Tetrahedron Letters 57 (2016) 1605–1609

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Fused dual boron core based BODIPY dyes: synthesis and optical character

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ARTICLE INFO

Article history:
Received 18 December 2015
Revised 23 February 2016
Accepted 29 February 2016
Available online 3 March 2016

Keywords:
BODIPY dyes
Dual boron core
Red-shift emission
Stokes' shift
Schiff's base

ABSTRACT

Here we report that two boron dipyrromethene derivatives (**BNB-1** and **BNB-2**), bearing double boron atomic centers, have been synthesized and characterized. The additional boron atom was introduced into the skeleton of typical BODIPY dyes through the reaction of $BF_3 \cdot Et_2O$ and the two ligands, phenol and Schiff's base. The maximum emission wavelength of both dyes moved to 584–603 nm with the larger Stokes' shift ($\Delta\lambda \approx 40$ nm). Moreover, less solvent polarity dependence of the Stokes' shift (40 ± 6 nm) was found in different organic solvents. Furthermore, fluorescent lifetime and CV methods were also performed to explore the photophysical and electrochemical behaviors of both dyes.

Introduction

It has been a hot investigation in recent years that the design and synthesis of small-molecular fluorescent dyes are applied for chemosensors, fluorescent label reagents, and nonlinear optical materials. Boron dipyrromethene (BODIPY) and its derivatives are classical organic fluorophores with high luminescent efficiency, relatively sharp fluorescence peaks, and advantageous photostability.[1–5] These BODIPY dyes have worked as energy/electron donors or acceptors in different donor–acceptor sensors. With the demands of the probes or sensitizers in chemosensor and corresponding devices, several modifying strategies about BODIPY dyes were developed: (1) electron-deficient and electron-rich substitutions on the *meso* site of BODIPYs provided the photo-induced electron transfer (PeT) process for designing fluorescent sensors and switches;[6–11] (2) the π-extended BODIPY dyes with longer emission wavelength were obtained by the Knoevenagel reaction or Heck coupling reaction. The formed fluorophores showed deep puncturing depth that is needed for optical bioimaging in vivo;[12–16] (3) Först resonance energy transfer was another powerful tool to enhance Stokes' shift and construct dual channel detection device. BODIPY can couple with other fluorophores and sensors in order to construct new optical cassettes;[17–19] (4) nucleophilic substitution on the boron core of BODIPY provided plenty of compounds with different photophysical properties. Until now, the aryl-, alkyl-, alkynyl-, and alkoxy-substituent of BODIPY has been reported in different fields;[20–22] (5) some researches introduced the N atom into the *meso* position of the BODIPY to give the far red/near infrared emission derivatives that could be used as the contrast agents and photodynamic therapy.[23–34]

Because the indole group has larger conjugated system than pyrrole, a series of indole-based BODIPY derivatives have been designed in our previous work.[35] These derivatives with red to near-infrared emission can work as fluorescent probes for different species. However, further exploration in expanding structures and optimizing photophysical properties of these derivatives have not been put forward. Hence, we described a new type of dual boron core BODIPY (**BNB-1** and **BNB-2**) on the basis of indole-based BODIPY, which integrated both typical BODIPYs and mini BODIPY analogs. As shown in Scheme 1, the second boron atom was induced in both dyes to construct the mini BODIPY moiety (blue square), which was fused on the typical BODIPY ring (yellow circle). The newly boron core fixated the Schiff's base and phenol of **BODIPY-OH**, which could keep rigidity and enhance the planarity of the structure. Furthermore, we introduced the methoxy moiety as an electron donor into the *para* position of Schiff's base of **BNB-1**. Then, we employed the ^{1}H NMR spectra to study the charge distribution on both dyes. UV–vis and emission spectra were employed to explore the behavior of the additional boron unit fused on the BODIPY dyes. The fluorescent quantum yield and lifetime were determined to confirm the role of an electron-rich group ($-OCH_3$)

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http://dx.doi.org/10.1016/j.tetlet.2016.02.109
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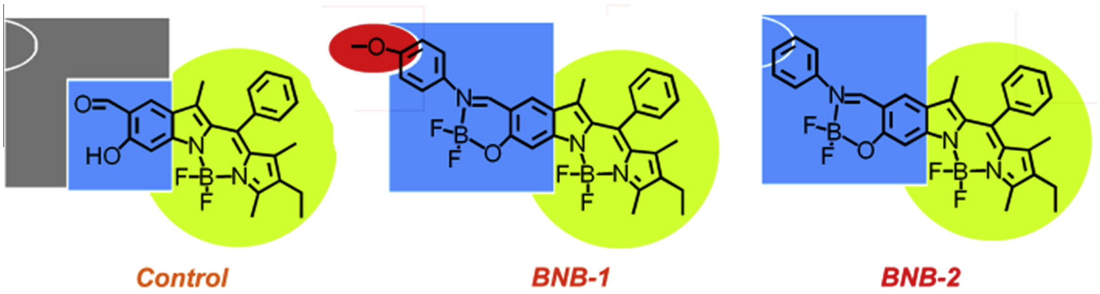
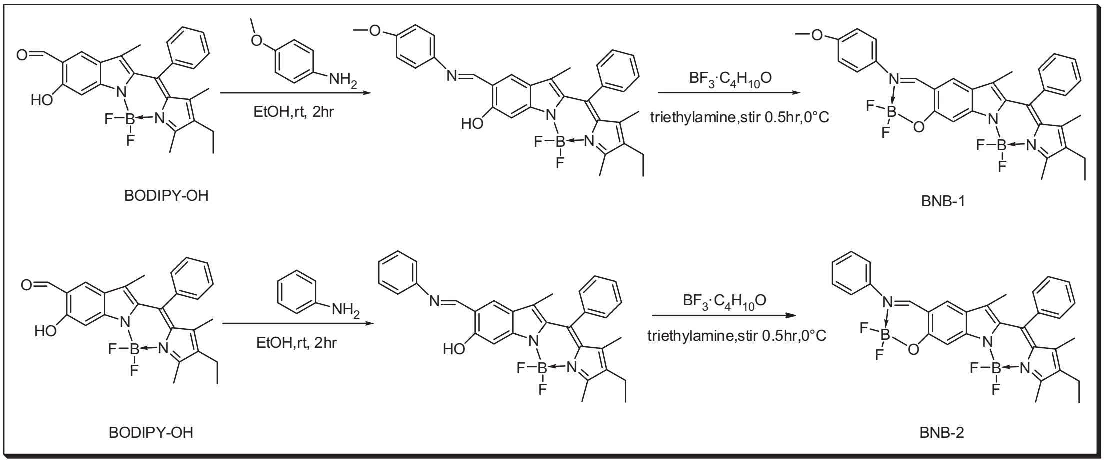


Scheme 1. Structures of the **BNB-1**, **BNB-2**, and control.



Scheme 2. Synthesis of **BNB-1** and **BNB-2**.

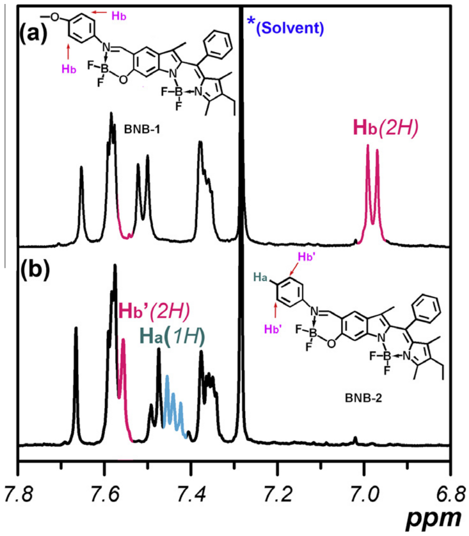


Figure 1. Low-field ^{1}H NMR of **BNB-1** and **BNB-2**.

in these BODIPY dyes. Finally, the CV test was also performed to discuss the difference of the electronic properties between **BNB-1** and **BNB-2**.

Results and discussion

As shown in Scheme 2, **BNB-1** and **BNB-2** were prepared by a simple method. The condensation of the **BODIPY-OH** with the *p*-anisidine and aniline in ethanol under room temperature for 2 h produced the corresponding Schiff's bases of **BNB-1** and **BNB-2**, respectively. Then, both kinds of the Schiff's bases reacted with $BF_3 \cdot OEt_2$ under ice-bath for half an hour to gain the targets (**BNB-1** and **BNB-2**). The structures of both targets were characterized by ^{1}H NMR, ^{13}C NMR, and HRMS spectra in Supporting information.

Figure 1 described the difference between the ^{1}H NMR spectra of **BNB-1** and **BNB-2**. **BNB-1** gave the double peak at high field that assigned to the protons on the phenyl moiety (H_b; 6.95 and 6.97 ppm). Without methoxy group, the corresponding signals of **BNB-2** were found at 7.556 ppm (H_b'). Moreover, **BNB-2** had one more proton on the phenyl moiety than **BNB-1**, which could be found at 7.42–7.45 ppm (blue color in Fig. 1b). The HRMS spectrum showed a peak at m/z 584.2303 for **BNB-1** and 554.2175 for **BNB-2** (Figs. S6 and S9), which were consistent with the calculated values (584.2304 for $[M-H]^-$ of **BNB-1** and 554.2198 for $[M-H]^-$ of **BNB-2**).

Compared with the proton H_a of **BNB-2** (Fig. 1), the methoxy group of **BNB-1** showed electronic donor property, it caused the difference between **BNB-1** and **BNB-2**. For the investigation of the photophysical properties of **BNB-1** and **BNB-2** in different solvents, UV–vis and fluorescence spectra were performed in Figure 2. As Figure 2a shown, the absorption peak around 350 nm was assigned to the Schiff's base ligand of **BNB-1**. The absorption peak of **BNB-1** was stronger than the one of **BODIPY-OH** that indicated the planarity of **BNB-1** was better than **BODIPY-OH**. The similar phenomenon could also be found in **BNB-2** (Fig. S10).

In Figure 2b, the maximum absorption bands of **BODIPY-OH** shifted from 527 nm to 549 nm with different polarity of solvents. The similar variation was found in **BNB-1** and **BNB-2** but in a longer wavelength region. As shown in Figures 2a and S10e, the maximum absorption bands of **BNB-1** and **BNB-2** ranged from