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# Decorating BODIPY with Three- and Four-Coordinate Boron Groups

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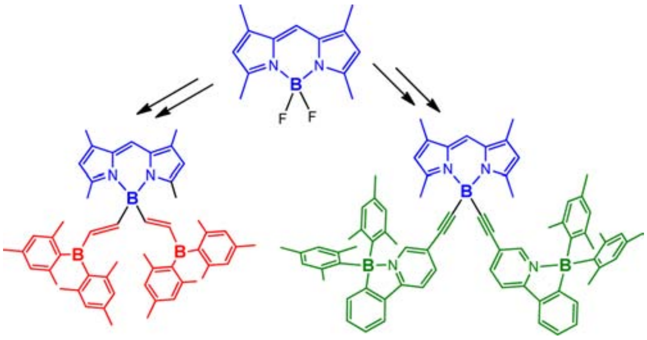
## ABSTRACT



**Two new BODIPY derivative molecules decorated by a Lewis acidic BMes$_2$(vinyl) group and a photochromic four-coordinate boryl chromophore, respectively, have been synthesized. Significant mutual influence on photophysical and photochemical properties by the different boron-containing units has been observed.**

BODIPY (boron dipyrromethene) dyes and derivatives are well-known to display interesting photophysical properties and high photostability, enabling their applications in bioimaging, biolabeling, or probes, etc.[1,2] Although most BODIPY dyes are brightly fluorescent in solution, they are usually poor emitters in the solid state. This is caused mostly by "self-absorption" due to the very small Stokes' shift and large overlap of BODIPY's absorption and emission spectra. Furthermore, because of the flat conjugated core, the BODIPY fluorophores normally pack tightly in the solid state, resulting in strong intermolecular interactions, leading to significant luminescent quenching.[2−6] Because of the low fluorescence quantum efficiencies in the solid state (either as a pure solid or in a solid matrix), BODIPY dyes are not suitable for use in applications such as emitters for organic light emitting diodes (OLEDs). To address this deficiency, several research teams have used the strategy of introducing bulky substituent groups including BMes$_2$-phenyl or *p*-BMes$_2$-ph-alkynyl[6] (Mes = mesityl) or aliphatic chains at the *meso* and/or 2,6-positions to strengthen steric hindrance, thus inhibiting intermolecular aggregations.[3−6] This strategy is somewhat effective in improving the solid-state emission quantum efficiency of certain BODIPY dyes. Nonetheless, because the fluorescence of BODIPY originates from the BODIPY core, bulky substituents at *meso* and/or 2,6-positions often have a significant impact on the emission energy, making the BODIPY chromophore more prone to decay from the excited state via nonradiative pathways, such as vibrational and/or rotational relaxation.[1a]

With the aim of tuning the photophysical properties of BODIPY, especially to increase the emission quantum efficiency in the solid state, we designed and synthesized two new molecules **B3a** and **B3b** (Scheme 1). In **B3a**, a

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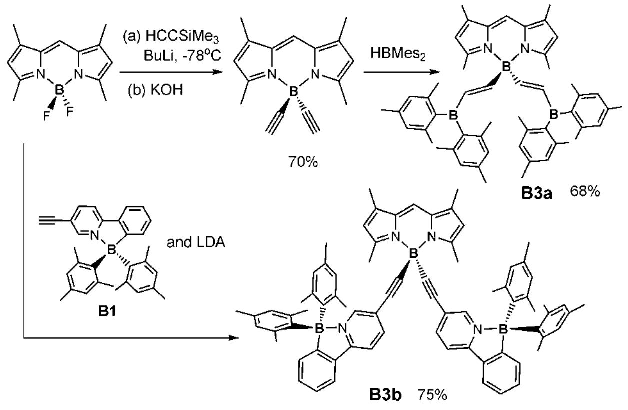
BMes$_2$-vinyl group is attached to the BODIPY core while in **B3b** a four-coordinate boron group, B(ppy)Mes$_2$-alkynyl, is attached to the BODIPY core. BODIPY functionalization by these two boryl groups has not been reported previously. These two molecules allow us to examine the impact of three- and four-coordinate boryl groups on the photophysical properties of the BODIPY core. Further, because the BMes$_2$-vinyl group is Lewis acidic[7] and the B(ppy)Mes$_2$-alkynyl unit is photochromic,[8] these two molecules allow us to examine the influence of the BODIPY core on the anion sensing ability of the three-coordinate boron and the photochromic properties of the N,C-chelate boron unit.

**Scheme 1.** Synthetic Procedures for **B3a** and **B3b**



The syntheses of **B3a** and **B3b** are accomplished according to Scheme 1. For **B3a**, the bis-acetylide BODIPY compound was synthesized first. This precursor compound was connected to the BMes$_2$ unit via a hydroboration reaction with BMes$_2$H using well-established literature procedures,[9] producing **B3a** in good yield. For the synthesis of compound **B3b**, the N,C-chelate precursor compound[8a,b] **B1** was reacted with LDA first,[10] followed by the addition of the parent BODIPY compound, producing **B3b** in 75% yield. **B3a** and **B3b** were fully characterized by $^{1}$H, $^{13}$C, and $^{11}$B NMR spectra, HRMS, and elemental analyses. The two distinct types of boron centers in **B3a** and **B3b** were observed in the $^{11}$B NMR spectra. For **B3a**, no *cis*-isomer with respect to the olefin bond was observed. Both compounds are as stable as the difluoro BODIPY parent molecule toward air and moisture.

The crystal structures of both compounds were determined by single-crystal X-ray diffraction analysis.[11] The crystals of both compounds are very thin and small and diffract poorly. As a result, the quality of the crystal data are poor. Nonetheless, the key structural features of both compounds were established unambiguously and are shown in Figures 1 and 2, respectively. The boron atom of the BODIPY core in both compounds has the typical B–N (average, 1.56 Å) and B–C (average 1.60 Å) bond lengths, comparable to those of previously reported BODIPY compounds.[1–6] The B–C$_{\text{vinyl}}$ bonds in **B3a** are much shorter (average 1.54 Å) than those of the BODIPY core, and the B–C$_{\text{(mesityl)}}$ (average 1.59 Å), which can be attributed to the $\pi$-conjugation of the three-coordinated B atom with the olefin carbon atoms. In fact, the C$_{\text{Mes}}$–B–C$_{\text{Mes}}$ plane is essentially coplanar with the plane of B-vinyl with an average dihedral angle of 9.5°. The B–N and B–C bond lengths of the N,C-chelate units in **B3b** are about 0.1 Å longer than the those of the BODIPY core, caused by the steric congestion imposed by the bulky mesityls.

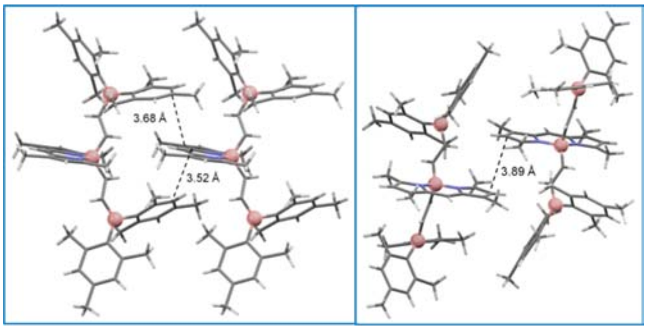


**Figure 1.** Crystal structure of **B3a** showing intermolecular interactions between mesityls and the BODIPY core (left) and between two neighboring BODIPY units (right). The boron atoms are shown as pink spheres. Key: blue, nitrogen; gray, carbon.

The most important features revealed by the crystal structures are the two distinct intermolecular interaction patterns for the two compounds. As shown in Figure 1, in the crystal lattice of **B3a**, the BODIPY unit is sandwiched between two mesityl groups with the shortest atomic separation distances being 3.52 and 3.68 Å, respectively. The shortest separation distance between two neighboring BODIPY units in **B3a** is 3.89 Å. In contrast, the BODIPY core units in **B3b** are all paired up with the average separation distance between two BODIPY planes being ~3.50 Å (Figure 2), an indication of strong $\pi$-stacking interactions. The distinct packing patterns by **B3a** and **B3b** may be partially attributed to the shape of these two

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(11) CCDC 901543 (**B3a**) and 901544 (**B3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

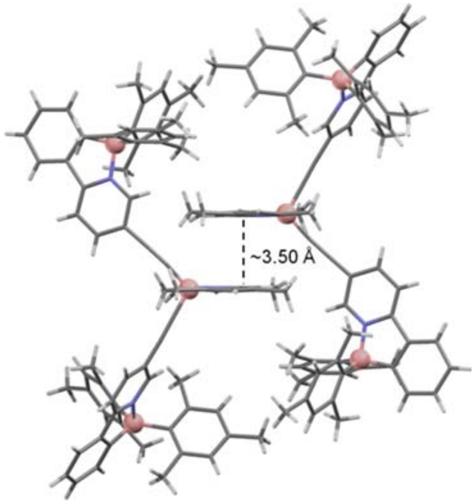

**Figure 2.** Crystal structure of **B3b** showing intermolecular interactions between two neighboring BODIPY units. The boron atoms are shown as pink spheres. Key: blue, nitrogen; gray, carbon.

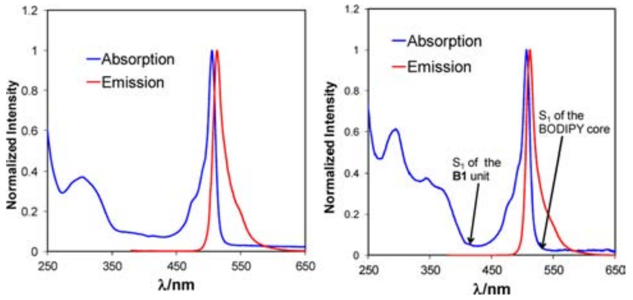

**Figure 3.** Absorption and fluorescence spectra of **B3a** (left) and **B3b** (right) in $CH_2Cl_2$.

molecules, one being approximately linear and the other being V-shaped, and are expected to have a significant impact on their luminescent properties in the solid state.

As shown by Figure 3, although the absorption spectra contain significant contributions from vinylborane or **B1** chromophores, **B3a** and **B3b** share a similar emission profile and identical emission maximum ($\lambda_{max}$ = 510 nm), similar to that of the parent difluoride BODIPY molecule, thus attributable to the BODIPY core.[12] Furthermore, the emission energy of both compounds was found to be independent of excitation energy. The lack of emission from the **B1** unit[8] ($\lambda_{max}$ = ~500 nm) in **B3b** can be attributed efficient internal energy transfer from the **B1** unit to the BODIPY core due to the extensive overlap of the absorption peak of the BODIPY core and the fluorescent peak of the **B1** unit. TD-DFT computational data also confirmed that the lowest excited states of **B3a** and **B3b** with significant oscillator strengths are indeed dominated by electronic transitions of the BODIPY core (Supporting Information). Both compounds have very impressive emission quantum efficiencies (~100%, see the Supporting Information), much higher than the previously reported $BMes_2$-functionalized BODIPY at the *meso* or 2,6-positions[6] and display little dependence on concentration in solution. However, they do display distinct doping concentration-dependent luminescence in the solid-state blends with PMMA (poly(methyl methacrylate) as shown in Figure 4.

At the 5 wt % doping level, the emission spectrum of **B3a** resembles closely the solution spectrum with $\lambda_{max}$ = 512 nm and an impressive quantum efficiency of 0.32, which is much higher than the previously reported highest quantum yield (25%) for BODIPY derivatives in PMMA.[5a] At 25 and 50 wt % doping levels, the $\lambda_{max}$ shifts to 520 and 531 nm, respectively, coupled with a substantial broadening of the spectrum and a decrease of the quantum efficiency (0.30 and 0.18, respectively). At doping levels above 75%, the $\lambda_{max}$ is further red-shifted to ~540–550 nm, and the emission peak is dominated by excimer emission with a drastic decrease of quantum efficiency (see the Supporting Information). The neat **B3a** film has a broad emission band with $\lambda_{max}$ at ~560 nm and a quantum efficiency of 0.05, albeit weak, a significant enhancement, compared to the parent difluoro BODIPY, which is nonemissive at all either as neat films or powders. The doping concentration-dependent fluorescence in PMMA displayed by **B3a** may be attributed to molecular aggregations and intermolecular interactions as revealed by the crystal structure shown in Figure 1.

The behavior of **B3b** is quite different. At 5 wt % doping concentration, the PMMA film of **B3b** appears green but with an emission intensity and a quantum efficiency too low to be determined by our integration sphere. As the doping concentration increases to 25 wt %, the emission color of **B3b** becomes red with $\lambda_{max}$ at ~630 nm, which is about 120 nm red-shifted, compared to the solution fluorescence spectrum. This red shift is much more dramatic than that observed in **B3a**. Most importantly, further increasing of the doping concentration does not cause further change the emission spectrum. The highest quantum efficiency of **B3b** in PMMA films was observed to be 0.10 at the 50 wt % doping level, much lower than that of **B3a**–PMMA films at the same doping level. The peculiar concentration-dependent behavior of **B3b** in PMMA films can be explained by the "stacked dimer" formation, shown in Figure 2, which becomes dominant and persistent at doping levels greater than 25 wt %. The red emission band displayed by **B3b** can therefore be assigned to excimer emission of the $\pi$-stacked BODIPY dimer.[13] The distinct concentration-dependent behavior of **B3a** and **B3b** in the solid state illustrates that the fluoride substitution in

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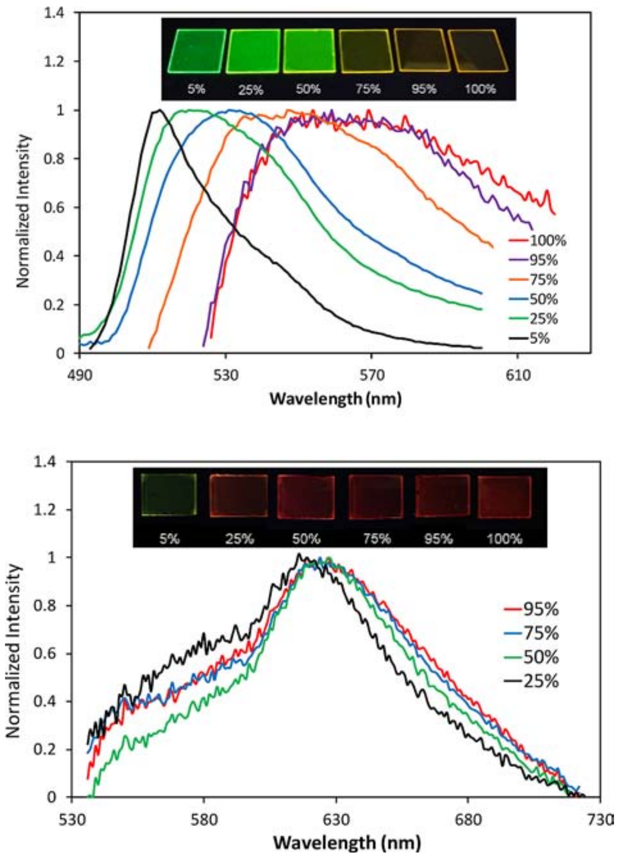

**Figure 4.** Fluorescence spectra of **B3a** (top) and **B3b** (bottom) doped PMMA films and neat films (100%) (the fluorescence spectrum of the 5 wt % of **B3b**-doped film could not be obtained due to the very weak signal). Inset: photographs showing the fluorescence colors of the **B3a**- or **B3b**-doped PMMA or neat films.

BODIPY by a BMes$_2$-vinyl and a B(ppy)Mes$_2$-alkynyl can be used as an effective strategy to control/influence the solid state luminescence properties of BODIPY.

The impact of the boryl substituents on the electronic properties of the BODIPY can be further evidenced by the reduction potentials of **B3a** and **B3b**. The first reduction peak of both compounds is characteristic of BODIPY reduction. However, the first reduction potential of **B3a** ($-1.95$ V, relative to FeCp$_2$$^{0/+}$) is much more negative than that of **B3b** ($-1.72$ V), indicating that despite the lack of direct $\pi$-conjugation between the boryl and the BODIPY core the boryl substituents do have a significant impact on the BODIPY unit. This may be explained by the much greater electron affinity of the **B1** unit that is known to have a much more positive reduction potential[8a,b] than the BMes$_2$(vinyl) unit[14] does. In agreement with the electrochemical data, DFT computational results show that the LUMO of both compounds is localized on the BODIPY unit with the energy level of **B3b** being about 0.30 eV lower than that of **B3a** (Supporting Information).

To examine the impact of the BODIPY unit on the Lewic acidity of the BMes$_2$-vinyl group in **B3a** and the photochromic properties of of the **B1** unit in **B3b**, we carried out fluoride titration for **B3a** and photoisomerization experiments for **B3b**, respectively. The addition of TBAF to the THF solution of **B3a** resulted in a partial quenching of the BODIPY absorption and emission peak in the UV−vis and fluorescence spectra, respectively, with binding strength similar to those observed previously for typical BMes$_2$(vinyl) compounds.[15] This observation supports that although fluorescence of **B3a** is dominated by the BODIPY unit, it is electronically coupled to the BMes$_2$-(vinyl) unit. TD-DFT also supports that the singlet excited states (S$_1$ and S$_2$, which are very close in energy) responsible for the observed fluorescence do have appreciable contributions from the charge transfer transition of BMes$_2$-vinyl to BODIPY (see ESI).

In the photoisomerization experiments, compound **B3b** was irradiated in toluene or C$_6$D$_6$ at 365 nm (the charge-transfer band responsible for photoisomerization of **B1**) and the solution was monitored by UV−vis and $^1$H NMR spectra. After extended irradiation, no change was observed for the solution of **B3b** by either UV−vis or NMR spectra. This lack of any photochromic activity by the **B1** unit can be attributed to a fast and efficient intramolecular energy transfer from the **B1** unit to the BODIPY core since the optical energy gap of **B1** (~3.0 eV) is much greater than that of BODIPY (~2.3 eV) (Figure 3), which completely intercepts the excitation energy, thus blocking photoisomerization of the **B1** unit.

In summary, two new BODIPY molecules decorated by a BMes$_2$(vinyl) unit and an N,C-chelate boryl unit, respectively, have been achieved. Unlike substitution at the *meso* or the 2,6-positions of the BODIPY core that significantly shifts the emission energy, the difluoro substitution by a BMes$_2$-vinyl or a B(ppy)Mes$_2$-alkynyl group does not shift the emission energy of the molecule in solution, compared to the difluoro BODIPY parent molecule. Both molecules have ~100% emission quantum efficiencies in solution and display distinct doping concentration-dependent fluorescence in a PMMA matrix. The BMes$_2$(vinyl) unit greatly enhances BODIPY fluorescence efficiency in a PMMA matrix while the photoreactivity of the N,C-chelate boryl unit is switched off completely by BODIPY via intramolecular energy transfer.

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**Supporting Information Available.** Synthetic and characterization details, crystal structural data, solid-state luminescent quantum efficiencies at various doping levels, TD-DFT data, and CV and TBAF titration data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.