



Synthesis and photo-property of 2-cyano boron-dipyrromethene and the application for detecting fluoride ion



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ABSTRACT

Three 2-cyano boron-dipyrromethene (BODIPY) based derivatives (**CB1–CB3**) have been synthesized and characterized. The photophysical properties of these compounds are investigated by means of UV/Vis absorption and fluorescence spectroscopy. **CB1–CB3** exhibit small Stokes shift and high fluorescence quantum yield. Noticeably, **CB2** with styrene moieties at 5-position of BODIPY displays absorption alternation with maximum of 120 nm red-shift upon addition of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as a base, giving remarkable color change which can be detected by naked eye. Meanwhile, the compound **CB3** shows high selectivity toward fluoride ion via fluorescence quenching mechanism by release of the masked phenolate form of **CB2** through fluoride ion induced deprotection reaction. It also exhibits fast signal response time (30 s) and excellent selectivity over other competing analytes, making it a good candidate as colorimetric sensor for fluoride sensing.

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1. Introduction

As anions play a fundamental and important role in many chemical and biological processes, the design and synthesis of probe for the detection of anions with high selectivity and sensitivity have attracted intensive interest.¹ Fluoride ion has been proved to be very important anion in dental care and in the treatment of osteoporosis.² However, excessive intake of fluoride ion can cause fluorosis on human and animal kidney damage, leading to urinary tract stones.³ In this context, many colorimetric and fluorescent fluoride probes have been designed and reported.^{4–6} For those various sensors, hydrogen bonding between proton donor and fluoride⁴ and fluoride–boron interaction between organoboron-derivatives and fluoride⁵ have been frequently investigated and utilized for the recognition. Meanwhile, the reaction-based sensor based on the formation of F–Si bond has also been designed and applied with very high selectivity.⁶

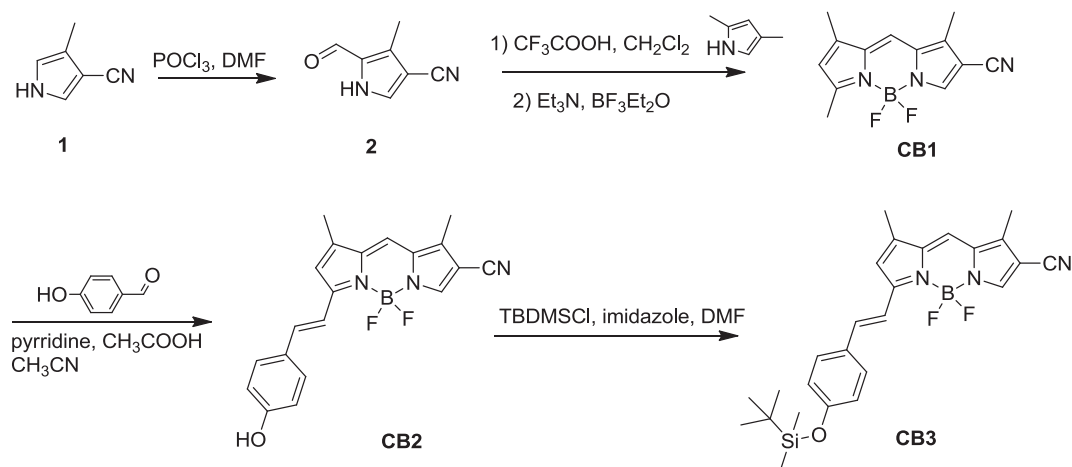
Recently, boron-dipyrromethene (BODIPY) derivatives have attracted much interest due to their unique photophysical properties, such as strong absorption in the visible and near-IR ranges, high fluorescence quantum yield and excellent photo-stability. The easy synthesis, potential for derivatization and excellent photophysical properties of BODIPY compounds make it be utilized in

broad fields such as fluorescent dyes, cation and anion sensors, drug delivery agents, light harvesting systems and photodynamic therapy.⁷

Several new BODIPY compounds with functionalization at all the positions of BODIPY core have been synthesized.^{8–13} For example, all position of BODIPY compound can be halogenated and given the halogenated BODIPYs which have been used as building blocks to synthesize different types of new BODIPY derivatives through metal-catalyzed cross-coupling reaction and nucleophilic substitution reaction.⁸ Recently, Boens et al. developed the synthesis of arylated BODIPY by the metal-catalyzed direct C–H arylation.⁹ The methyl groups at 3, 5-positions of BODIPYs can be subjected to the Knoevenagel reaction with electron-rich aromatic aldehydes owing to their strong nucleophilic character, generating conjugated styrene moieties on BODIPYs.¹⁰ Ziessel and co-workers reported a library of highly stable C-BODIPY and E-BODIPY dyes by C or O atoms subunits in place of the usual fluorine atoms.¹¹ The formyl groups can be introduced at 2-/6- position of BODIPY by using POCl₃/DMF reagents and further transformed for the synthesis of new BODIPY derivatives.¹² The amines and carboxylic acid groups can also be directly introduced to BODIPY, which can be used for ligation reaction with proteins or DNA-derivatives.¹³ Therefore, a newly modified BODIPY with a novel functional group would be interesting and useful in organic synthesis and sensing applications.

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Cyano as a special and versatile functional group can be hydrolyzed to carboxylic acid and reduced to amines. As a result, the Cyano-modified BODIPY can be activated and applied to the biological labeling. The *meso*-cyano modified BODIPYs have been synthesized and their fluorescence and absorbance spectra show approximate 60 nm red-shift comparing with simply alkyl-substituted BODIPYs, which is attributed to the net stabilization of the LUMO level, hence the decrease of energy gap induced by the cyano group.^{14,7b} However, this spectral phenomenon is not observed in the reported 2, 6-cyano modified BODIPYs.¹⁵ In this work, we have synthesized three 2-cyano-modified asymmetric BODIPY derivatives **CB1**–**CB3** through CF₃COOH-catalyzed condensation of 5-formyl-4-methyl-pyrrole-3-carbonitrile with 2, 4-dimethyl pyrrole (Scheme 1). A styrene moiety at Bodipy 5-position in **CB2** is introduced by the Knoevenagel reaction between **CB1** and an aromatic aldehyde. All three compounds display good chemical stability and fluorescence properties. The **CB2** is converted to the phenolate form from the neutral phenol states when the strong base (DBU) is added, which generates remarkable color change and fluorescence decrease. **CB3** shows high selectivity for detecting fluoride ion as colorimetric sensor based on the de-protective reaction. On the other hand, the cyano group in **CB3** renders the Si–O band cleavage by fluoride faster to realize short response time.



Scheme 1. Synthesis routes of compounds **CB1**, **CB2** and **CB3**.

2. Result and discussion

2.1. Synthesis of compound **CB1**–**CB3**

Three 2-cyano BODIPY derivatives were synthesized according to the procedure shown in Scheme 1. The compound **2** was synthesized by using POCl₃/DMF reaction with 4-methyl-pyrrole-3-carbonitrile (compound **1**) as the starting material.¹⁶ The Bodipy derivative **CB1** was obtained through the TFA-catalyzed condensation reaction of **2** with 2,4-dimethyl-pyrrole according to BODIPY formation procedure using Et₃N and BF₃·Et₂O. The compound **CB2** was obtained by condensation reaction of the compound **CB1** with 4-hydroxybenzaldehyde under AcOH and pyridine. Finally, compound **CB3** was obtained by the reaction of compound **CB2** with *tert*-butyldimethylchlorosilane (TBDMSCl) in the presence of imidazole. Those compounds were further confirmed and characterized by ¹H, ¹³C NMR spectra and HR-MS measurements.

2.2. Absorption and fluorescence properties of compounds **CB1**–**CB3**

The absorption spectra and fluorescence spectra of compounds **CB1**–**CB3** were performed in various solvents. As showed in Fig. 1, Fig. S1–2 and Table 1, these CN-modified compounds **CB1**, **CB2** and **CB3** show the typical BODIPY platform photophysical characteristics with a narrow and strong absorption band around 480 and 550 nm, respectively, which is corresponded to the S₀–S₁ transition. The absorption maximum of **CB1** exhibits a slight hypsochromic shift with about 17 nm when solvent is changed from toluene (492 nm) to acetonitrile (475 nm). Similarly, the emission spectrum also shows minor solvent-dependent shift with decreased fluorescence quantum yields (from 0.74 in toluene to 0.59 in methanol), which is consistent with the general behavior of other BODIPY chromophores. Due to the styrene substitution at the 5-position of BODIPY, the absorption spectra of **CB2** and **CB3** have absorption maximum at 550 nm and the maximum shift of absorbance spectra is only 6 nm and 19 nm for **CB2** and **CB3**, respectively. Similar to their absorption spectra, their fluorescence spectra also show minor solvent-dependent shift and the maximum emission wavelength in 560–580 nm range.

The un-cyano substituted BODIPY compound **B1**¹⁸ and **B2** were also synthesized and their photo properties were studied. As shown in Fig. S3–S4 and Table S1, compound **B1** and **B2** exhibit a similar narrow and strong absorption band around 490 and 560 nm, respectively. Compared with **B1** and **B2**, 2-CN BODIPY compounds **CB1** and **CB2** show a slight blue-shift with 10 nm and the larger Stokes shifts (31 nm in MeOH for **CB2**), as observed from the absorbance and fluorescence spectra, which is attribute to the presence of the cyano group.

Due to the acidic phenol group in **CB2**, the deprotonation reaction in the presence of organic base could occur. It was found that the conversion of phenol group to phenolate form in **CB2** could be achieved by simply adding DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in solution, the UV/Vis absorption spectra display a quite large red shift. As showed in Fig. 2, **CB2** treated with 10 equiv of DBU in CH₃CN exhibits obvious absorption alternation with maximum red-shift from 545 nm to 653 nm, resulting in remarkable solution color change from orange to blue. It is attributed to

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