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一种新型 pH 荧光探针:中位-吡啶取代的硼二吡咯亚甲基(BDP)染料的合成、结构与光谱性质研究

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摘要:本文报道了一种新型中位-吡啶取代的硼-二吡咯亚甲基(BDP)染料的合成与晶体结构表征,发现中位-吡啶环与因达省平面几乎正交,其二面角为 88.2°。同时对它的吸收和稳态荧光性质研究表明:当溶液的酸性增强时,化合物的荧光减弱,pK_a 为 2.24。该化合物在可见光激发下,可以作为比较灵敏的 pH 荧光探针。

关键词:硼-二吡咯亚甲基;晶体结构;荧光;pH 探针
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meso-Pyridine Substituted Boron-dipyrromethene (BDP) Dye as a pH Probe: Synthesis, Crystal Structure and Spectroscopic Properties

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Abstract: A new boron-dipyrromethene (BDP) dye with pyridine subunit at *meso*-position has been synthesized and structurally characterized by X-ray diffraction crystal structure analysis. The *meso*-pyridine ring is nearly perpendicular to the indacene plane with torsion angle being 88.2°. Its absorption and steady-state fluorescence properties are investigated. The compound shows strong fluorescent quenching upon increasing the solution acidity. The pK_a value calculated from the pH dependent fluorescence emission spectra is 2.24. It can be used as a pH probe excited with visible light. CCDC: 297327.

Key words: boron-dipyrromethene; crystal structure; fluorescence; pH probe

Recently, boron-dipyrromethene (BDP) dyes have received considerable attentions because of their valuable photophysical properties such as high photostability, high absorption coefficients, high fluorescent quantum yield and photoexcitable with visible light[1]. These properties have led to numerous applications in the field of laser dyes[2~8], optical devices[9~16], fluorescent sensors[17~23], and molecular probes[21]. A lot of BDP-based fluorescent probes with dialkyaminophenyl, phenolic, naphtholic and calyxarene subunits at *meso*-position have been designed for the detection of proton or metal ions[24~29]. In our previous work, we have reported on the chemical, structural and properties of a series of BDP dyes[30,31]. As an extension of this research program and in connection with our current interest, we report the synthesis, structure and spectroscopic properties of a pyridine substituted BDP dye: 4,4-difluoro-8-(4′-pyridinyl)1,3,5,7-tetramethyl-4-bora-3*a*, 4*a*-diaza-*s*-indacene. Its absorption and steady-state fluorescence properties have been investigated. Protonation of the pyridine

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moiety at low pH in MeOH-H_2O (1∶1 *V*/*V*) solution quenches its fluorescence intensity dramatically.

1 Experimental

1.1 Instruments

^{1}H NMR spectrum was recorded on a Bruker DRX500 spectrometer and referenced to the residual proton signals of the solvent. UV-Vis absorption spectra were carried out on a UV-3100 spectrophotometer. Elemental analyse for C, H and N was performed on a Perkin-Elmer 240C elemental analyzer. Mass spectrum was measured with a Bruker Daltonics Autoflex Ⅱ ™ MALDI TOF spectrometer. Melting point was determined with a Reichert Thermometer apparatus. Fluorescence spectra were measured on an Aminco Bowman 2 Luminescence spectrophotometer with a xenon arc lamp as the light source. The fluorescence quantum yields (ϕ_f) were determined relative to rhodamine 6G in water (λ_{ex}=488 nm, ϕ_f=0.76) with an absorbance below 0.1 at the excitation wavelength[32]. Fluorometric titration measurement was carried out in MeOH-H_2O (1:1 *V*/*V*) by gradually adding microliter of H^+ (c=10^{-2} mol·L^{-1} of $HClO_4$) to the dye solution (c=10^{-5} mol·L^{-1}).

1.2 Reagents and materials

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. All air- and moisture-sensitive reactions were carried out under nitrogen atmosphere in oven-dried glassware. Dichloromethane was distilled over calcium hydride. Triethylamine was obtained by simple distillation. The solvents used for photophysical measurements were of spectroscopic grade without further purification.

1.3 Crystal structure determination

Single crystal of the title compound with dimensions of 0.39 mm × 0.34 mm × 0.23 mm was selected for the measurement. The unit cell parameters and data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293 K using the ω-2θ scan mode. The data were corrected for Lorenz and polarization effects. The structure was solved by the direct method and refined on F^2 by full-matrix least-squares method. All nonhydrogen atoms were corrected anisotropically. All hydrogen atoms were treated as riding on their attached atoms. All calculations and molecular graphics were done by using the SHELXTL-2000 program package[33]. Detailed information about the crystal data and structure determination for the title compound are summarized in Table 1. The selected bond distances and angles are listed in Table 2.

Table 1 Crystal data and structure refinement for 1

Empirical formula	$C_{18}H_{18}BF_2N_3$	μ_{calc} / mm^{-1}	0.096
Formula weight	325.16	Temperature / K	298(2)
Crystal size / mm	0.39 × 0.34 × 0.23	*F*(000)	1 360
Crystal system	Monoclinic	Reflections collected	15 093
Space group	$P2_1/c$	Independent reflections (R_{int})	5 675 (0.136 7)
Z	4	θ range for data collection / (°)	1.79~25.05
a / nm	2.503 0(15)	Index ranges	$-25 \leqslant h \leqslant 29, -8 \leqslant k \leqslant 8, -24 \leqslant l \leqslant 22$
b / nm	0.681 1(6)	R_1, wR_2	0.098 1, 0.243 1
c / nm	2.085 7(17)	Absorption correction	ψ-scan
β / (°)	114.62(5)	Refinement method	Full-matrix least-squares on F^2
V / nm^3	3.232(4)	Goodness-of-fit on F^2	1.237
ρ_{calc} / (Mg·m^{-3})	1.336	Largest diff. peak and hole / (e·nm^{-3})	330 and −416

Table 2 Selected bond lengths (nm) and bond angle (°)

F(1)-B(1)	0.137 9(6)	N(2)-B(1)	0.155 3(6)	N(5)-B(2)	0.153 4(6)
F(2)-B(1)	0.137 4(6)	N(3)-C(17)	0.134 5(6)	N(6)-C(35)	0.133 5(6)
F(3)-B(2)	0.139 4(5)	N(3)-C(13)	0.138 4(5)	N(6)-C(31)	0.140 7(5)
F(4)-B(2)	0.136 7(6)	N(3)-B(1)	0.154 2(6)	N(6)-B(2)	0.154 6(6)

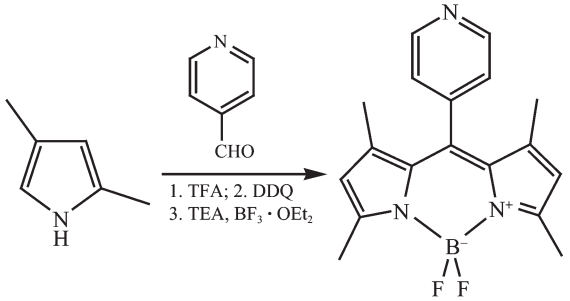
Continued Table 2

N(2)-C(11)	0.133 4(6)	N(5)-C(29)	0.134 3(6)	N(2)-C(7)	0.138 8(5)
N(5)-C(25)	0.140 7(5)				
F(2)-B(1)-F(1)	110.9(4)	C(17)-N(3)-C(13)	107.8(3)	N(3)-C(13)-C(6)	118.8(3)
F(2)-B(1)-N(3)	110.8(4)	C(17)-N(3)-B(1)	125.9(4)	N(3)-C(13)-C(14)	108.3(3)
F(1)-B(1)-N(3)	109.3(4)	C(13)-N(3)-B(1)	126.4(4)	N(3)-C(17)-C(16)	109.2(4)
F(2)-B(1)-N(2)	109.3(4)	C(19)-N(4)-C(23)	115.5(4)	N(3)-C(17)-C(18)	122.2(4)
F(1)-B(1)-N(2)	109.3(4)	C(29)-N(5)-C(25)	109.0(3)	N(4)-C(19)-C(20)	124.6(4)
N(3)-B(1)-N(2)	107.2(3)	C(29)-N(5)-B(2)	125.5(3)	N(4)-C(23)-C(22)	124.3(4)
F(4)-B(2)-F(3)	109.7(3)	C(25)-N(5)-B(2)	125.5(3)	C(24)-C(25)-N(5)	119.9(3)
F(4)-B(2)-N(5)	110.6(4)	C(35)-N(6)-C(31)	107.9(3)	N(5)-C(25)-C(26)	107.0(3)
F(3)-B(2)-N(5)	110.4(4)	C(35)-N(6)-B(2)	126.1(3)	N(5)-C(29)-C(28)	108.3(4)
F(4)-B(2)-N(6)	109.9(4)	C(31)-N(6)-B(2)	126.0(3)	N(5)-C(29)-C(30)	122.8(4)
F(3)-B(2)-N(6)	109.3(4)	N(1)-C(1)-C(2)	124.8(4)	C(24)-C(31)-N(6)	119.5(4)
N(5)-B(2)-N(6)	106.8(3)	N(1)-C(5)-C(4)	123.6(5)	N(6)-C(31)-C(32)	108.1(3)
C(5)-N(1)-C(1)	116.7(4)	C(6)-C(7)-N(2)	120.6(4)	N(6)-C(35)-C(34)	109.3(4)
C(11)-N(2)-C(7)	108.4(4)	N(2)-C(7)-C(8)	107.0(3)	N(6)-C(35)-C(36)	122.8(4)
C(11)-N(2)-B(1)	126.9(4)	N(2)-C(11)-C(10)	109.6(4)	C(7)-N(2)-B(1)	124.6(3)
N(2)-C(11)-C(12)	123.2(5)				

CCDC: 297327.

1.4 Preparation of compound 1

The title compound was prepared by condensation of 4-formylpyridine (1 mmol) with 2,4-dimethylpyrrole (2 mmol) in CH_2Cl_2 (10 mL) using trifluoroacetic acid (TFA) (Scheme 1). After oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1mmol) and treatment with triethylamine (3 mL) and boron trifluoride etherate ($BF_3 \cdot Et_2O$, 3 mL). The crude product was purified by silica-gel column chromatography ($CHCl_3$:petroleum ether=1:9) and recrystallization in $CHCl_3$/hexane. Slow diffusion of diethyl ether vapor into a $CHCl_3$ solution of the compound, affords red block crystals in 36% yield; m.p. >250 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.398 (s, 6H), 2.547 (s, 6H), 5.595 (s, 2H), 7.334 (dd, 2H, ^3J=4.5 Hz, ^4J=1.6 Hz), 8.790 (dd, 2H, ^3J=4.5 Hz, ^4J=1.6 Hz); MALDI-TOF MS: *m/z*: 325.19 (M^+); Anal. Calcd for $C_{18}H_{18}BF_2N_3$: C, 66.49; H, 5.58; N, 12.92 Found: C, 66.61; H, 5.64; N, 12.95; UV-Vis ($CHCl_3$) λ_{max}/nm 369, 472 and 502.



Scheme 1 Synthetic procedure for compound **1**

2 Results and discussion

2.1 Structural description

The single-crystal structure of compound **1** shows that there are two crystallographically independent molecules (A and B), only bond lengths and angles are slightly different. Therefore, the structure of molecular A is taken as an example to be described in detail.

The molecular plot and packing diagram of the title compound are shown in Fig.1 and 2, respectively. Compound **1** is crystallized in the monoclinic space group, $P2_1/c$. The bond lengths of F(1)-B(1) and F(2)-B(1) are 0.137 9(6) nm and 0.137 4(6) nm, respectively, whereas the bond lengths of N(2)-B(1) and N(3)-B(1) are 0.155 3(6) nm and 0.154 2(6) nm, respectively. The average bond angles of N-B-N and F-B-F angles are 107.2(3)° and 110.9(4)°, respectively. These data are in good agreement with the corresponding values of BF_2N_2 tetrahedron configurations in their analogues[30,31]. The bond lengths of N(2)-C(11) (0.133 4(6) nm) and N(3)-

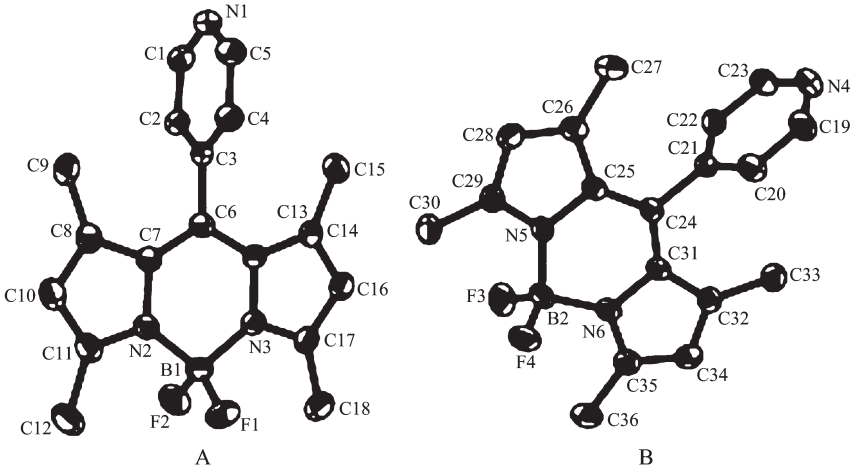


Fig.1 Molecular structure of **1** with thermal ellipsoids shown at 30% probabitity

C(17) (0.134 5(6) nm) are significantly shorter than the bond lengths of N(2)-C(7) (0.138 8(5) nm) and N(3)-C(13) (0.138 4(5) nm). The central six-membered ring containing B-N2-C7-C6-C13-N3 is almost coplanar with the adjacent pyrrole rings with the average deviation from the mean plane is 0.000 52 nm, indicating that π-electrons strongly delocalize within the indacene plane. The two fluorine atoms in the compound occupy apical positions relative to the mean plane of the indacene ring system. The meso-pyridine ring is almost perpendicular to the indacene plane with torsion angle of 88.2°.

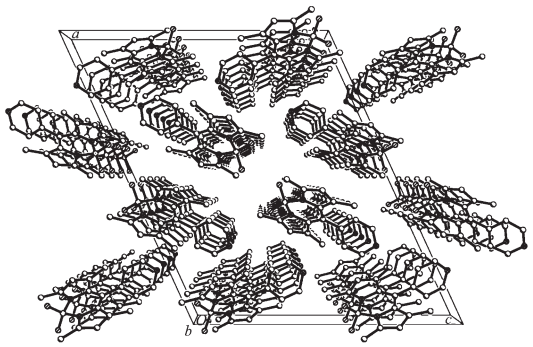


Fig.2 Molecular packing in the crystal structure along the *b*-axis

All the molecules are parallel each other with head-to-head orientation (Fig.2). The *meso*-pyridyl ring of one molecule is nearly orthogonal to the indacene plane of the other, therefore no π-π stacking interactions can be observed.

2.2 Absorption and fluorescent spectroscopy

The absorption and steady-state fluorescence emission spectra in MeOH/H_2O (1:1 *V*/*V*) are shown in Fig.3. The absorption spectrum features with a strong, narrow band centered at 502 nm and a shoulder on the high-energy side centered at about 472 nm, which is typical for the conventional BDP derivatives carrying only alkyl substituents on the indacene core. A considerably weaker and broad absorption band is observed at about 369 nm, which can be ascribed to the $S_0 \rightarrow S_2$ transition[19].

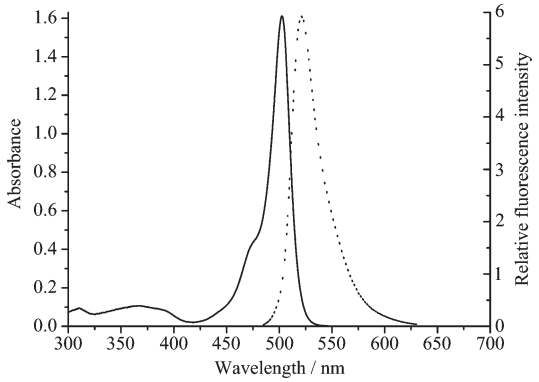


Fig.3 UV-Vis absorption (solid line) and fluorescence emission spectra (dotted line) in MeOH/H_2O (1:1 *V*/*V*) (λ_{ex}=472 nm)

Compound **1** exhibits a strong green fluorescence in aqueous solution MeOH/H_2O (1:1 *V*/*V*) (ϕ_f=0.51), which is attributed to the transition from the singlet excited state of the boradiazindacene to the ground state[34,35]. Gradually adding the H^+ to its solution in MeOH/H_2O (1:1 *V*/*V*), the emission intensity decreased significantly while the emission maxima centered at 521 nm remain unchanged (Fig.4). The quenching is due to the oxidative photoinduced electron transfer

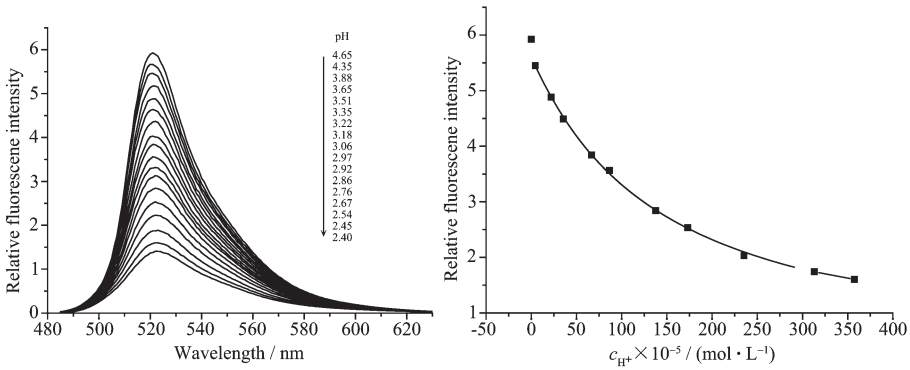


Fig.4　Emission spectra compound **1** (left) (λ_{ex}=472 nm) in MeOH/H_2O (1∶1 *V*/*V*) as a function of pH and fluorescene titration curve (right) in MeOH/H_2O (1∶1 *V*/*V*) as a function of c_{H^+} (λ_{em}=521 nm, λ_{ex}=472 nm)

(PET) from the excited BDP to the protonated pyridyl group[34,35]. The ground-state acidity constant K_a value is determined by fluorimetric titration as a function of pH using the fluorescence emission spectra (Fig.4). Nonlinear curve fitting Eq.(**1**) to the fluorescence data (*F*) recorded as a function of pH yield values of *n* (the stoichiometry of H^+ binding to the aniline), K_a, the fluorescence signals F_{max} and F_{min} at maximal and minimal c_{H^+}, respectively. Fitting Eq.(**1**) to the steady-state fluorescence data *F* with *n*, K_a, F_{max} and F_{min} as freely adjustable parameters gives valued of *n* close to **1**, indicating that one proton is bound per pyridine molecule. Therefore, from which the estimated values of pK_a are obtained as 2.24. Such a high proton-induced fluorescence quenching makes the dye into a very sensitive fluorescent probe for pH measurements.

$$F=\frac{F_{max}c_{H^+}^{\ n}+F_{min}K_a}{K_a+c_{H^+}^{\ n}} \qquad (1)$$

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