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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.

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 fluoride[4] and fluoride-boron interaction between organoboron-derivatives and fluoride[5] 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 Knoevengal 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 $POCl_3$/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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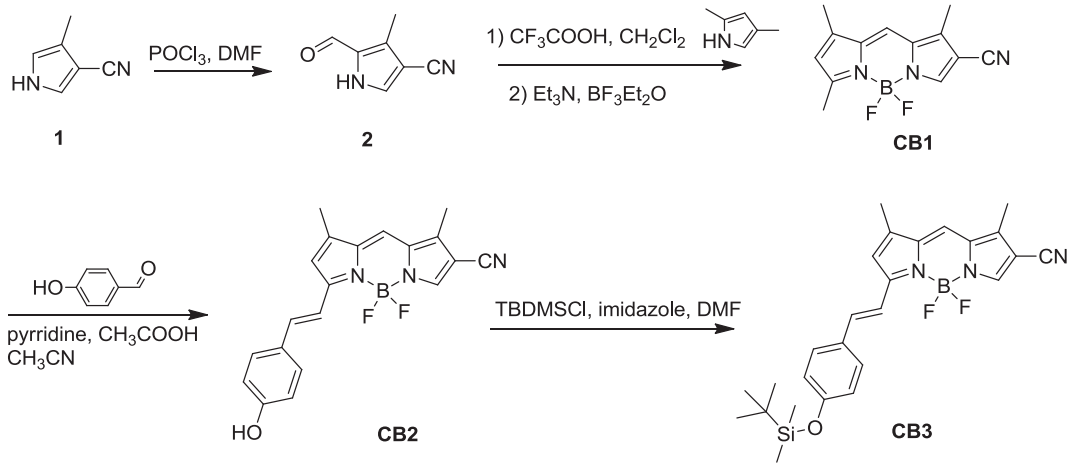
Cyano as a special and versatile functional group can be hydrolyzed to carboxylic acid and reduced to aminies. As a result, the Cyano-modified BODIPY can be activated and applied to the biological labeling. The *meso*-cyano modified BODIPYs have been synthesized and their fluorescence and absorbance 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 CF_3COOH-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 Knoevengal 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.

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.



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 $POCl_3$/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 Et_3N and $BF_3{\cdot}Et_2O$. The compound **CB2** was obtained by condensation reaction of the compound **CB1** with 4-hydroxybenzaldehyde under AcOH and pyridine. Finally, compound C**B3** 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, ^{13}C NMR spectra and HR-MS measurements.

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 CH_3CN 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

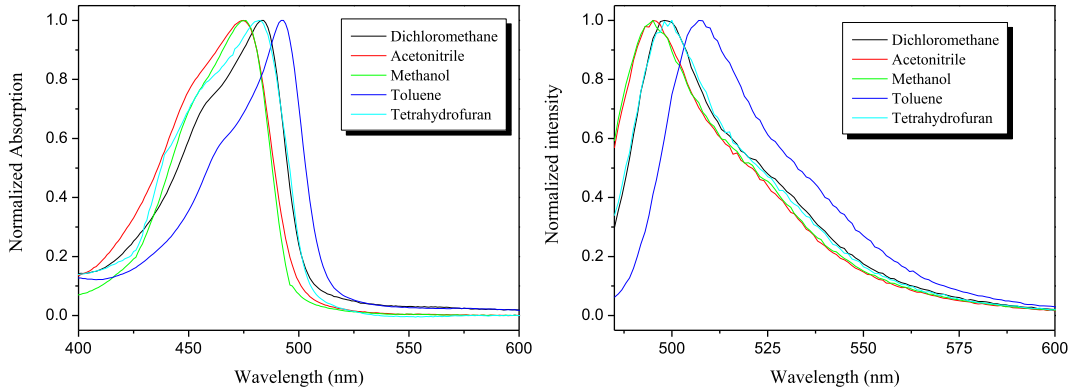


Fig. 1. Normalized absorption spectra and fluorescence spectra of compound **CB1** in different solvent.

Table 1
Spectroscopic data for compounds **CB1**–**CB3** in various solvents

2-CN BODIPY	Solvent	λ_{abs}/nm	λ_{em}/nm	Stokes shift/nm	Φ_f[a]
CB1	Toluene	492	507	15	0.74
	CH_2Cl_2	483	498	15	0.63
	THF	482	500	18	0.64
	MeOH	476	495	19	0.59
	MeCN	475	495	20	0.63
CB2	CH_2Cl_2	551	570	19	0.38
	THF	555	582	27	0.23
	MeOH	546	577	31	0.18
	MeCN	545	573	28	0.29
CB3	Toluene	562	578	16	0.50
	CH_2Cl_2	553	575	22	0.46
	THF	550	571	21	0.57
	MeOH	542	566	24	0.45
	MeCN	543	570	27	0.47

[a] The Φ_f values was determined using fluorescein (0.85 in 0.1N NaOH)[17] as a standard.

occurrence of a strong intramolecular charge transfer (ICT) from phenolate unit to the conjugated BODIPY core. Similar to the reported BODIPYs bearing phenolic subunits, such large red-shift results in a decrease in the emission intensity. Based on the above results, compound **CB3** is designed as colorimetric sensor for detecting fluoride by fluoride-induced Si–O bond cleavage reaction.

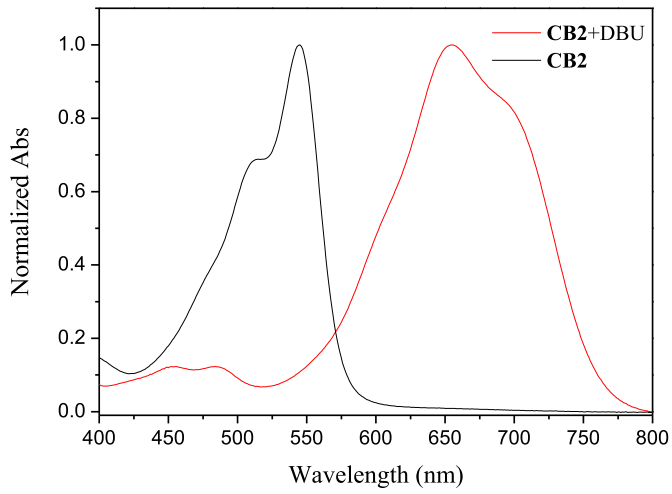


Fig. 2. The Normalized absorption spectra of compound **CB2** in CH_3CN containing no and organic base DBU (10 equiv).

2.3. TBDMS deprotective reaction based response of CB3 to fluoride ion

Fig. 3 displays the UV–vis absorption titration of compound **CB3** with various amount of fluoride ion in CH_3CN at room temperature. With increasing equivalence of fluoride ion (using TBAF), the intensity of the absorption maximum at 543 nm gradually decreased, concomitant with the formation of a new band centered at 653 nm, with an isosbestic point at 570 nm. Correspondingly, the absorption alternation of 110 nm red-shift results in the solution distinct color change from pink to blue, which can be directly observed by naked eyes. The absorption band at 653 nm is similar to that characteristic absorption of phenolate form of **CB2** (Fig. 2), where is attributed to the F^- promoted deprotection of **CB3** to generate phenolate form as that of **CB2**.

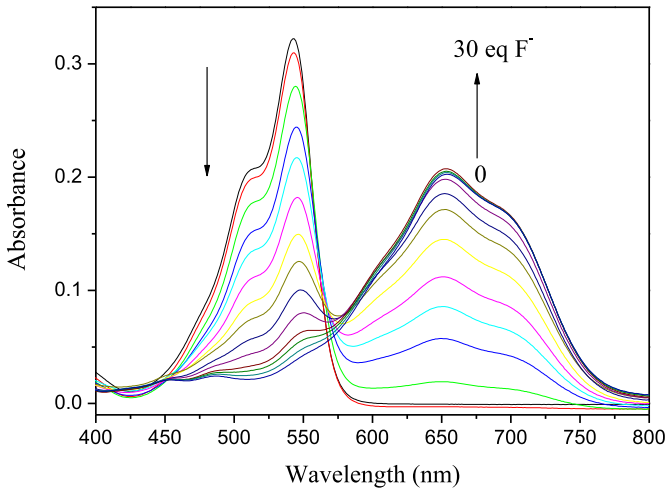


Fig. 3. The absorption spectra change of compound **CB3** (5 μM) with various concentration of TBAF (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 24, 28, 30 equiv) in CH_3CN.

The fluorescence response of **CB3** in CH_3CN toward various amount of fluoride ion was also performed at room temperature. As shown in Fig. 4, upon the addition of TBAF, the fluorescence intensity at 570 nm was remarkably decreased, which was almost linearly quenched with increasing added amount of F^- and 95% of the fluorescence intensity was quenched upon addition of about 25 equiv of fluoride ion. This result originates from the formation of non-emissive phenolate form of **CB2** by the F^- promoted deprotection of **CB3**.

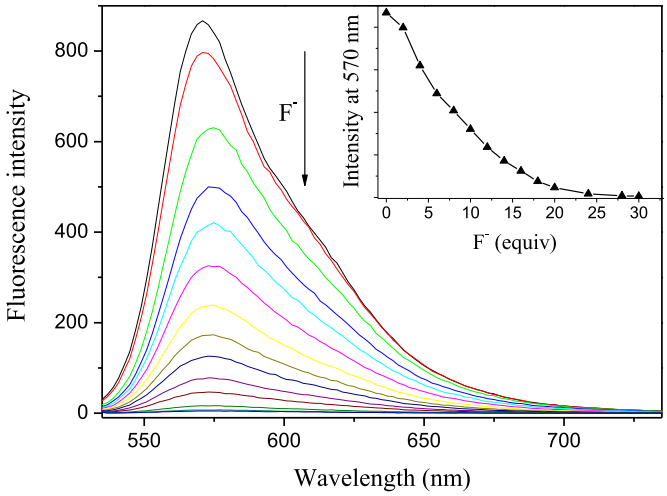


Fig. 4. The fluorescence spectra change of compound **CB3** (5 μM) with various concentration of TBAF (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 24, 28, 30 equiv) in CH_3CN. Inset: fluorescence intensity changes (at 570 nm) of **CB3** with various amounts of F^-.

Kinetics profile of the fluorescence response of **CB3** toward fluoride ion was studied by time-dependent fluorescence spectra. As is shown in Fig. 5, the quenching of fluorescence-intensity is largely dependent on the concentration of fluoride ion in the solution at room temperature. The F^- promoted de-protection maybe it is an equilibrium, since less equivalence did not promote further fluorescence quenching after 2 min. As a result, large excess of F^- anion is necessary to drive the equilibrium to the right, afforded a quicker and more dramatic fluorescent decrease response. The **CB3** didn't show any noticeable change in the emission intensities at 563 nm in the absence of F^- within 5 min. In contrast, **CB3** was quantitatively consumed in the presence of 25 or 30 equiv of F^- within 30 s and the observed rate constant (k_{obs}) was obtained to be 0.14 or 0.18 s^{-1}, respectively, which is faster than the reported compound.[6b] Therefore, **CB3** for the detection of F^- in CH_3CN could be achieved in 30 s at room temperature.

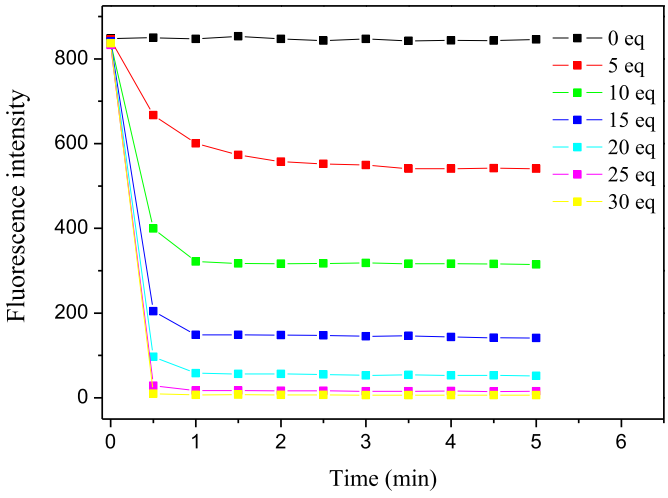
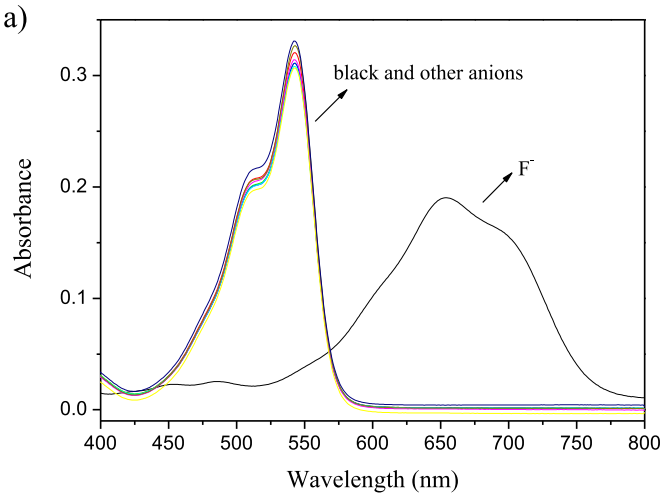


Fig. 5. The time dependent of fluorescence intensity change at 570 nm of compound **CB3** (5 μM) with different equiv of TBAF in CH_3CN.

The selectivity of compound **CB3** toward fluoride ion is impressively high due to the specific reactivity of Si–O band cleavage induced with F^-. As shown in Fig. 6a, the large absorption red-shift



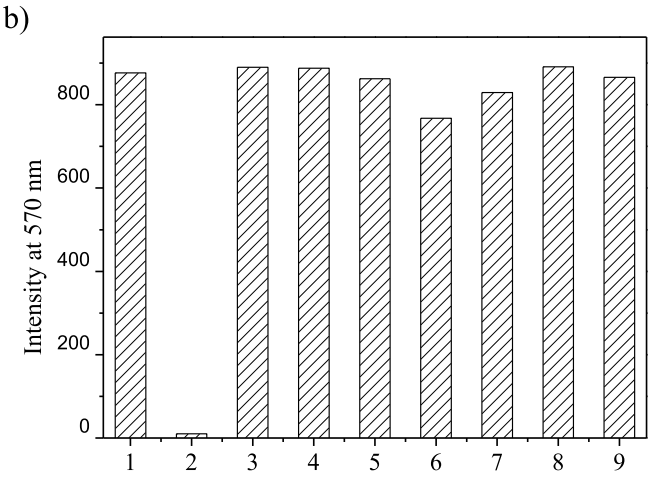


Fig. 6. (a) The absorption spectra of compound **CB3** (5 μM) with F^- (25 equiv) and other anions (25 equiv) including Cl^-, Br^-, I^-, $H_2PO_4^-$, HPO_4^{2-}, N_3^-, NO_3^- and OH^- in CH_3CN. (b) The fluorescence intensity at 570 nm of **CB3** (5 μM) in the absence and presence of 25 equiv of various anions in CH_3CN: 1, free; 2, F^-; 3, Cl^-; 4, Br^-; 5, I^-; 6, $H_2PO_4^-$; 7, N_3^-; 8, NO_3^-; 9, OH^-.

was only observed with the addition of F^-, whereas the addition of various other anions such as Cl^-, Br^-, I^-, $H_2PO_4^-$, N_3^-, NO_3^- and OH^- did not show any change in the absorption spectra. Meanwhile, the color of **CB3** solution changed from orange to blue with addition of F^- and the other anions didn't induce any color change as showed in Fig. 7. The fluorescence response of **CB3** toward various anions is

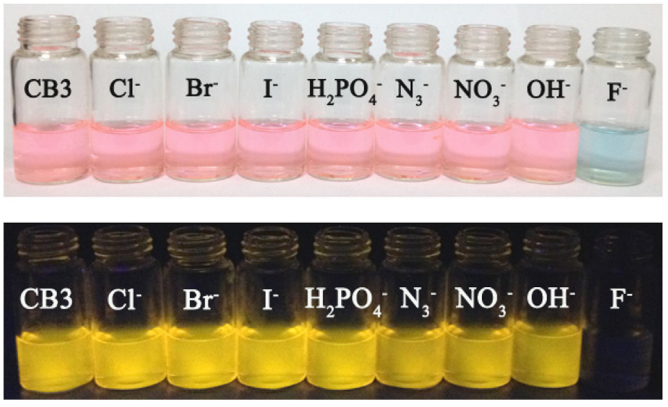


Fig. 7. Colorimetric changes (up) and Fluorescence photographs (down) of compound **CB3** (5 μM) with 25 equiv of various anions in CH_3CN.

shown in Fig. 6b. **CB3** showed strong fluorescence intensity at 570 nm, and the fluorescence change didn't take place upon addition of 25 equiv of Cl^-, Br^-, I^-, $H_2PO_4^-$, N_3^-, NO_3^- and OH^-. Only the introduction of F^- resulted in the remarkable fluorescence quenching and this response could also be observed by naked eyes under a hand-held UV lamp from Fig. 7. These results indicate the excellent selectivity of **CB3** towards F^- over other competitive anions.

3. Conclusion

In summary, we have synthesized and investigated three 2-cyano modified asymmetric BODIPY derivatives **CB1**–**CB3**, which show typical photophysical behavior of BODIPY derivatives with small Stokes shift and high fluorescence quantum yield. The **CB2** turns into the phenolate form upon adding base (DBU) and exhibits remarkable color change and fluorescence decrease owing to the strong intramolecular charge transfer. Accordingly, the **CB3** is designed and applied as a colorimetric sensor for detecting fluoride ion. **CB3** shows excellent selectivity owing to the specific F^- deprotective reaction and rapid response time (30 s) due to the electron-withdrawing cyano group in BODIPY core. These cyano-substituted BODIPY can be further modified and show their potential in the biological labeling in our following work.

4. Experimental

4.1. Reagents and instrumentation

Solvents for organic synthesis were reagent grade, and were dried prior to use. 4-Methyl-pyrrole-3-carbonitrile was prepared as described in the literature.[16] Other chemicals were purchased from commercial sources and used as received. Double distilled water was used throughout the experiments.^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ with a Varian operating at 400 MHz and 100 MHz, respectively and chemical shifts were reported in ppm using tetramethylsilane (TMS) as internal standard. FT-IR spectra were measured with a Bruker Vector22 Infrared Spectrometer. Mass spectra were obtained with a Micromass GCF TOF mass spectrometer. UV–vis absorption and fluorescence emission spectra were performed at room temperature with a Shimadzu UV-2450 UV–vis spectrometer and Shimadzu RF 5301 PC spectrophotometer, respectively. Fluorescence quantum yield was determined using fluorescein (Φ_f=0.85 in 0.1N NaOH) [17] as a reference.

4.2. Synthesis

*4.2.1. Synthesis of compound **2**.* $POCl_3$ (4 ml, 43 mmol) was added dropwise to DMF (3.4 ml, 43 mmol) in an ice bath for 5 min, then the solution was stirred for additional 1 h at 25 °C. Compound **1** (3 g, 28.3 mmol) in DMF (12 ml) was added slowly. The mixture was stirred at 25 °C for 1 h, then poured into ice water. The precipitated light yellow solid was collected by filtration and purified by silica gel column chromatography to give compound **2** (2.8 g, 74%) as white solid. R_f=0.30 (ethyl acetate/petroleum ether 1/2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 9.70 (s, 1H), 7.45 (d, J=2.8 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 134.4, 130.2, 129.6, 114.1, 97.8, 9.4. IR (KBr, cm^{-1}): 3253 (m), 2225 (m), 1654 (s), 1417 (s), 1361 (m), 800 (s). FTMS (EI) calcd for M^+ $C_7H_6N_2O$: 134.0480, found 134.0480.

*4.2.2. Synthesis of compound **CB1**.* To a stirred solution of compound **2** (0.4 g, 3 mmol) and 2,4-dimethyl-1H-pyrrole (0.29 g, 3 mmol) in CH_2Cl_2 (40 ml) was added CF_3COOH (3 drops). The mixture was stirred at 25 °C for 6 h triethylamine (3.0 ml, 21.2 mmol) and $BF_3\cdot OEt_2$ (3.1 ml, 24.2 mmol) were added and the reaction was stirred for 5 h. The mixture was washed with water and brine. The organic layers was dried Na_2SO_4, filtered and evaporated. The residue was purified by silica gel column chromatography to give compound **CB1** (0.36 g, 47%) as black solid. R_f=0.33 (ethyl acetate/petroleum ether 1/2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.22 (s, 1H), 6.31 (s, 1H), 2.62 (s, 3H), 2.40 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 148.2, 139.5, 139.0, 138.3, 129.9, 123.4, 122.0, 114.9, 99.7, 15.6, 11.6, 10.4. IR (KBr, cm^{-1}): 3432 (m), 2926 (m), 2219 (m), 1611(s), 1415 (s), 1260 (s), 1090 (s), 972 (m). FTMS (EI) calcd for M^+ $C_{13}H_{12}N_3BF_2$: 259.1092, found 259.1088.

*4.2.3. Synthesis of compound **CB2**.* To a stirred solution of compound **CB1** (0.17 g, 0.66 mmol) and 4-hydroxybenzaldehyde (0.1 g, 0.79 mmol) in CH_3CN (10 ml) was added CH_3COOH (0.26 g) and pyridine (0.33 g). The mixture was stirred at 70 °C for 30 min where the reaction was completed by TLC monitored. Then the solvent was evaporated by vacuum. Water (20 ml) was added and the solution was extracted with EtOAc (15 ml×3). The combined organic layers was washed with brine, dried over Na_2SO_4 and evaporated under vacuum. The residue was purified by silica gel column chromatography to give compound **CB2** (0.11 g, 46%) as violent solid. R_f=0.21 (ethyl acetate/petroleum ether 1/1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.35 (s, 1H), 8.14 (s, 1H), 7.93 (d, J=16 Hz, 1H), 7.86 (s, 1H), 7.56 (d, J=8.4 Hz, 2H), 7.24–7.29 (m, 2H), 6.90 (d, J=8.4 Hz, 2H), 2.41 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.0, 161.3, 148.0, 145.8, 140.0, 139.0, 136.9, 131.0, 130.5, 126.8, 121.0, 120.1, 116.8, 116.3, 115.6, 113.9, 11.8, 10.4. IR (KBr, cm^{-1}): 3431 (m), 2924 (m), 2224 (m), 1601 (s), 1418 (s), 1265 (s), 1152 (m), 1066 (m). FTMS (ESI) calcd for $[M+Na]^+$ $C_{20}H_{16}ON_3BF_2Na$: 386.1250, found 386.1242.

*4.2.4. Synthesis of compound **CB3**.* A mixture of compound **CB2** (80 mg, 0.22 mmol), *tert*-butyldimethylchlorosilane (TBDMSCl, 66 mg, 0.44 mmol) and imidazole (45 mg, 0.66 mmol) in DMF (5 ml) was stirred at room temperature for 6 h under N_2. After the reaction completed, water (20 ml) was added and the solution was extracted with EtOAc (15 ml×3). The combined organic layers was washed with brine, dried over Na_2SO_4 and evaporated under vacuum. The residue was purified by silica gel column chromatography to give compound **CB3** (45 mg, 43%) as violent solid. R_f=0.46 (ethyl acetate/petroleum ether 1/2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.55 (d, J=8.8 Hz, 2H), 7.47 (s, 2H), 7.11 (s, 1H), 6.89 (d, J=8.8 Hz, 2H), 6.85 (s, 1H), 2.41 (s, 3H), 2.37 (s, 3H), 0.99 (s, 9H), 0.24 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 158.7, 146.4, 143.7, 139.6, 138.3, 136.9, 130.3, 130.2, 128.5, 120.8, 118.9, 118.8, 115.6, 115.2, 99.3, 25.6, 18.3, 11.7, 10.4, −4.3. IR (KBr, cm^{-1}): 3337 (m), 2927 (m), 2221 (m), 1610 (s), 1419 (s), 1266 (s), 1156 (m). FTMS (ESI) calcd for $[M+Na]^+$ $C_{26}H_{30}ON_3BF_2SiNa$: 500.2116, found 500.2112.

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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.tet.2015.10.081.

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