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Synthesis, characterization and fluorescence properties of boron difluoride pyridyl-β-diketonate derivatives

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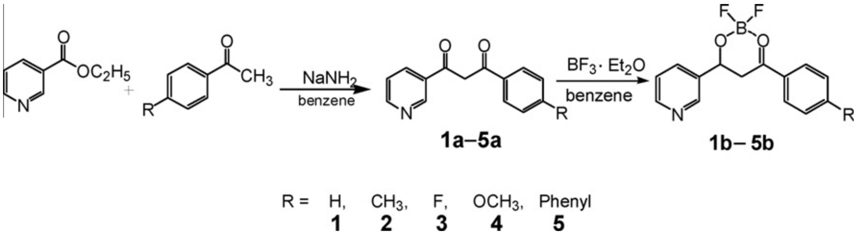
HIGHLIGHTS

- ▶ Synthesis and characterization of the pyridyl-β-diketones and its BF_2 complexes.
- ▶ Fluorescence properties of boron difluoride pyridyl-β-diketonate derivatives.
- ▶ Intense fluorescence of BF_2 complexes under UV radiation and high quantum yield.

GRAPHICAL ABSTRACT

Some new boron difluoride pyridyl-β-diketonate derivatives were synthesized by Claisen condensation of aryl methyl ketones with ethyl nicotinate and followed by complexation with boron trifluoride etherate. Their optical properties were studied by UV–vis absorption and fluorescence spectroscopy.



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ABSTRACT

Five pyridyl-β-diketones were synthesized by Claisen condensation of ethyl nicotinate with various aryl methyl ketones in benzene in the presence of sodium amide as the base, and then reacted with boron trifluoride diethyl etherate in dichloromethane to afford some new boron difluoride pyridyl-β-diketonate derivatives. The compounds obtained were characterized using FTIR, ^1H NMR, elemental analysis and mass spectrometry. Their optical properties were studied in DMF by UV–vis absorption and fluorescence spectroscopy. The results showed that these boron complexes exhibited intense fluorescence in the blue–green region (420–490 nm) under UV radiation with a relatively high quantum yield. Especially, compounds **4b** and **5b** displayed much higher quantum yield as compared to compounds **1b**, **2b** and **3b**.

Introduction

In recent years, organic electroluminescent devices have attracted considerable investigations to develop different materials and various devices [1,2]. It is well known that complex compounds of boron difluoride with β-diketonate ligands containing aromatic cycles at the carbonyl carbon atoms possess intense luminescence with high quantum yields, two-photon absorption and large molar extinction coefficients, which leads to their use as fluorescent probes, laser dyes, light-emitting diodes, and nonlinear optics [3–6]. By far, the synthesis and photoluminescence properties of many boron difluoride β-diketonate derivatives were reported [7,8]. In addition, some solid-state structures of boron difluoride complexes with β-diketones were also studied [9,10]. Recently, we have reported spectroscopic properties of some new diaroylmethanatoboron difluoride derivatives [11]. As a continuation of our previous work, herein we describe the synthesis and characterization of some novel boron difluoride pyridyl-β-diketonate derivatives. The variety of the aromatic substituent groups for the chelate ring enable the study of varying electronic effects on their luminescence properties and intense emission [3,12,13]. Therefore,

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we introduce the electron-donating 4-methyl, 4-methoxyl, electron-withdrawing 4-fluoro and 4-phenyl groups into the aromatic substituents of the chelate ring (Fig. 1) for investigating their spectroscopic and fluorescent properties.

Experimental

Materials

Ethyl nicotinate was prepared by our group according to the literature [14]. Acetophenone, 4-methylacetophenone, 4-fluoroacetophenone, 4-methoxy-acetophenone, 4-phenylacetophenone, quinine sulfate and sodium amide were purchased from Shanghai Chemical Reagent Company Ltd. (Shanghai, China). Other reagents used were of analytical grade, and were used without further purification.

Methods and instruments

Infrared spectra were recorded on a Nicolet FTIR 5700 spectrophotometer with KBr pellets. ^{1}H NMR spectra were measured on an Avance III™ 300 MHz NB Digital NMR spectrometer in $CDCl_3$ or DMSO-d_6 solution with TMS as internal standard. Electrospray ionization mass spectra (ESI-MS) were performed with a Finnigan LCQ Advantage Max spectrometer. Elemental analysis (C, H, N) was performed with a Perkin–Elmer 2400 elemental analyzer. Melting points were determined using X-4 digital melting-point apparatus and are uncorrected.

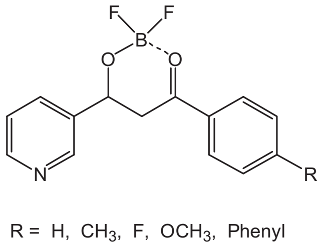
The UV–vis spectra were obtained with Hitachi U-3010 spectrophotometer. The emission spectra of the sample were carried out on a Hitachi F-4500 Fluorescence spectrophotometer. The Φ values were determined according to literature method using quinine sulfate in 0.1 mol L^{-1} sulfuric acid ($\Phi_s = 0.55$, $\lambda_{ex} = 366$ nm, at room temperature) as a standard [15]. The fluorescence quantum yields Φ were calculated from the relation shown in the following equation:

$$\Phi_u = \frac{F_u}{F_s} \times \frac{A_s}{A_u} \times \frac{n_u^2}{n_s^2} \times \Phi_s \tag{1}$$

where the subscripts u and s denote test and standard respectively, Φ is the fluorescence quantum yield, A is the absorbance at the excitation wavelength, F is the integrated emission spectrum, and n is the refractive index for the solvent.

General procedure for the synthesis of the pyridyl-β-diketones (**1a**–**5a**)

The mixture of sodium amide (1.4 g, 36 mmol) and ethyl nicotinate (6.65 g, 44 mmol) in benzene (50 mL) was placed in a three-necked, round-bottom flask fitted with a reflux condenser and heated to 50 °C. Then a solution of aryl methyl ketones (22 mmol) in benzene was added dropwise to the mixture. The reaction mixture was stirred at 80 °C for about 7 h until the dark yellow product precipitated. The precipitate was filtered off and washed with 5% acetic acid until pH = 6. The crude products were recrystallized from ethanol (95%) to obtain the pyridyl-β-diketones. Compounds **1a**–**5a** were confirmed by elemental analysis, FTIR, ^{1}H NMR, and mass spectroscopy (the data are in the Supplementary Information).



R = H, CH_3, F, OCH_3, Phenyl
1 2 3 4 5

Fig. 1. Structures of boron difluoride pyridyl-β-diketonate derivatives **1b**–**5b**.

General procedure for the synthesis of the boron complexes (**1b**–**5b**)

To a solution of the pyridyl-β-diketones (2.2 mmol) in dry dichloromethane (25 mL), boron trifluoride diethyl etherate (0.42 mL, 3.3 mmol) was added dropwise. The reaction mixture was stirred at 40 °C for 5 h. After removal of the solvent, the residue was filtered and washed with dichloromethane. The solid was sublimated at 200 °C under 10^{-3} mmHg to obtain the boron complexes. The title compounds **1b**–**5b** were characterized by elemental analysis, FTIR, ^{1}H NMR, and mass spectroscopy (the data are in the Supplementary Information).

Results and discussion

Synthesis of boron difluoride pyridyl-β-diketonate derivatives

The synthetic procedure was accomplished in two steps (Scheme S1). Firstly, the pyridyl-β-diketones **1a**–**5a** were prepared via Claisen condensation of the aryl methyl ketones with ethyl nicotinate using sodium amide as the condensing agent. Secondly, the boron difluoride complexes **1b**–**5b** were obtained by reacting the pyridyl-β-diketones with boron trifluoride diethyl ether ($BF_3{\cdot}Et_2O$) in dichloromethane. The crude products were isolated by simple filtration. The pure boron complexes were provided by sublimation at 200 °C under 10^{-3} mmHg. The advantages of this synthetic procedure were the easily available starting materials, mild reaction and high purity products.

Spectroscopic characterization

The IR spectra of the title compounds showed several weak vibrations in the range of 3100–3050 cm^{-1} assigned to the stretching vibrations for unsaturated C—H. Strong absorption bands in the regions of 1603–1592 cm^{-1} and 1549–1524 cm^{-1} were due to the C═O and enolic C═C stretching vibrations [16,17]. The strong absorptions in the region of 1368–1364 cm^{-1} belonged to the B—O stretching vibrations and those in the region of 1179–1032 cm^{-1} were attributed to the B—F and B—O stretching vibrations [16,18]. Obviously, these results indicated that the boron complexes of the pyridyl-β-diketones with boron trifluoride were formed.

The ^{1}H NMR spectra of boron difluoride pyridyl-β-diketonate derivatives show pronounced changes in comparison with those of the pyridyl-β-diketones. In the pyridyl-β-diketones, the keto-CH_2 protons displayed a single peak at $\delta = 4.61$–4.69 ppm, the vinylic protons exhibited a single peak at $\delta = 6.81$–6.91 ppm and the enolic protons revealed a single peak at $\delta = 16.72$–16.88 ppm. But in their boron complexes, the ^{1}H NMR spectra did not show the presence of not only the enolic proton but also the keto-CH_2 proton signals. Only their vinylic protons exhibited a single peak at $\delta = 7.99$–8.14 ppm. However, these proton signals were shifted 1.18–1.26 ppm to lower field with respect to the corresponding vinylic signal in the parent enol [16,17], which due to the withdraw of electronic density from the chelate ring by the fluorine atoms.

The ESI mass spectra of the title compounds **1b**–**5b** were measured and compared to confirm elemental compositions. The molecular ion peaks for these compounds were observed in agreement with the Nitrogen Rule.

Photo-physical properties

UV–vis absorption spectra

For UV–vis absorption measurements, the concentration of compounds **1a**–**5a** and **1b**–**5b** was 1.0×10^{-5} mol L^{-1}. Their spectra in DMF are shown in Fig. 2 and their spectra data are summarized in Table 1. The results showed that there were a strong broad absorption bands at 346–355 nm and 366–402 nm in compounds **1a**–**5a** and **1b**–**5b**, respectively. The longest absorption maxima of compounds **1b**–**5b** are red shifted about 20–50 nm as compared to those of compounds **1a**–**5a**, which assigned to π–π^* transitions in the conjugated ring system by the BF$_2$-chelating moiety.

Fluorescence spectra

The fluorescence spectra of compounds **1b**–**5b** were also recorded in DMF at a concentration of 1.0×10^{-5} mol L^{-1}. Their emission spectra are shown in Fig. 3 and their spectra data are summarized in Table 2. The maximal emission peaks of the boron complexes are mainly located at about 420–490 nm. These compounds yield blue or green emission in DMF solution at room temperature. Among these boron difluoride pyridyl-β-diketonate complexes, it can be noted that the emission spectra of substituted phenyl compounds were shifted to the red. Especially, compounds **4b** and **5b**, where the benzene is linked by methoxyl and phenyl groups, respectively, emit at higher wavelengths than other compounds.

The highest fluorescence intensity in these boron difluoride complexes was found for Boron difluoride 1-(4-methoxyphenyl)-3-(3-pyridyl)-1,3-propandionate (**4b**). The intensity of fluorescence decreased in the sequence, **4b** > **5b** > **2b** > **3b** > **1b**. The introduction of the electron-donating 4-methyl and 4-methoxyl groups into the benzene ring in the boron complexes resulted in a higher fluorescence intensity. Meanwhile, the introduction of the electron-withdrawing 4-fluoro group did not caused an obvious change of fluorescence intensity. However, the introduction of 4-phenyl group sharply increased the fluorescence intensity, which due to much larger π-conjugated systems.

Fluorescence quantum yields

The fluorescence quantum yields (Φ_u) of compounds **1b**–**5b** were referenced to that of quinine sulfate as a fluorescence standard because of the similarity between its absorption and fluorescence spectra with those of the boron complexes. The quantum yield data are tabulated in Table 2. The results revealed that the 4-position substituted group of benzene ring had a significant effect on their fluorescence quantum yield in boron difluoride pyridyl-β-diketonate derivatives. Especially, compounds **4b** and **5b** exhibited much higher quantum yield (Φ_u = 0.72 and 0.65, respectively) than that of other boron complexes, resulting from the larger donor character of the methoxyl moiety and larger π-conjugated system of the phenyl moiety. This result is in accordance with the literature [3].

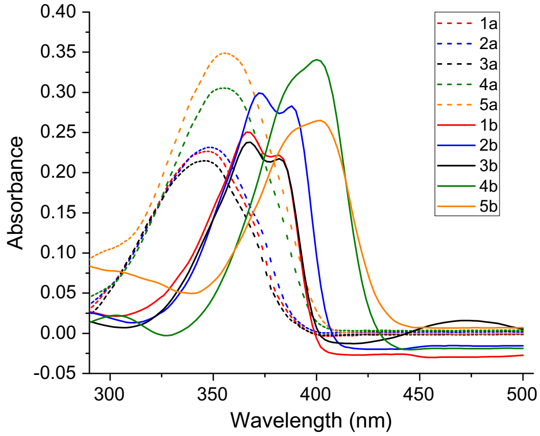


Fig. 2. UV–vis spectra for compounds **1a**–**5a** (dotted lines) and **1b**–**5b** (solid lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
UV–vis spectra data for compounds **1a**–**5a** and **1b**–**5b**.

Compound	λ_{max} (nm)	log ε_{max}	Compound	λ_{max} (nm)	log ε_{max}
1a	347	4.35	**1b**	366	4.40
2a	348	4.36	**2b**	372	4.48
3a	346	4.33	**3b**	368	4.38
4a	355	4.48	**4b**	400	4.53
5a	355	4.54	**5b**	402	4.42

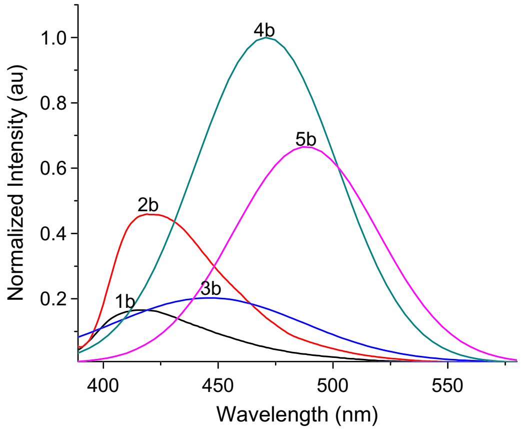


Fig. 3. Normalized emission spectra for compounds **1b**–**5b**.

Table 2
Fluorescence spectra data and quantum yields for compounds **1b**–**5b**.

Compound	λ_{ex} (nm)	λ_{em} (nm)	Φ_u
1b	366	417	0.17
2b	372	419	0.43
3b	368	446	0.36
4b	400	471	0.72
5b	402	487	0.65

Conclusions

In conclusion, several new boron difluoride pyridyl-β-diketonate derivatives were synthesized and their structures were confirmed by FTIR, ^{1}H NMR, elemental analysis and MS spectrometry. From the emissive properties, it was concluded that these boron complexes exhibited intense fluorescence in the blue–green region (420–490 nm) with a relatively high quantum yield. Especially, compounds **4b** and **5b** displayed much higher quantum yield (Φ_u = 0.72 and 0.65, respectively) as compared to compounds **1b**, **2b** and **3b**. The introduction of the electron-donating and π-conjugated groups into the aromatic substituents of the chelate ring can remarkably increase the fluorescence intensity of the boron complexes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.11.102.

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