

## 检测氢离子的荧光探针:含稠合外环的硼-二吡咯亚甲基染料的合成、光谱和电化学性质研究

徐海云<sup>1,2</sup> 沈 珍<sup>\*,1</sup>

(<sup>1</sup> 南京大学配位化学国家重点实验室,化学化工学院,南京 210093)

(<sup>2</sup> 商丘师范学院化学系,商丘 476000)

**摘要:** 本文合成了 3 个新型中位分别为 *N,N*-二甲基苯胺、对-甲氧基苯基或苯基取代的含稠合外环的硼-二吡咯亚甲基染料。研究了它们的吸收光谱、稳态荧光光谱和电化学性质;采用荧光光谱滴定方法研究了它们在强极性溶剂中对氢离子的响应;将氢离子滴加到 *N,N*-二甲基苯胺取代的硼-二吡咯亚甲基染料(**1**)的 CH<sub>3</sub>CN-H<sub>2</sub>O(1:1, V/V)溶液中,其溶液的荧光显著增强;染料 **1** 在可见光激发下,可以作为酸性 pH 范围内检测氢离子的荧光探针。

**关键词:** 硼-二吡咯亚甲基染料;稠合外环;氢离子识别;电子转移;荧光探针

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## Fluorescent Probe for H<sup>+</sup>: Synthesis, Spectroscopic and Electrochemical Studies of Exocyclic Ring-Fused Boron Dipyrromethene Dyes

XU Hai-Yun<sup>1,2</sup> SHEN Zhen<sup>\*,1</sup>

(<sup>1</sup> *School of Chemistry and Chemical Engineering, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China*)

(<sup>2</sup> *Department of Chemistry, Shangqiu Normal College, Shangqiu, Henan 476000, China*)

**Abstract:** Three new exocyclic ring-fused boron-dipyrromethene (BDP) dyes with *N,N*-dimethylaniline, *p*-methoxyphenyl or phenyl subunit at *meso*-position were synthesized. Their absorption, steady-state fluorescence and electrochemical properties were investigated. The spectrofluorometric titrations were performed to examine their responsive abilities to H<sup>+</sup> in strong polar solvent. The dimethylanilino-substituted BDP dye **1** showed a large fluorescence enhancement upon adding H<sup>+</sup> to its CH<sub>3</sub>CN-H<sub>2</sub>O (1:1, V/V) solution. BDP **1** can be used as a fluorescent probe for H<sup>+</sup> in the acidic pH range excited with visible light.

**Key words:** Boron-dipyrromethene (BDP) dyes; fused exocyclic rings; H<sup>+</sup> recognition; electron transfer, fluorescent sensor

In recent years, boron-dipyrromethene (BDP) dyes have received increasing attentions because of their superior photostability to fluorescein<sup>[1]</sup>, insensitivity towards pH value and solvent polarity<sup>[2]</sup>, and sufficiently high lipophilicity to permeate cell membranes, as well

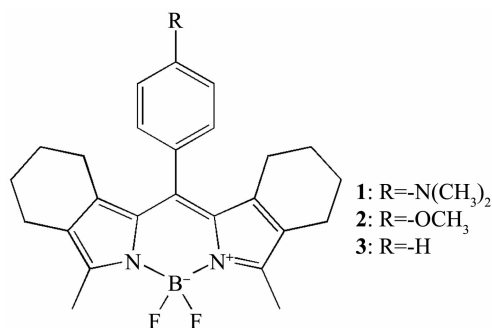
as high molar extinction coefficients, high fluorescence quantum yields approaching unit, photoexcitation with visible light and accessible structural modification<sup>[3]</sup>. These valuable properties have brought out various applications in the field of laser dyes<sup>[4]</sup>, fluorescent

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\*通讯联系人。E-mail: zshen@nju.edu.cn, xuhyun@163.com

sensors<sup>[5]</sup>, optical devices<sup>[6]</sup> and dopants in liquid crystals<sup>[7]</sup>. A lot of BDP derivatives substituted with phenolic, naphtholic, dialkylaminopheny, calix[4]-arene subunits at meso-position show interesting photoinduced electron transfer (PET) mediated fluorescence off/on switch, thus acting as probes for pH sensing in the alkaline region, the acidic region and the near neutral region, respectively<sup>[8]</sup>. To the best of our knowledge, examples of BDP analogous fused with exocyclic rings, especially at positions 1, 2, 6, 7 are very rare<sup>[9-10]</sup>. As our increasing interest in BDP-based fluorescent molecular sensors or switches and an extension of our previous research work<sup>[9-12]</sup>, we report here three new exocyclic ring-fused boron-dipyrromethene (BDP) dyes substituted with *N,N*-dimethylaniline (**1**), *p*-methoxyphenyl (**2**) or phenyl (**3**) subunit at *meso*-position. Their photophysical properties have been investigated by steady-state absorption and emission spectroscopy. Moreover, the binding behavior of **1** and **2** with  $H^+$  in acetonitrile- $H_2O$  (1:1, *V/V*) has been spectroscopically examined and their redox features have been also studied.



## 1 Experimental

### 1.1 Instruments

Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. Melting points were determined with a Reichert Thermover apparatus without correction. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX500 spectrometer and referenced to the residual proton signals of the solvent. The Mass spectra were measured with a Bruker Daltonics Autoflex II™ MALDI-TOF spectrometer. IR spectra were recorded on Bruker Vector 22 spectrometer with KBr pellets in the 4 000~400 cm<sup>-1</sup>

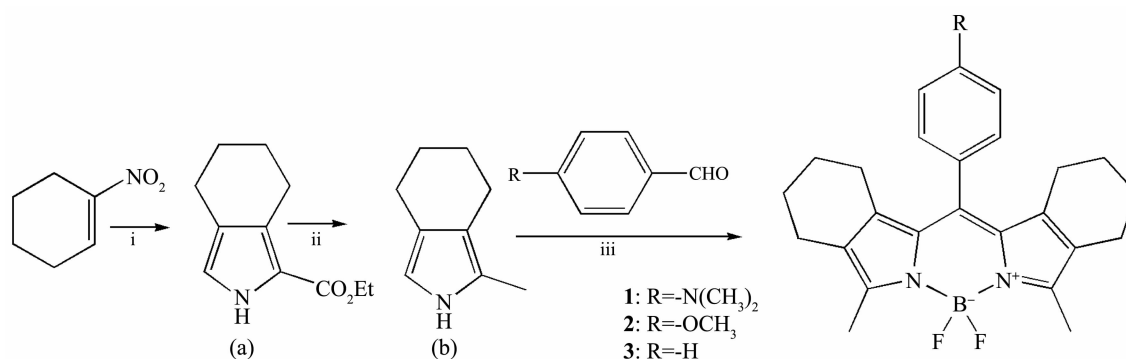
region. UV-Visible spectra were carried out on a UV-3100 spectrophotometer. Fluorescence spectra were measured on an Aminco Bowman 2 Luminescence spectrophotometer with a xenon arc lamp as the light source. The fluorescence quantum yields ( $\Phi_f$ ) were determined relative to rhodamine 6G in water ( $\lambda_{ex}$ =488 nm,  $\Phi_f$ =0.76) with an absorbance below 0.1 at the excitation wavelength<sup>[13]</sup>. The reported complex stability constant  $K_s$  of probe **1** with  $H^+$  was determined by gradually adding microliter of  $H^+$  ( $c=10^{-2}$  mol·L<sup>-1</sup> of HClO<sub>4</sub>) to a dilute solution (typically  $c=10^{-5}$  mol·L<sup>-1</sup>) of dye **1** in CH<sub>3</sub>CN- $H_2O$  (1:1, *V/V*). Cyclic voltammetry were carried out in 0.1 mol·L<sup>-1</sup> TBAP (tetra-*n*-butylammonium perchlorate) in acetonitrile on a Perkin-Elmer electrochemical analysis system model 283 with a platinum disk as the working electrode, Ag/AgCl as the quasi-reference electrode, and a platinum wire as the counterelectrode. Redox potentials were referenced internally against ferrocenium/ferrocene ( $Fc^+/Fc$ ). All measurements were performed under an inert atmosphere with a scan rate of 250 mV·s<sup>-1</sup> at room temperature.

### 1.2 Reagents and materials

All air- and moisture-sensitive reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Unless otherwise noted, all reagents or solvents were obtained from commercial suppliers and used as received without further purification. Dry dichloromethane was obtained by refluxing and distilling over CaH<sub>2</sub>. Dry tetrahydrofuran (THF) was distilled from sodium/benzophenone. Triethylamine was obtained by simple distillation. Acetonitrile used for the electrochemical studies was distilled from CaH<sub>2</sub>. The solvents used for photophysical measurement were of spectroscopic grade without further purification. Chromatographic purifications were conducted by using 40~200  $\mu$ m silica gel obtained from Merck. Thin-layer chromatography (TLC) was performed on silica gel plates coated with fluorescent indicator. 2-Ethoxycarbonyl-4,5,6,7-tetrahydroisoidole (**a**) was synthesized according to the literature<sup>[14]</sup>.

### 1.3 Synthesis

#### 1.3.1 2-methyl-4,5,6,7-tetrahydro-2*H*-isoidole (**b**)



Reaction conditions: (i) CNCH<sub>2</sub>CO<sub>2</sub>Et, DBU in dry THF at r.t.; (ii) LiAlH<sub>4</sub> in dry THF, reflux; (iii) TFA, DDQ, (Et)<sub>3</sub>N, BF<sub>3</sub>OEt<sub>2</sub>, in dry CH<sub>2</sub>Cl<sub>2</sub> at r.t.

Scheme 1 Synthetic route for **1**, **2** and **3**

LiAlH<sub>4</sub> (1.14 g, 30 mmol) powder was added in small portions to a stirred solution of ethyl 4,5,6,7-tetrahydro-2*H*-isoinidole-1-carboxylate **a** (579 mg, 3 mmol) in dry THF (200 mL) under nitrogen. The reaction mixture was refluxed for 3 h. After cooling to room temperature, water (50 mL) was added dropwise and the resulting mixture was filtered through a Celite pad, which was washed with EtOAc (3×30 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2×20 mL). The combined organic layer was washed with water (5×30 mL) and brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by chromatography on silica using CHCl<sub>3</sub> as solvent. The first fraction was collected to give **b** (0.27 g) as a pale red liquid with a 67% yield.

### 1.3.2 General procedure for the preparation of **1**~**3**

Compound **b** (2 mmol) and aldehyde [4-(dimethylamino)benzaldehyde (**1**), 4-methoxybenzaldehyde (**2**), or benzaldehyde (**3**)] (1 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (120 mL) under nitrogen. One drop of trifluoroacetic acid (TFA) was added, and the solution was stirred at room temperature in the dark for 2~4 h (until TLC showed complete consumption of aldehyde). A solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added, and the stirring was continued for additional 1 h. The reaction mixture was then treated with absolute triethylamine (3 mL) and boron trifluoride etherate (3 mL). After the mixture was stirred for another 1 h, a deep green fluorescence was observed in the mixture.

The reaction mixture was washed with water (3×50 mL) and brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated at reduced pressure. The crude product was purified by column chromatography on silica-gel and recrystallization from CHCl<sub>3</sub>/hexane.

**1**: red crystals (214 mg, yield 48%). m.p. >250 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.07 (d, 2H, *J*=8.1 Hz), 6.79 (broad s, 2H), 3.06 (s, 6H), 2.49 (s, 6H), 2.35 (t, 4H, *J*=6.1 Hz), 1.72 (m, 4H), 1.62 (m, 4H), 1.44 (t, 4H, *J*=2.8 Hz); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): 151.8, 150.1, 141.3, 139.6, 131.0, 129.3, 128.6, 128.3, 112.7, 40.84, 24.66, 23.63, 22.97, 21.79, 12.68; IR (KBr): ν<sub>max</sub>/cm<sup>-1</sup> 1547, 1482 (C=C, C=N), 1200 (B-F); MS (MALDI-TOF): *m/z*: 448.20 [M+H]<sup>+</sup>; elemental analysis calcd. (%) for C<sub>27</sub>H<sub>32</sub>BF<sub>2</sub>N<sub>3</sub>: C 72.49, H 7.21, N 9.39; found: C 72.42, H 7.29, N 9.32.

Compound **2** was prepared from the reaction of **b** (0.27 g, 2 mmol) with 4-methoxybenzaldehyde (0.14 g, 1 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (120 mL) under nitrogen atmosphere and purified by flash chromatography (silica gel, 5% EtOAc/petroleum ether), followed by recrystallization from CHCl<sub>3</sub>/hexane to give red crystals in 18% yield. m.p. 194 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ=7.16 (d, 2H, 8.6Hz), 6.99 (d, 2H, 8.6Hz), 3.90(s, 3H), 2.49(s, 6H), 2.35(t, 4H, 6.2Hz), 1.65(t, 4H, 3.9Hz), 1.61 (m, 4H), 1.43 (m, 4H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): 156.42, 153.17, 141.23, 139.66, 130.64, 129.88, 128.69, 128.11, 116.30, 52.65, 24.58, 23.46, 22.88, 21.74, 12.74; IR (KBr): ν<sub>max</sub>/cm<sup>-1</sup> 1548, 1480(C=C, C=N), 1201 (B-F); MS (EI): *m/z* (%): 434.71 (100) [M<sup>+</sup>]; elemental

analysis calcd.(%) for  $C_{27}H_{29}BF_2N_2O$ : C 71.90, H 6.73, N 6.49; found: C 71.82, H 6.70, N 6.54.

Compound **3** was synthesized analogously by the reaction of benzaldehyde (0.11 g, 1 mmol) with **b** (0.27 g, 2 mmol) in dry  $CH_2Cl_2$  (120 mL), and purified by column chromatography (silica gel, 5% EtOAc/petroleum ether), recrystallized from  $CHCl_3$ /hexane to give red solid in 30% yield. m.p. 170 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$ =7.28~7.49 (m, 5H), 2.47 (s, 6H), 2.34 (t, 4H,  $J$ =6.0 Hz), 1.75 (t, 4H,  $J$ =10 Hz), 1.59 (m, 4H); 1.40(m, 4H); IR (KBr):  $\nu_{max}/cm^{-1}$  1 549, 1 480(C=C, C=

N), 1 202 (B-F); MS (EI):  $m/z$ (%): 404.23 (100) [ $M^+$ ]; elemental analysis calcd.(%) for  $C_{25}H_{27}BF_2N_2$ : C 72.27, H 6.73, N 6.93; found: C 72.14, H 6.82, N, 6.88.

## 2 Results and discussion

### 2.1 Spectroscopic properties

The absorption and emission properties of BDPs **1~3** in nonpolar and polar solvents are listed in Table 1, and the absorption and steady-state fluorescence emission spectra of dye **1** in the determined solvents are shown in Fig.1.

Table 1 Absorption and emission properties of **1~3** in hexane and acetonitrile at 298 K

Compounds	Solvent	$\epsilon_{max}$ (abs) <sup>a</sup> / (mol <sup>-1</sup> ·L·cm <sup>-1</sup> )	$\lambda_{abs}$ / nm	$\lambda_e$ / nm	$\Phi_f$	Stokes shift / nm
<b>1</b>	Hexane	97 000	523	542	0.92	19
	$CH_3CN$	11 1300	522	540	0.02	18
<b>2</b>	Hexane	71 000	524	543	0.91	18
	$CH_3CN$	78 000	522	540	0.82	18
<b>3</b>	Hexane	35 000	525	542	0.79	17
	$CH_3CN$	46 000	522	539	0.74	17

<sup>a</sup> Estimated errors in  $\epsilon_{max}$  are within 500 mol<sup>-1</sup>·L·cm<sup>-1</sup>.

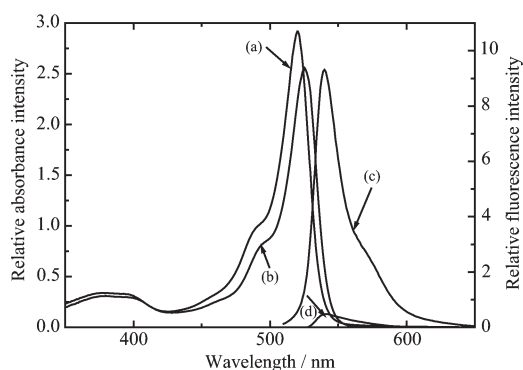


Fig.1 Absorption spectra of dye **1** in hexane (a) and  $CH_3CN$  (b) and the emission spectra of **1** in hexane (c) and  $CH_3CN$  (d) at 298 K ( $\lambda_{ex}$ =490 nm)

As can be seen from Table 1, the molar absorption coefficients ( $\epsilon_{max}$ ) for these exocyclic ring-fused BDP derivatives are relatively high and lie in 35 000~111 300 mol<sup>-1</sup>·L<sup>-1</sup>·cm<sup>-1</sup> range, and the nature of the *para*-substituent (R) in the phenyl group at *meso*-position of BDPs **1~3** has no essential effect on their absorption and emission maxima. In addition, the maximal band positions in the absorption and emission spectra do not show any particular trend as a function of solvent polarity, only being slightly shifted

hypsochromically with increasing the solvent polarity, which is consistent with the general behavior of BDP chromophore. On the other hand, the longest absorption or emission bands for BDPs **1~3** are shifted to the red of 10~20 nm relative to those described BDP dyes carrying only alkyl substituents on the BDP core<sup>[15]</sup> owe to the introduction of the fused exocyclic rings on the pyrrole side.

The steady-state absorption spectrum of **1** features with a strong, narrow band centered around 524 nm and a shoulder on the shorter wavelength side centered at about 496 nm, which is typical for the conventional BDP derivatives carrying only alkyl substitutes on the indacene core<sup>[2a]</sup>. A considerably weaker and broad absorption band is observed at about 390 nm, which can be attributed to the  $s_0-s_2$  transition<sup>[16]</sup>. The absorption spectra of **2** and **3** are, in general, similar to those of **1** in the used solvents.

Excitation of **2** yields the typical fluorescence spectra (Fig.2) features of the classical BDP, with a narrow and slightly Stokes-shifted band of mirror image shape. The intensity and position of the fluorescent spectra are almost independent of the solvent polarity,

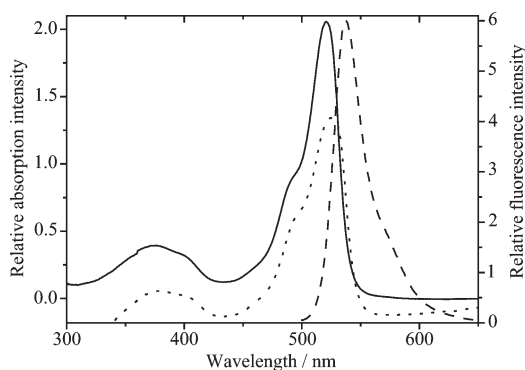


Fig.2 Absorption of dye **2** in hexane (dotted line) and  $\text{CH}_3\text{CN}$  (solid line) and emission spectra of **2** in  $\text{CH}_3\text{CN}$  (dashed line) ( $\lambda_{\text{ex}}=490\text{ nm}$ ), the emission spectra of dye **2** in hexane, similar to that in  $\text{CH}_3\text{CN}$ , are omitted for better clarity

indicating that emission occurs from the weakly polar, relaxed Franck-Condon excited state. The emission spectra of **3** are almost the same as those of **2** in the determined solvents

In contrary to its absorption spectra, the emission spectra of **1** are strongly solvent-dependent. In hexane, the localized, narrow LE emission maximum around 542 nm is strong and shaped like the mirror image of the absorption spectra, which strongly resemble those of **2** and **3**. In acetonitrile, the fluorescence of **1** from this LE emission is strongly quenched (Fig.1) due to the photoinduced electron transfer (PET) from the nitrogen atom of the *p*-dimethylamino-substituted phenyl group to the excited BDP chromophore, while dye **2** or dye **3** display a strong fluorescence emission independent of

the nature of the studied solvents.

## 2.2 Fluorimetric titrations of **1** and **2** with $\text{H}^+$

In acetonitrile-water solvent, all of the features (including position, shape, height) of the absorption spectra of dye **1** and dye **2** are essentially  $\text{H}^+$  independent, indicating that the effect of protonation on the absorption behavior of **1** and **2** is only barely, with a slight bathochromic shift in the absorption maxima. However, the effect of  $\text{H}^+$  binding on the emission spectrum of **1** is very large.

As seen from Fig.3, the fluorescence emission intensity ( $F$ ) is only dependent on  $\text{H}^+$  and increases significantly with increasing  $c_{\text{H}^+}$  while the emission maxima centered at 540 nm are almost invariant, with only a slight bathochromic shift. Upon binding of  $\text{H}^+$  with the dimethylamino group, *p*-alkylamino-substituted phenyl moiety on meso-position of the BDP core becomes substituted with an electron acceptor rather than with an electron donor in such a way that any PET is strongly inhibited, which means that the quenching fluorescence is again revived. The association constants  $K_s$  for the interaction  $\text{H}^+$  with **1** in acetonitrile-water is determined by the nonlinear curve-fitting analysis of the fluorescence titration data ( $F$ ) recorded as a function of  $c_{\text{H}^+}$  (Fig.3b) according to Eq. (1), where the fluorescence signals  $F_{\text{min}}$  is the initial fluorescence value of **1**, and  $F_{\text{max}}$  is the maximum fluorescence value in the presence of  $\text{H}^+$  ( $F_{\text{max}}$  can not be accurately determined, it can be left as a floating

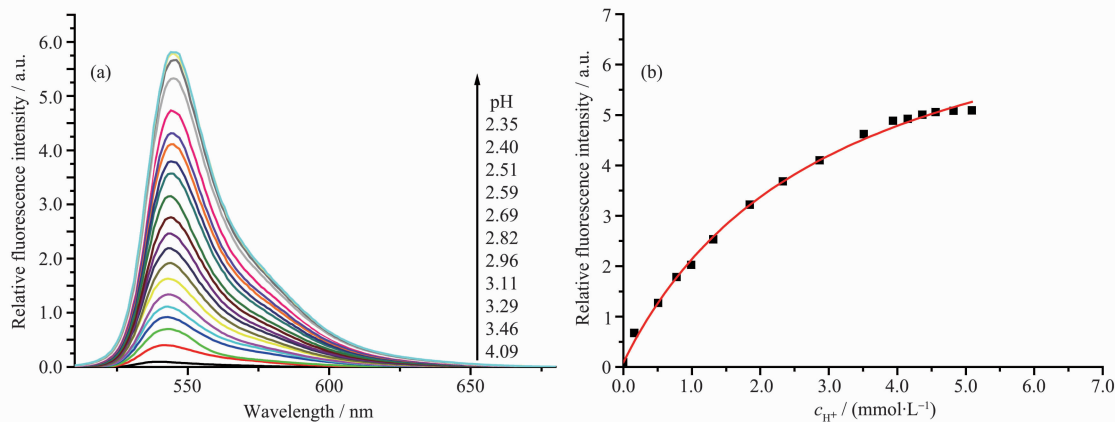


Fig.3 (a) Variations in fluorescence intensity of a solution of dye **1** in  $\text{CH}_3\text{CN-H}_2\text{O}$  (1:1, V/V) as a function of pH value; (b) Fluorescence titration curve of dye **1** in  $\text{CH}_3\text{CN-H}_2\text{O}$  (1:1, V/V) as a function of  $c_{\text{H}^+}$  is obtained from Fig.3a ( $\lambda_{\text{em}}=540\text{ nm}$ ,  $\lambda_{\text{ex}}=490\text{ nm}$ ), and the solid line represents the best fits with eq 1 to the fluorimetric titration data of dye **1**



parameter in the analysis).

$$F = (F_{\max} c_{\text{H}^+} K_s + F_{\min}) / (1 + K_s c_{\text{H}^+}) \quad (1)$$

The estimated  $K_s$  value of a well-defined 1:1 stoichiometry of  $\text{H}^+$  binding to the aniline moiety of **1** is found to be  $333 \text{ mol}^{-1} \cdot \text{L}$ . Therefore, the corresponding  $\text{p}K_a$  (here,  $K_a$  is the acid dissociation constant of the ammonium form of **1**) is determined as 2.52 including in the normal ranges of values reported for other 8-dimethylaminophenyl-substituted BDP analogues<sup>[17]</sup> or related donor-acceptor-substituted biaryl dyes, such as *p*-anthracene-9-yl-dimethyl-aminobenzene ( $\text{p}K_a=2.50$  in ethanol-water 4:1, V/V)<sup>[18]</sup> or 4-dimethyl-amino-4'-cyano-biphenyl ( $\text{p}K_a=2.35$  in ethanol-water 1:1, V/V)<sup>[19]</sup>.

To study the influence of added salt on the steady-state fluorescence of dye **1**, we recorded pH value-dependent emission spectra of dye **1** under various conditions. The results are shown in Fig.4, indicating that the fluorescence intensity change of dye **1** is nearly insensitive to added salt in the concentration range studied.

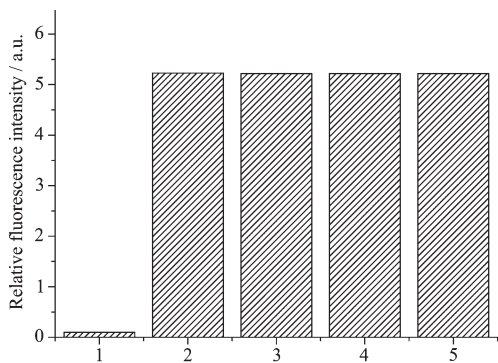


Fig.4 pH value-dependent emission spectra of dye **1** in the absence/presence of other ions in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (1:1, V/V) solution ( $\lambda_{\text{em}}=540 \text{ nm}$ ,  $\lambda_{\text{ex}}=490 \text{ nm}$ )

However, addition of  $\text{H}^+$  into  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (1:1, V/V) solution of **2** did not bring about any significant changes in the fluorescence emission spectra, with only a slight bathochromic shift (Fig.5). This insensitive behavior of **2** to  $\text{H}^+$  is due to the weaker electron donating ability of its *p*-alkoxy-substituted phenyl moiety than *p*-alkylamino-substituted moiety of **1**, which leads to the immunity of **2** against the activation

of an electron-transfer (ET) process even in more polar solvents, and therefore it is difficult to accurately assess its binding constant with  $\text{H}^+$ . Obviously, **2** is not suitable for fluorescent pH indicator based on the design principle of PET while **1** can be served as a very sensitive fluorescence off/on probe for detecting traces of free (solvated) protons in polar solvents considering its high cation induced fluorescence enhancement factor  $F_{\max}/F_{\min}$ .

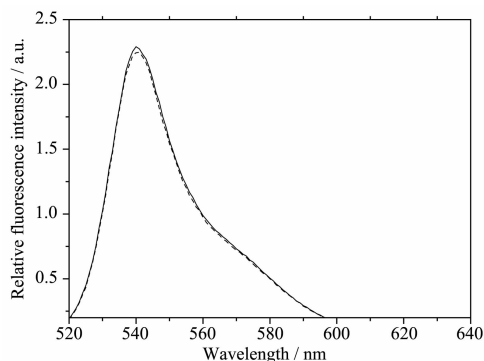


Fig.5 Fluorescence spectra of dye **2** in the absence (dashed line) and presence of 40 equiv of  $\text{H}^+$  in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (solid line)

### 2.3 Electrochemical properties

The redox properties of **1**, **2** and **3** were examined by cyclic voltammetry in  $0.1 \text{ mol} \cdot \text{L}^{-1}$  TBAP in acetonitrile. Each of dyes **1**, **2** and **3** displays a one-electron reversible reduction wave at  $-1.696 \text{ mV}$  (vs  $\text{Fc}^+/\text{Fc}$ ) and a one-electron reversible oxidation wave at  $565 \text{ mV}$ , which are close to those of the conventional BDP dyes. This may be due to reduction and oxidation only centering at the BDP core, independent of the substituted groups at *meso*-position of the BDP core.

The thermodynamic driving force ( $\Delta G_{\text{ET}}$ ) for the excited state electron transfer in polar media can be described by the Rehm-Weller equation<sup>[20]</sup> (Eq. (2)) where  $E_{1/2}(\text{D}^+/\text{D})$  and  $E_{1/2}(\text{A}/\text{A}^-)$  are the ground-state oxidation potential of the receptor and the reduction potential of the electron-deficient fluorophore, respectively,  $E_{00}$  is the zero-zero transition energy of the excited state donor-acceptor pair ( $\text{D}-\text{A}^*$ ),  $E_c$  is the Coulomb stabilization energy of the radical ion pair  $\text{D}^+-\text{A}^-$ .

$$\Delta G_{\text{ET}} = E_{1/2}(\text{D}^+/\text{D}) - E_{1/2}(\text{A}/\text{A}^-) - E_{00} - E_c \quad (2)$$

Here, a second oxidation wave appearing at  $228$

mV for **1** is assigned to the oxidation of the attached dimethylamino substituted phenyl moiety at *meso*-position of the BDP core while the oxidation potential of *p*-methoxy-substituted phenyl moiety for **2** is much larger and can not be detected under this experimental conditions. To assess the feasibility of PET within the dyes, we took the value of dimethoxybenzene (1 150 mV vs  $\text{Fc}^+/\text{Fc}$ ) as a model for **1** and **2**.  $E_c$  is taken as 0.1

eV<sup>[21]</sup>. As can be seen from the calculated values of  $\Delta G_{\text{ET}}$  for these compounds summarized in Table 2, light-induced electron transfer within **1** is thermodynamically favorable while the opposite result is obtained for **2**. All these findings are in good agreement with the experimental observations that only compound **1** shows a significant PET fluorescence quenching.

**Table 2** Redox potentials and electron-transfer parameters of **1**, **2** and **3** in acetonile (potentials in mV vs  $\text{Fc}^+/\text{Fc}$ )

Compounds	$E_{1/2}^{(\text{ox})} / \text{mV}$	$E_{1/2}^{(\text{ox})} / \text{mV}$	$E_{1/2}^{(\text{ox})} / \text{mV}$	$E_{00} / \text{eV}$	$E_c / \text{eV}$	$\Delta G_{\text{ET}} / \text{eV}$
<b>1</b>	-1 712	588	228 <sup>b</sup>	2.36	0.1	-0.520
<b>2</b>	-1 692	558	1 150 <sup>c</sup>	2.30	0.1	0.442 <sup>c</sup>
<b>3</b>	-1 694	560		2.36		

<sup>a</sup> According to Eq.(2); <sup>b</sup> *p*-dimethylamino-substituted phenyl group at the *meso*-position of BDP **1**; <sup>c</sup> Value of dimethoxybenzene.

### 3 Conclusion

Three new exocyclic ring-fused boron-dipyrromethene (BDP) dyes with *N,N*-dimethylaniline, *p*-methoxyphenyl or phenyl subunit at *meso*-position were synthesized by a one-pot, three-step procedure, and their spectroscopic and electrochemical properties were also investigated. Their longest wavelength absorption or emission band is red shifted 15~20 nm compared to that of the classic BDP dyes. Dye **2** displays a strong fluorescence emission with poor response to  $\text{H}^+$ , irrespective of the solvent polarity, whereas dye **1** exhibits very weak residual fluorescence in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  solution, and its fluorescence intensity considerably enhanced upon adding of  $\text{H}^+$ . BDP **1** can be used as a fluorescent probe for  $\text{H}^+$  in the acidic pH range excited with visible light.

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