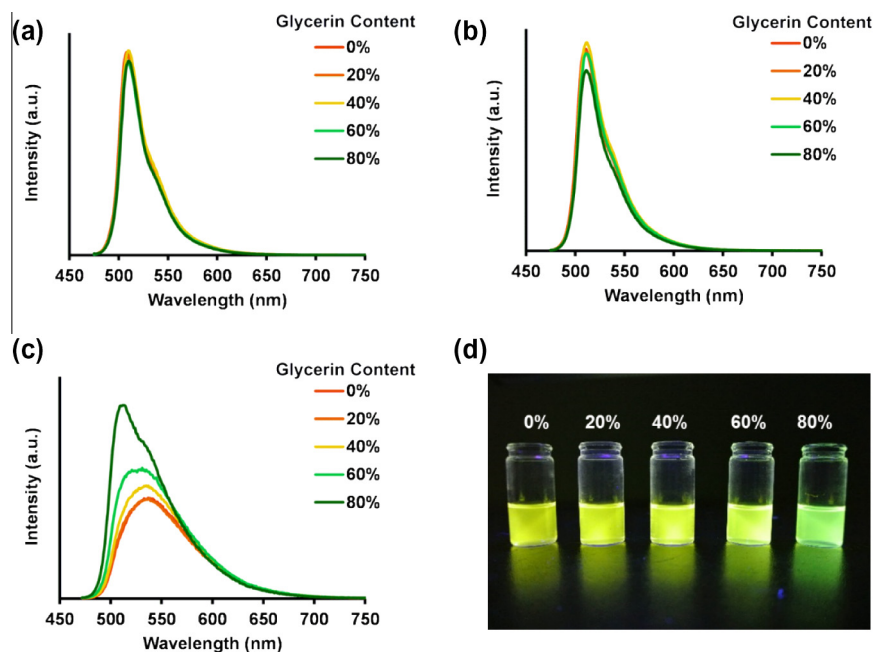


Figure 4. PL spectra of (a) **B0**, (b) **B1**, and (c) **B2** in variable viscosity solutions. (d) Photographs of the solution samples of **B2** under UV irradiation (365 nm).

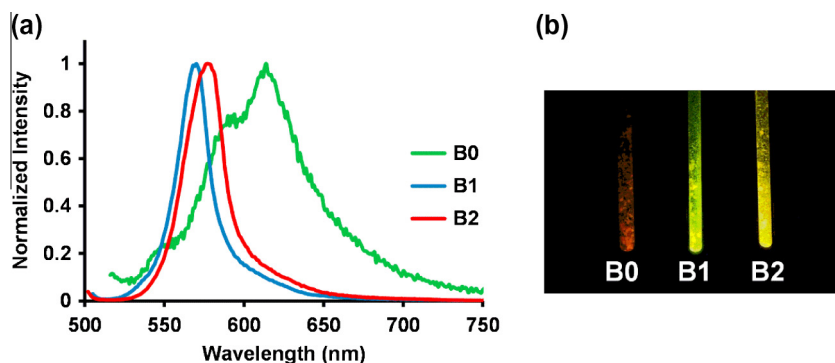


Figure 5. (a) PL spectra of **B0**, **B1**, and **B2** in the solid state. (b) Photographs of the powder samples of **B0**, **B1**, and **B2** under UV irradiation (365 nm).

Table 2
Emission properties of the modified BODIPYs in the solid state

	λ_{em}^a (nm)	Φ_{PL}^b	τ^c (ns)
B0	614	0.09	4.46
B1	569	0.25	4.10 (52%) 7.37 (48%)
B2	577	0.30	3.50 (76%) 22.5 (24%)

Parentheses represent the proportion of each element.

^a Excited at the corresponding λ_{abs} in their solutions.

^b Determined as an absolute value.

^c Excited at 375 nm.

in BODIPY should be valid for enhancing the solid-emissive property. It is proposed that the steric hindrance of the phenyl group could play a significant role in the inhibition of ACQ of BODIPY.

In conclusion, this manuscript describes the valid strategy for obtaining the solid-emissive property from BODIPYs. By selecting the organometallic reactions, the number of substituents in the boron center in BODIPY can be modulated. By introducing phenyl groups into the boron atom in the BODIPY, the planarity of the six-membered ring including boron was lowered. In addition, because of the molecular motion at the phenyl group, the peak broadening and the decrease in emission quantum yields were

induced in the solution state. However, interestingly, these substituents played a favorable role in improving the solid-emissive properties of BODIPY. It was clearly demonstrated that the introduction of the phenyl groups was valid for avoiding the concentration quenching by inhibiting the intermolecular interaction in the solid state. In addition, the molecular motion was suppressed in the solid state. As a result, the solid emission with the sharp and unimodal peak can be accomplished. From these data, we can say that the minimum modification method was accomplished for solid emission based on BODIPY without modification at the ligand moiety. It is implied that the solid emission might be obtained with our strategy based on the conventional BODIPY derivatives such as deep red or NIR-emissive molecules which are useful for the direct application not only to organic opto-electronics devices but also to the bioimaging probes.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2015.10.072>.

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