



Synthesis, structures and photophysical properties of boron–fluorine derivatives based on pyridine/1,8-naphthyridine



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ABSTRACT

Three boron–fluorine complexes **B1**–**B3** containing pyridine/1,8-naphthyridine were synthesized and structurally characterized. Compounds **B1** and **B2** exhibited strong fluorescence in solution and solid state. The solvent-dependent luminous properties and large Stokes shift in solution could be explained by intramolecular charge transfer, which is confirmed by time-dependent density functional theory calculation. The absolute quantum yield of **B1** in powder form reached 0.48 because of inhibiting planar $\pi\cdots\pi$ stacking. Single-crystal X-ray diffraction analyses of **B1** and **B2** revealed that weak intermolecular C–H \cdots F and H \cdots π interactions hinder further stacking of $\pi\cdots\pi$ dimers, consequently preventing aggregation-induced quenching. Complex **B3**, composed of boron–dipyrromethene and 1,8-naphthyridine fluorophore, had potential applications as a pH ratiometric fluorescent sensor.

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1. Introduction

Organoboron complexes are well known as one group of most important fluorescent dyes because of their tunable emission wavelengths [1–3] and high fluorescence quantum yields [4]. In particular, boron dipyrromethene (BODIPY) derivatives have played significant roles in many fields including fluorescent indicators [5], energy-transfer cassettes [6], laser dyes [7], and photodynamic therapy [8]. However, typical BODIPYs suffer from aggregation-induced quenching (ACQ) caused by their small Stokes shift and tight $\pi\cdots\pi$ packing in the solid state, which severely limits their applications as electroluminescence materials [9]. Generally, two promising strategies are employed to avoid ACQ in solid state, that is, aggregation-induced emission [10,11] and introduction of bulky groups [12]. Although the methods are effective to enhance solid emission, the energy of excited fluorophores will greatly exhaust via nonradiative decay, resulting in low quantum yields in solution [13]. Thus, it is still a challenge to obtain emissive BODIPY derivatives both in solution and solid state.

Naphthyridine derivatives are widely applied as biological probes and assembled supramolecular systems because of its diverse coordination modes and multiple hydrogen-bonded self-assembly ability [14,15]. However, BF₂ core complexes based on 1,8-naphthyridine unit have been little explored. Recently, we have reported a series of emissive 1,8-naphthyridine-BF₂ complexes that exhibit diverse attractive photophysical properties [4,16,17]. Herein, we synthesized three boron complexes **B1**–**B3** containing pyridine/1,8-naphthyridine, and their spectroscopic behaviors were investigated. Both **B1** and **B2** displayed strong emission in the solid state due to weak intermolecular C–H \cdots F and H \cdots π interactions. Although **B3** was not fluorescent in solid state, it exhibited pH-dependent solution-emission spectra by protonation of naphthyridine upon excitation at 330 nm, indicating that **B3** could act as a pH ratiometric fluorescent sensor.

2. Experimental section

2.1. Materials and instrumentations

All starting materials were purchased commercially as reagent grade and used as received unless otherwise mentioned. Dichloromethane was distilled over calcium hydride. The solvents used for spectroscopic measurements were of HPLC grade. 2-(4,5-

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diphenyl-1*H*-imidazol-2-yl)pyridine (**L1**) and 2-(pyridin-2-yl)-1*H*-phenanthro[9,10-*d*]imidazole (**L2**) were synthesized according to the literature methods [18]. 1,8-naphthyridine-2-carbaldehyde was obtained by the previously reported procedure [19].

¹H and ¹³C spectra were recorded on a Bruker Avance 400 spectrometer in CDCl₃ at room temperature. Electrospray Ionization (ESI) mass spectra were obtained on a Finnigan LCQ quadrupole ion trap mass spectrometer. UV–Vis absorption spectra were recorded using a Hitachi U-3010 spectrophotometer. Emission and excitation spectra were obtained on a Hitachi F-4500 Fluorescence Spectrophotometer. The fluorescence quantum yields in solution were measured relative to quinine sulfate in 0.1 M sulfuric acid aqueous solution ($\lambda_{\text{ex}} = 345 \text{ nm}$, $\Phi_{\text{F}} = 0.546$) at room temperature. The quantum yield was calculated by using Equation (1), where subscripts std denotes standard, Φ is quantum yield, I is the integrated emission intensity, A is the absorbance, and n is the refractive index.

$$\Phi_{\text{sample}} = \Phi_{\text{std}} \left(\frac{A_{\text{std}}/A_{\text{sample}}}{I_{\text{sample}}/I_{\text{std}}} \right) \left(\frac{n_{\text{sample}}/n_{\text{std}}}{I_{\text{std}}/I_{\text{sample}}} \right)^2 \quad (1)$$

Solid-state fluorescence quantum yields were measured using an integrating sphere F-3018 (HORIBA JOBIN YVON) equipped to the Spex 1681 Fluorolog-2 Model F111 spectrophotometer. The pH measurements were performed utilizing a Mettler-Toledo FE20K pH meter. Single crystals of **B1** and **B2** suitable for X-ray diffraction were grown by slow evaporation of solutions of the samples in CHCl₃. The diffraction data were collected on a Rigaku R-AXIS RAPID IP X-Ray diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.071073 \text{ nm}$) at 293 K. The structures were solved by direct methods and refined by full-matrix least-squares methods on all F^2 data (SHELX-97). CCDC-855326 (**B2**) contains the supplementary crystallographic data for this paper [20]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2. Synthetic procedures

Synthetic procedures of **B1–B3** were depicted in Scheme 1.

2.2.1. Synthesis of BF₂{2-(4,5-diphenyl-1*H*-imidazol-2-yl)pyridine} (**B1**)

At room temperature, triethylamine (2 mL) was added to a stirred mixture of **L1** (297 mg, 1.0 mmol) in dry CH₂Cl₂ (30 mL) under N₂.

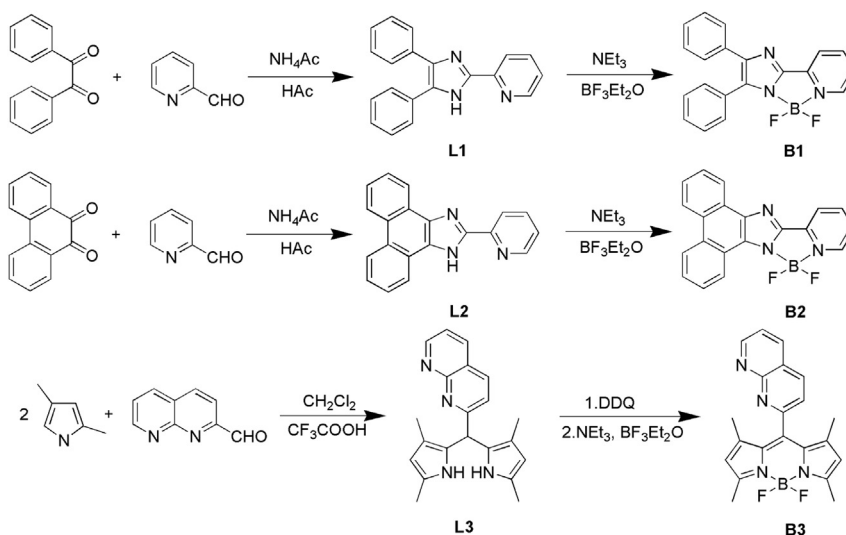
After 5 min, boron trifluoride etherate (2 mL, 15.7 mmol) was added dropwise. The solution was stirred overnight. The reaction was quenched by adding water (20 mL) and the mixture was extracted with CH₂Cl₂ (2 × 50 mL). The organic phase was dried by anhydrous Na₂SO₄, and concentrated to dryness on a rotary evaporator. The crude product was purified by silica gel column chromatography (CH₂Cl₂/EtOH, 20/1, v/v) to yield **B1** as yellow solid (150 mg, 43%). ¹H NMR (400 MHz, CDCl₃) 8.45 (d, $J = 5.6 \text{ Hz}$, 1H), 8.24–8.16 (m, 1H), 8.09 (d, $J = 8.1 \text{ Hz}$, 1H), 7.66–7.60 (m, 2H), 7.60–7.55 (m, 2H), 7.50 (t, $J = 6.2 \text{ Hz}$, 1H), 7.42–7.27 (m, 6H) ppm (Fig. S1); ¹³C NMR (101 MHz, CDCl₃) 145.88, 145.58, 145.17, 144.65, 141.30, 134.76, 134.47, 130.80, 128.76, 128.63, 128.38, 128.17, 127.32, 122.73, 117.67 ppm (Fig. S2). ESI-MS m/z calcd. for C₂₀H₁₄BF₂N₃ (M+H)⁺ 346.1; found 346.2. Anal. calcd. for C₂₀H₁₄BF₂N₃: C, 69.63; H, 4.09; N, 12.18; found: C, 69.57; H, 4.10; N, 12.22.

2.2.2. BF₂{2-(pyridin-2-yl)-1*H*-phenanthro[9,10-*d*]imidazole} (**B2**)

The synthesis is analogous to **B1** with **L2** as the starting material. The product was obtained as a brown yellow solid. Yield: 30%. ¹H NMR (400 MHz, CDCl₃) 8.69 (dd, $J = 19.1, 8.9 \text{ Hz}$, 3H), 8.59 (d, $J = 5.3 \text{ Hz}$, 1H), 8.47 (d, $J = 7.9 \text{ Hz}$, 1H), 8.25 (d, $J = 5.9 \text{ Hz}$, 2H), 7.76–7.62 (m, 4H), 7.58 (s, 1H) ppm (Fig. S3); ¹³C NMR (101 MHz, CDCl₃) 146.31, 144.80, 143.53, 141.74, 129.72, 128.86, 127.63, 127.46, 127.29, 126.61, 125.94, 123.74, 123.69, 123.63, 123.49, 123.30, 122.63, 118.78 ppm (Fig. S4); ESI-MS m/z calcd. for C₂₀H₁₂BF₂N₃ (M+H)⁺ 344.1; found 344.2. Anal. calcd. for C₂₀H₁₂BF₂N₃: C, 70.03; H, 3.52; N, 12.25; found: C, 70.10; H, 3.55; N, 12.20.

2.2.3. 8-(1,8-naphthyridine)-1,3,5,7-tetramethyl-4,4-difluoroboradiazaindacene (**B3**)

1,8-Naphthyridine-2-carbaldehyde (370 mg, 2.3 mmol) was dissolved in dry CH₂Cl₂ (200 mL). 2,4-Dimethylpyrrole (456 mg, 4.8 mmol) and one drop of trifluoroacetic acid were added under N₂ atmosphere. The mixture was stirred at room temperature in the dark for 3 h. After oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (1.01 g, 2.3 mmol), triethylamine (TEA) (4 mL) and BF₃·Et₂O (5 mL) were added dropwise to the mixture. The reaction solution was stirred for another 3 h, and the brown mixture was washed with water and brine, dried over anhydrous magnesium sulfate and concentrated at reduced pressure. The crude product was purified by silica-gel column chromatography (petroleum/EtOAc = 10:1, v/v) to yield **B3** as red solid, 130 mg, yield 15%. ¹H NMR (400 MHz, CDCl₃) δ 9.24 (d, $J = 2.3 \text{ Hz}$, 1H), 8.38 (d,



Scheme 1. Synthetic procedures and chemical structures of **B1–B3**.

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