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Synthesis and spectroscopic properties of some new difluoroboron bis-β-diketonate derivatives





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HIGHLIGHTS

- Synthesis and characterization of the bis-β-diketones and their difluoroboron complexes.
- Spectroscopic properties of difluoroboron bis-β-diketonate derivatives.
- Fluorescence behavior and quantum yields for difluoroboron complexes under UV radiation.

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ABSTRACT

Six new bis- β -diketones (RCOCH₂CO-C₇H₇N-COCH₂COR) were synthesized from 3,5-diacetyl-2,6-dimethylpyridine via Claisen condensation with the corresponding esters, and then reacted with boron trifluoride etherate to afford difluoroboron bis- β -diketonate derivatives. Their spectroscopic properties were investigated by UV-vis, FTIR, ¹H NMR and fluorescence spectroscopic techniques. It was found that these boron complexes exhibited violet or blue fluorescence emission at 422–445 nm and possessed high extinction coefficients. The results indicate that the extending π -conjugation can increase the fluorescence intensity and quantum yield for these boron complexes. Especially, the compound **2b** displayed the stronger fluorescence intensity and the highest fluorescence quantum yield ($\Phi_u = 0.94$) in these boron compounds. However, compounds **2c** and **2d** had the lower fluorescence intensity and quantum yield as a result of the heavy atom effect of the chlorine atom in the molecules.

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Introduction

In the past decade, the design and synthesis of stable tetracoordinate difluoroboron complexes have been attracted attention due to their outstanding photophysical and photochemical properties [1,2]. Especially, the difluoroboron bis- β -diketonate complexes are classic fluorescent molecules with large molar extinction coefficients, two-photon absorption cross sections and high emission quantum yields [3,4]. Their features have been widely explored as imaging cells fluorophores [5], photochemical reagents [6], semiconductors [7], laser dyes [8], organic light-emitting diodes [9] and many other modern technologies. Recently, the photophysical and photochemical properties of some novel difluoroboron β -diketonates were reported [10–12]. In addition, we also have investigated photoluminescence behavior of some new difluoroboron complexes with β -diketone ligands [13,14].

But until now the difluoroboron bis- β -diketonate compounds have been little studied. As an extension of this work, herein we present the synthesis and spectroscopic properties of six difluoroboron complexes with the new bis- β -diketones. Structures of the obtained compounds were demonstrated by means of FT-IR, NMR, MS, elemental analysis, UV-vis and fluorescence spectroscopy.

Experimental

Materials and methods

3,5-Diacetyl-2,6-dimethylpyridine was prepared by our group according to the method described in the literature [15,16]. Substi-

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tuted benzoic acid esters, potassium and quinine sulfate were purchased from Shanghai Chemical Reagent Company Ltd. (Shanghai, China). Boron trifluoride diethyl etherate was purchased from Sigma Chemical Co. Other reagents were of analytical grade purity and used without further purification.

Elemental analysis (C, H, N) was determined with a Perkin– Elmer 2400 elemental analyzer. Infrared spectra were performed on a Nicolet FTIR 5700 spectrophotometer with KBr pellets. ¹H NMR and ¹³C NMR spectra were recorded on an Avance IIITM 300 MHz NB Digital NMR spectrometer in CDCl₃ or DMSO–d₆. Electrospray ionization mass spectra (ESI–MS) were determined with a Finnigan LCQ Advantage Max spectrometer. Melting points were measured using X-4 digital melting-point apparatus and are uncorrected.

The optical properties of the obtained compounds were investigated with UV-vis absorbance and fluorescence spectroscopies in DMSO solution. The emission spectra of the samples were carried out on a Hitachi F-4500 Fluorescence spectrophotometer. The UV-vis spectra were obtained with Hitachi U-3010 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 [17]. The fluorescence quantum yield (Φ_u) was calculated by 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.

Synthetic methods

The difluoroboron complexes were synthesized in two steps (Scheme 1). Firstly, the bis- β -diketone ligands **1a–1f** were prepared via Claisen condensation of 3,5-diacetyl-2,6-dimethylpyridine with the appropriate esters using potassium tert-butanolate as the condensing agent in benzene. Secondly, the difluoroboron complexes **2a–2f** were obtained by reacting the bis- β -diketones with an excess of boron trifluoride diethyl ether (BF₃·Et₂O) in dichloromethane. The crude products were isolated by filtration and recrystallized from DMF–CHCl₃ (1:1) solution to give the title compounds **2a–2f**.

Synthesis of bis- β -diketone ligands **1a**–**1f**

A suspension of freshly cut potassium (1.56 g, 40 mmol) in tertbutanol (30 mL) was placed in a 100 mL round bottom flask with stirring and the mixture was heated up to 80 °C. After the potassium was completely exhausted, the excess tert-butanol was evaporated under reduced pressure and the white residue was dissolved in benzene (20 mL). To this solution a mixture of 3,5-diacetyl-2,6dimethyl-pyridine (1.19 g, 10 mmol) and the required ester (25 mmol) in benzene (30 mL) was slowly added. The mixture was stirred at room temperature for 24 h and then poured into 100 mL ice-water. The aqueous layer was adjusted to pH = 6 and the products were precipitated. The resulting precipitates were filtered and recrystallized from acetone to give bis- β -diketones (**1a**-**1f**).

1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(butane-1,3-dione)(**1a**): Colorless needle crystals, yield 45%, mp 89–90 °C; ¹H NMR (300 MHz, CDCl₃): δ 15.88 (s, br, 2H, enol OH), 7.86 (s, 1H, Py—H), 5.88 (s, 2H, enol CH), 2.73 (s, 6H, Py—CH₃), 2.20 (s, 6H, CH₃); ¹³C NMR (300 MHz, CDCl₃): δ 193.2, 185.6, 158.2, 136.0, 128.8, 100.8, 25.5, 24.0; IR (KBr): v 3441 (w), 3020 (m), 2980 (m), 1599 (s), 1513 (s), 1432 (s), 1374 (w), 1228 (s), 1148 (m), 1080 (m), 1024 (m), 933 (m), 832 (m), 768 (m) cm⁻¹; ESI–MS *m/z*: 276.12 [M+1]⁺; Anal. Calcd. for C₁₅H₁₇NO₄: C 65.44, H 6.22, N 5.09; found C 65.69, H 6.20, N 5.07.

3,3'-(2,6-dimethylpyridine-3,5-diyl)bis(1-phenylpropane-1,3dione) (**1b**): White crystals, yield 59%, mp 158–159 °C; ¹HNM R (300 MHz, CDCl₃): δ 16.59 (s, br, 2H, enol OH), 8.05 (s, 1H, Py–H), 7.96 (d, *J* = 8.8 Hz, 4H, Ar–H), 7.55–7.47 (m, 6H, Ar–H), 6.56 (s, 2H, enol CH), 2.81 (s, 6H, Py–CH₃); ¹³C NMR (300 MHz, CDCl₃): δ 187.7, 185.4, 158.2, 136.0, 134.7, 132.9, 129.6, 128.8, 127.3, 97.2, 24.1; IR (KBr): v 3443 (w), 3053 (m), 2939 (w), 1597 (s), 1502 (s), 1424 (s), 1381 (w), 1250 (s), 1184 (m), 1091 (m), 926 (m), 819 (m), 773 (m), 685 (m) cm⁻¹; ESI–MS *m/z*: 400.13 [M+1]⁺; Anal. Calcd. for C₂₅H₂₁NO₄: C 75.17, H 5.30, N 3.51; found C 75.28, H 5.28, N 3.53.

3,3'-(2,6-dimethylpyridine-3,5-diyl)bis(1-(2-chlorophenyl)propane-1,3-dione) (**1c**): White powder, yield 65%, mp 160–162 °C; ¹H NMR (300 MHz, CDCl₃): δ 16.10 (s, br, 2H, enol OH), 8.07 (s, 1H, Py—H), 7.70–7.67 (m, 2H, Ar—H), 7.49–7.38 (m, 6H, Ar—H), 6.48 (s, 2H, enol CH), 2.82 (s, 6H, Py—CH₃); ¹³C NMR (300 MHz, CDCl₃): δ 186.4, 186.2, 158.8, 136.5, 135.4, 132.1, 131.9, 130.8, 130.2, 128.9, 127.1, 102.4, 24.3; IR (KBr): v 3431 (w), 3079 (m), 2980 (w), 1594 (s), 1498 (s), 1448 (m), 1388 (w), 1248 (s), 1173 (m), 1035 (m), 950 (m), 804 (m), 765 (s) cm⁻¹; ESI–MS *m/z*: 468.12 [M]⁺; Anal. Calcd. for C₂₅H₁₉Cl₂NO₄: C 64.12, H 4.09, N 2.99; found C 63.95, H 4.11, N 2.98.

3,3'-(2,6-dimethylpyridine-3,5-diyl)bis(1-(4-chlorophenyl)propane-1,3-dione) (**1d**): White powder, yield 51%, mp 187–188 °C; ¹H NMR (300 MHz, CDCl₃): δ 16.53 (s, br, 2H, enol OH), 8.03 (s, 1H, Py—H), 7.90 (d, *J* = 8.7 Hz, 4H, Ar—H), 7.47 (d, *J* = 8.7 Hz, 4H, Ar—H), 6.51 (s, 2H, enol CH), 2.80 (s, 6H, Py—CH₃); ¹³C NMR (300 MHz, CDCl₃): δ 187.4, 184.2, 158.4, 139.3, 136.0, 133.1, 129.4, 129.1, 128.6, 97.1, 24.1; IR (KBr): v 3442 (w), 3066 (m), 2939 (w), 1592 (s), 1500 (s), 1477 (m), 1393 (w), 1253 (m), 1177 (m), 1095 (s), 806 (m), 725 (m) cm⁻¹; ESI–MS *m/z*: 468.25 [M]⁺; Anal. Calcd. for C₂₅H₁₉Cl₂NO₄: C 64.12, H 4.09, N 2.99; found C 64.29, H 4.07, N 2.98.

3,3'-(2,6-dimethylpyridine-3,5-diyl)bis(1-(4-fluorophenyl)propane-1,3-dione) (**1e**): Bright yellow crystals, yield 46%, mp 177–179 °C; ¹H NMR (300 MHz, CDCl₃): δ 16.58 (s, br, 2H, enol OH), 8.02 (s, 1H, Py–H), 8.01–7.96 (m, 4H, Ar–H), 7.18 (m, 4H, Ar–H), 6.50 (s, 2H, enol CH), 2.80 (s, 6H, Py–CH₃); ¹³C NMR (300 MHz, CDCl₃): δ 187.0, 184.8, 167.4, 164.0, 158.3, 136.0, 131.2, 131.1, 129.9, 129.7, 129.4, 116.2, 115.9, 97.0, 24.1; IR (KBr): v 3445 (w), 3057 (m), 2961 (w), 1602 (s), 1515 (s), 1350 (w), 1237 (s), 1157 (m), 1096 (m), 831 (m), 769 (m) cm⁻¹; ESI–MS *m/z*: 436.24



Scheme 1. Synthetic routes of compounds 1a-1f and 2a-2f.

 $[M+1]^{+}$; Anal. Calcd. for $C_{25}H_{19}F_2NO_4$: C 68.96, H 4.40, N 3.22; found C 69.11, H 4.38, N 3.24.

3,3'-(2,6-dimethylpyridine-3,5-diyl)bis(1-(4-(tert-butyl)phenyl) propane-1,3-dione) (**1f**): White crystals, yield 48%, mp 154–156 °C; ¹H NMR (300 MHz, CDCl₃): δ 16.62 (s, br, 2H, enol OH), 8.03 (s, 1H, Py—H), 7.90 (d, *J* = 8.7 Hz, 4H, Ar—H), 7.51 (d, *J* = 8.7 Hz, 4H, Ar—H), 6.53 (s, 2H, enol CH), 2.80 (s, 6H, Py—CH₃), 1.39 (s, 18H, C(CH₃)₃); ¹³C NMR (300 MHz, CDCl₃): δ 187.3, 185.5, 158.1, 156.9, 136.0, 132.0, 129.7, 127.2, 125.8, 97.1, 35.1, 31.1, 24.0; IR (KBr): v 3441 (w), 3057 (m), 2961 (m), 2863 (m), 1600 (s), 1500 (s), 1480 (m), 1388 (m), 1259 (m), 1186 (m), 1130 (m), 842 (m), 792 (m) cm⁻¹; ESI–MS *m/z*: 512.39 [M+1]⁺; Anal. Calcd. for C₃₃H₃₇NO₄: C 77.47, H 7.29, N 2.74; found C 77.64, H 7.26, N 2.75.

Synthesis of difluoroboron complexes 2a-2f

To a solution of bis- β -diketone ligands **1***a*–**1***f* (2.0 mmol) in dichloromethane (40 mL), the excess boron trifluoride diethyl etherate (1.0 mL, 7.9 mmol) was added dropwise. The reaction mixture was stirred for 6 h under reflux. The solvent was removed in vacuo and the precipitates were filtered off, washed with dichloromethane. The crude products were recrystallized from DMF-CHCl₃ (1:1) solution to obtain difluoroboron complexes **2***a*–**2***f* in good yields.

Difluoroboron 1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(butane-1,3dionate) (**2a**): White powder, yield 71%, mp 209–210 °C; ¹H NMR (300 MHz, DMSO–*d*₆): δ 8.49 (s, 1H, Py–H), 6.34 (s, 2H, C=CH), 2.79 (s, 6H, Py–CH₃), 2.23 (s, 6H, CH₃); IR (KBr): v 3030 (w), 2983 (m), 1582 (s), 1501 (s), 1395 (s), 1248 (m), 1200 (s), 1078 (s), 869 (w), 808 (w) cm⁻¹; ESI–MS *m*/*z*: 371.53 [M+1]⁺; Anal. Calcd. for C₁₅H₁₅B₂F₄NO₄: C 48.57, H 4.08, N 3.78; found C 48.76, H 4.07, N 3.79.

Difluoroboron 3,3'-(2,6-dimethylpyridine-3,5-diyl)bis(1-phenylpropane-1,3-dionate) (**2b**): Yellow powder, yield 76%, mp 272– 273 °C; ¹H NMR (300 MHz, DMSO- d_6): δ 8.77 (s, 1H, Py−H), 8.25 (d, *J* = 8.0 Hz, 4H, Ar−H), 7.83–7.72 (m, 6H, Ar−H), 7.37 (s, 2H, C=CH), 2.80 (s, 6H, Py−CH₃); IR (KBr): v 3078 (m), 2971 (w), 1572 (s), 1490 (s), 1458 (m), 1397 (s), 1250 (m), 1187 (s), 1057 (s), 832 (m), 780 (m), 693 (m) cm⁻¹; ESI–MS *m*/*z*: 496.01 [M+1]⁺; Anal. Calcd. for C₂₅H₁₉B₂F₄NO₄: C 60.66, H 3.87, N 2.83; found C 60.87, H 3.86, N 2.84.

Difluoroboron 3,3'-(2,6-dimethylpyridine-3,5-diyl)bis(1-(2-chlorophenyl) propane-1,3-dionate) (**2c**): White powder, yield 86%, mp 99–101 °C; ¹H NMR (300 MHz, DMSO– d_6): δ 8.80 (s, 1H, Py–H), 7.88 (d, *J* = 7.5 Hz, 2H, Ar–H), 7.75–7.63 (m, 6H, Ar–H), 7.59 (s, 2H, C=CH), 2.84 (s, 6H, Py–CH₃); IR (KBr): v 3051 (m), 2926 (w), 1578 (s), 1489 (s), 1442 (m), 1388 (s), 1282 (m), 1233 (m), 1177 (s), 1075 (s), 813 (m), 772 (m), 711 (m) cm⁻¹; ESI–MS *m*/*z*: 564.39 [M+1]⁺; Anal. Calcd. for C₂₅H₁₇B₂Cl₂F₄NO₄: C 53.25, H 3.04, N 2.48; found C 53.46, H 3.02, N 2.48.

Difluoroboron 3,3'-(2,6-dimethylpyridine-3,5-diyl)bis(1-(4-chlorophenyl) propane-1,3-dionate) (**2d**): Light yellow powder, yield 71%, mp > 300 °C; ¹H NMR (300 MHz, DMSO- d_6): δ 8.85 (s, 1H, Py—H), 8.37–7.94 (m, 4H, Ar—H), 7.39–7.33 (m, 4H, Ar—H), 7.13 (s, 2H, C=CH), 2.85 (s, 6H, Py—CH₃); IR (KBr): v 3088 (m), 2947 (w), 1573 (s), 1487 (s), 1421 (m), 1374 (m), 1240 (m), 1188 (s), 1071 (s), 1050 (s), 821 (m), 705 (m) cm⁻¹; ESI–MS *m*/*z*: 564.45 [M+1]⁺; ESI–MS *m*/*z*: 564.19 [M+1]⁺; Anal. Calcd. for C₂₅H₁₇B₂Cl₂F₄-NO₄: C 53.25, H 3.04, N 2.48; found C 53.43, H 3.05, N 2.49.

Difluoroboron 3,3'-(2,6-dimethylpyridine-3,5-diyl)bis(1-(4-fluorophenyl) propane-1,3-dionate) (**2e**): Yellow powder, yield 88%, mp > 300 °C; ¹H NMR (300 MHz, DMSO- d_6): δ 8.87 (s, 1H, Py—H), 8.18 (m, 4H, Ar—H), 7.57 (m, Hz, 4H, Ar—H), 7.18 (s, 2H, C=CH), 2.81 (s, 6H, Py—CH₃); IR (KBr): v 3054 (m), 2947 (w), 1572 (s), 1500 (s), 1390 (s), 1250 (m), 1163 (s), 1118 (m), 1080 (s), 852 (m), 810 (m), 746 (m) cm⁻¹; ESI–MS *m/z*: 531.91 [M+1]⁺; Anal.

Calcd. for $C_{25}H_{17}B_2F_6NO_4$: C 56.55, H 3.23, N 2.64; found C 56.68, H 3.24, N 2.65.

Difluoroboron 3,3'-(2,6-dimethylpyridine-3,5-diyl)bis(1-(4-(tertbutyl)phenyl) propane-1,3-dionate) (**2f**): Yellow powder, yield 79%, mp 182–184 °C; ¹H NMR (300 MHz, DMSO– d_6): 8.76 (s, 1H, Py–H), 8.18 (d, *J* = 8.7 Hz, 4H, Ar–H), 7.81 (d, *J* = 8.7 Hz, 4H, Ar–H), 7.37 (s, 2H, C=CH), 2.80 (s, 6H, Py–CH₃), 1.40 (s, 18H, C(CH₃)₃); IR (KBr): v 3089 (m), 2964 (m), 1577 (s), 1492 (s), 1494 (m), 1384 (s), 1264 (m), 1190 (s), 1052 (s), 811 (m), 691 (m) cm⁻¹; ESI–MS *m/z*: 607.98 [M+1]⁺; Anal. Calcd. for C₃₃H₃₅B₂F₄NO₄: C 65.27, H 5.81, N 2.31; found C 65.43, H 5.80, N 2.32.

Results and discussion

¹H NMR spectra

In the ¹H NMR spectra, the characteristic chemical shifts for the bis- β -diketone ligands and boron complexes are summarized in Table 1. From Table 1, the free bis- β -diketone ligands showed a singlet for the enolic protons at $\delta = 16.62-15.88$ ppm, the pyridine protons at $\delta = 8.07-7.86$ ppm and the methine protons at $\delta = 6.56-5.88$ ppm. However, the enolic proton signals were not observed in difluoroboron complexes **2a–2f**. Their methine proton and pyridine proton signals exhibited a single peak at $\delta = 5.88-7.59$ and $\delta = 8.49-8.87$ ppm, which shifted 0.46–1.11 ppm and 0.63–0.85 ppm, respectively, to lower field with respect to the corresponding proton signal in the free bis- β -diketone ligands. This is because of difluoroboron complexes formation arising from the electron-withdrawing effect of the chelate ring by the fluorine atoms [18]. In addition, the chemical shifts of other protons have few changes.

IR spectra

The IR spectra of difluoroboron complexes exhibited noticeable changes as compared with those of bis- β -diketone ligands. The characteristic, strong absorption bands of the free ligands and boron complexes are listed in Table 2. The free ligands **1a–1f** showed the strong absorption bands at 1602–1592 cm⁻¹ and 1515–1498 cm⁻¹ assigned to the C=O and enolic C=C stretching vibrations. However, the C=O and C=C absorption peaks of boron complexes **2a–2f** were at 1572–1582 cm⁻¹ and 1500–1487 cm⁻¹, which red-shifted 8–30 cm⁻¹ with respect to those of the corresponding bis- β -diketone ligands [**19**]. This is because that the C=O bonds were converted into the vibrating structure of the C=O \rightarrow BF₂ bond and C=O=BF₂ bond. Further information on the IR spectroscopy for boron complexes is given by the disappearance of corresponding O=H vibration band which exists in the free ligand due to the keto–enol tautomerism of the bis- β -diketones.

Table 1			
Comparison of ¹ H NMR	parameters	for compounds	1a–5a and 1b–5b.

Compound	δ(O —H), ppm	δ(Py—H), ppm	δ(C=C-H), ppm
1a	15.88	7.86	5.88
2a	-	8.49	6.34
1b	16.59	8.05	6.56
2b	-	8.77	7.37
1c	16.10	8.07	6.48
2c	-	8.80	7.59
1d	16.53	8.03	6.51
2d	-	8.85	7.13
1e	16.58	8.02	6.50
2e	-	8.87	7.18
1f	16.62	8.03	6.53
2f	-	8.76	7.37

Table 2
Comparison of the characteristic IR data for compounds 1a–5a and 1b–5b .

Compound	v(C==0), cm ⁻¹	v(C=C), cm ⁻¹	v(B—O), cm ⁻¹	$\nu(BF)$ and $\nu(BO)\text{, }cm^{-1}$
1a	1599 (s)	1513 (s)	1374	_
			(w, δ _{CH3})	
2a	1582 (s)	1501 (s)	1395 (s)	1200 (s), 1078 (s)
1b	1597 (s)	1502 (s)	-	-
2b	1572 (s)	1490 (s)	1397 (s)	1187 (s), 1057 (s)
1c	1594 (s)	1498 (s)	_	_
2c	1578 (s)	1489 (s)	1388 (s)	1177 (s), 1075 (s)
1d	1592 (s)	1500 (s)	-	-
2d	1573 (s)	1487 (s)	1374 (s)	1188 (s), 1071 (s)
1e	1602 (s)	1515 (s)	_	_
2e	1572 (s)	1500 (s)	1390 (s)	1163 (s), 1080 (s)
1f	1600 (s)	1500 (s)	1388	_
			(m, δ _{CH3})	
2f	1577 (s)	1492 (s)	1384 (s)	1190 (s), 1052 (s)

In addition, the strong absorptions of boron complexes in the region of 1397–1374 cm⁻¹ were due to the B—O stretching vibrations and those in the range of 1200–1052 cm⁻¹ were attributed to the B—F and B—O stretching vibrations [18,20]. Apparently, there were no strong absorption peaks in these regions for the bis- β -diketone ligands.

Absorption spectra

The absorption spectra data for compounds **1a–1f** and **2a–2f** in DMSO $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ in the UV region are summarized in Table 3. The results showed that boron complexes **2a–2f** exhibited high extinction coefficients $(2.74 \times 10^4 - 7.48 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$, which was typical of $\pi - \pi^*$ transitions. Compounds **1a–1f** and **2a–2f** have a strong broad absorption bands at 302–344 nm and 330–364 nm (Fig. 1), respectively. Obviously, the absorption maxima of the boron compounds are red-shifted about 4–28 nm compared to those of their corresponding parent bis- β -diketones, which derived from the extended π -conjugation by formation of the BF₂-chelating moiety.

Fluorescence spectra and quantum yields

The emission spectra of complexes **2a–2f** in DMSO $(2.0 \times 10^{-5} - \text{mol L}^{-1})$ are shown in Fig. 2 and their spectra data are summarized in Table 4. The results showed that these boron complexes yielded violet or blue emission at 422–445 nm in DMSO solution. Generally, an increase in π -conjugation length typically brings about a red shift of emission, change in fluorescence intensity and quantum yield [21]. In this experiment, the maximal emission peaks of complexes **2b–2f** with the extending conjugated benzene ring are red-shifted 15–23 nm compared to that of the complex **2a** containing a methyl unit in the molecules. And complexes **2b–2f** also displayed the significant increased fluorescence intensity and quantum yields, which was well consistent with the previous rule. But in complexes **2b–2f**, the substituted group of benzene ring exhibited a significant effect on their fluorescence intensity and quantum yields. The intensity of fluorescence decreased in the

Table 3						
UV-visible spectra	data	for	compounds	1a-1f	and	2a-2f

Compound	λ_{\max} (nm)	$\log \varepsilon_{\max}$	Compound	λ_{\max} (nm)	$\log \varepsilon_{\max}$
1a	302	4.79	2a	330	4.85
1b	340	4.83	2b	356	4.44
1c	326	4.67	2c	330	4.63
1d	344	4.65	2d	364	4.87
1e	340	4.57	2e	356	4.62
1f	344	4.60	2f	364	4.71



Fig. 1. UV-vis spectra for compounds **1a–1f** (dash lines) and **2a–2f** (solid lines) in DMSO $(2.0 \times 10^{-5} \text{ mol } L^{-1})$ solution.



Fig. 2. Normalized emission spectra for complexes $2a{-}2f$ in DMSO $(2.0\times10^{-5}\,{-}\,{\rm mol}\,L^{-1})$ solution.

sequence, 2f > 2b > 2e > 2d > 2c. Evidently, the introduction of the electron-donating tert-butyl substituent into the benzene ring in boron complexes resulted in a stronger fluorescence intensity and the introduction of the electron-withdrawing 4-fluoro, 2-chloro, 4-chloro substituents gave rise to an obvious decline of the fluorescence intensity. However, the complex **2e** with high electronegative 4-fluoro substituent in benzene ring exhibited

 Table 4

 Fluorescence spectra data and quantum yields for boron complexes 2a-2f.

Compound	λ_{ex} (nm)	$\lambda_{\rm em} ({\rm nm})$	Φ_u
2a	330	422	0.03
2b	356	442	0.94
2c	330	445	0.19
2d	364	438	0.16
2e	356	440	0.55
2f	364	437	0.46

the much stronger fluorescence intensity and quantum yields than complexes **2c** and **2d**, which owing to the heavy atom effect of the chlorine atom for complexes **2c** and **2d** [22]. Additionally, the complex **2b** displayed the highest fluorescence quantum yield ($\Phi_u = 0.94$) rather than the complex **2f** in these difluoroboron complexes. It might be explained by non-radiative deactivation of the energy of excited state as a result of its interaction with high frequency stretching vibrations of C—H groups [23], because of the present of six methyl groups in the compound **2f**.

Conclusions

In conclusion, we have synthesized some novel bis-β-diketone ligands (RCOCH₂CO-C₇H₇N-COCH₂COR, R = methyl, phenyl, 2-chlorophenyl, 4-chlorophenyl, 4-fluorophenyl and 4-tert-butylphenyl groups) and their difluoroboron complexes. The spectroscopic properties of these difluoroboron bis-β-diketonates were investigated by UV-vis, FTIR, ¹H NMR and fluorescence spectroscopic techniques. It was found that these boron complexes possessed high extinction coefficients and yielded violet or blue emission at 422-445 nm under UV radiation in DMSO solution. The extending π -conjugation can lead to a remarkably increased fluorescence intensity and fluorescence quantum yield in the difluoroboron complexes. The complexes 2b and 2f showed much stronger fluorescence intensity and higher quantum yield in these boron compounds; especially, the complex 2b exhibited the highest fluorescence quantum yield (Φ_u = 0.94). However, the fluorescence intensity and quantum yield for boron compounds 2c and 2d were obviously diminished, which attributed to the heavy atom effect of the chlorine atom in their molecules. These results provide a practical method on the design and synthesis of high intense fluorescent difluoroboron complex applicable to luminescence materials of chemical sensors and OEL devices.

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