A new difluoroboron bis-β-diketonate with high quantum yield and intense photoluminescence

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A new difluoroboron bis-β-diketonate was synthesized by Claisen condensation of 2-butanone with diethyl 2,6-pyridinedicarboxylate and followed by complexation with boron trifluoride etherate. Its structure was confirmed by elemental analysis, IR, NMR, ESI-MS and UV-vis spectroscopy. Its photoluminescence behavior was studied via fluorescence spectroscopy in solution and solid state. The results indicated that this complex had strong fluorescence emission in the visible with high quantum yield (Φ_u = 0.90) in DMSO solution. It exhibited the stronger photoluminescence intensity in the powder, and its emission peak was red-shifted 132 nm in comparison with that in solution, which due to the intermolecular interactions in the solid state. Meanwhile, its lifetime value (τ) was calculated according to the luminescence decay curve in the solid state.

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1. Introduction

β-Diketones are a class of classical ligands in inorganic chemistry for main group, transition metal, and rare earth complexes [1]. Recently, their difluoroboron complexes have been extensively studied due to the large molar extinction coefficients, first and second-order nonlinear optical properties, high fluorescence quantum yield, and ion sensing ability [2–4]. These difluoroboron complexes have found use as fluorescent probes, electroluminescent emitters, sensors, and lasers [4–6]. Furthermore, some authors reported synthesis, crystal structures, spectroscopic and photoluminescence properties of difluoroboron β-diketonate complexes [7–12]. However, the difluoroboron bis-β-diketonate compounds have been little studied [13,14]. In this communication, we report the synthesis and photoluminescence properties of a new difluoroboron bis-β-diketonate linked to the pyridine ring. Its structure was also confirmed by FT-IR, NMR, ESI-MS, elemental analysis and UV-vis spectroscopy.

2. Experimental

Measurement

Elemental analysis (C, H, N) was performed with a Perkin–Elmer 2400 elemental analyzer. The UV-vis spectra were obtained with Hitachi U-3010 spectrophotometer. Infrared spectra were recorded on a Nicolet FTIR 5700 spectrophotometer with KBr pellets. ^{1}H and ^{13}C NMR spectra were measured on an Avance III^{TM} 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. The emission spectra and fluorescence lifetime were measured on a Varian Cary Eclipse fluorescence spectrometer. The fluorescence quantum yield (Φ_u) was calculated by the following equation [15]:

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

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. The standard fluorophore for the quantum yield measurements was quinine sulfate in 0.1 mol L^{-1} sulfuric acid with Φ_s = 0.55 (λ_{ex} = 366 nm, at room temperature) [16].

Synthesis of the bis-β-diketone ligand

Diethyl 2,6-pyridinedicarboxylate (4.9 g, 22 mmol) was dissolved in toluene (50 mL) and freshly cut sodium (1.5 g, 65 mmol) was added to this solution with stirring. The mixture was heated to 110 °C till the sodium was molten. Then a solution of 2-butanone (3.2 g, 44 mmol) in toluene was added dropwise to the mixture. The reaction mixture was stirred and refluxed for about 4 h until the dark yellow solid formed. The mixture was cooled to room temperature and the solid was filtered. The solid was adjusted pH = 5 with dilute hydrochloric acid and collected by filtration. The crude product was recrystallized from ethanol to give the bis-β-diketone ligand as dark yellow crystals. Yield 29 %, mp 50–51 °C; IR (KBr): ν 3428(w), 3048(w), 2960 (m), 2862(m), 1607(s), 1564(s), 1479(s), 1440(s), 1303(m), 1250(m), 1065(m), 797(m), 764(m) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 15.72 (br s, 2H, enol OH), 8.24–8.15 (m, 3H, Py-H), 6.90 (s, 2H, enol CH), 4.35 (s, 0.4H, keto CH_2), 2.75–2.72 (q, 4H, CH_2), 1.15 (t, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.22, 179.76, 151.68, 138.09, 124.09, 96.08, 32.68, 9.44 ppm; ESI–MS m/z: 275.81 $[M+H]^+$. Anal. calcd. for $C_{15}H_{17}NO_4$: C 65.44, H 6.22, N 5.09; found C 65.69, H 6.24, N 5.06.

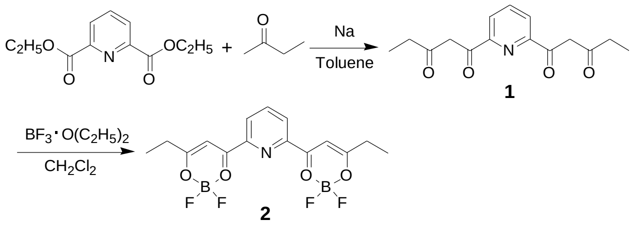
Synthesis of the difluoroboron complex *2*

Boron trifluoride diethyl etherate (0.77 mL, 6.0 mmol) was added dropwise to a solution of the bis-β-diketone ligand **1** (0.56g, 2.0 mmol) in dry dichloromethane (30 mL). The reaction mixture was stirred at room temperature for 3 h. The solution was concentrated, cooled down and the precipitate was filtered off, washed three times with dichloromethane. The solid product was sublimation at 200 °C under 10^{-3} mmHg to give the difluoroboron complex **2** as white crystalline powder. Yield 76 %, mp 229–230 °C; IR (KBr): ν 3036(w), 2952(m), 2897(m), 1602(s), 1535(s), 1443(s), 1373(s), 1306(s), 1150(s), 1052(s), 979(s), 830(s), 747(m) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 8.53 (d, 2H, Py-H, *J* = 7.5 Hz), 8.42–8.28 (m, 1H, Py-H), 7.63 (s, 2H, C=CH), 2.78 (q, 4H, CH_2), 1.21 (t, 6H, CH_3) ppm; ESI–MS m/z: 371.69 $[M+H]^+$. Anal. calcd. for $C_{15}H_{15}B_2F_4NO_4$: C 48.57, H 4.08, N 3.78; found C 48.78, H 4.05, N 3.71.

3. Results and discussion

Synthesis

Synthesis of the difluoroboron bis-β-diketonate complex was performed by following a two-step procedure (Scheme **1**). Firstly, the bis-β-diketone ligand was synthesized by Claisen condensation of 2-butanone with diethyl 2,6-pyridinedicarboxylate in toluene using sodium as the condensing agent. Secondly, the bis-β-diketone ligand treated with boron trifluoride diethyl ether (BF_3·Et_2O) in dichloromethane to give the title compound **2**.



*Scheme 1 Synthetic pathway for the difluoroboron complex **2**.*

Spectroscopic characterization

The difluoroboron complex exhibited the strong absorption bands at 1602 and 1535 cm^{-1} in the IR spectra, which attributed to the C=O and enolic C=C stretching vibrations [17,18]. The strong band assigned to the B–O stretching frequencies was observed at 1373 cm^{-1}. The absorptions at 1150 and 1052 cm^{-1} were due to the B–F and B–O stretching vibrations [12,14]. In the ^1H NMR spectra, the difluoroboron complex showed two obvious changes compared to the free ligand. One is that the chemical shift at 15.72 ppm in the bis-β-diketone ligand, which assigned to the proton of O–H in the keto-enol tautomerism of bis-β-diketone, disappeared completely in that of difluoroboron complex. The other is that the chemical shift at 6.90 ppm in the bis-β-diketone, which due to the vinylic proton in the keto-enol tautomerism of bis-β-diketone, moved to 7.63 ppm in the difluoroboron complex [17,19]. This can be explained by the effect of electronegative fluorine atoms on the electron density of the chelate ring of difluoroboron complex.

The electronic absorption spectra (Fig. 1) for the free ligand and difluoroboron complex were recorded in DMSO (1.0×10^{-5} mol·L^{-1}). From Fig. 1, the difluoroboron complex exhibited a high extinction coefficient (ε = 21250 M^{-1}·cm^{-1}) and its maximum absorption peak was red-shifted 14 nm in comparison with that of the free ligand, which assigned to π–π^* transition in the difluoroboron complex conjugated ring system.

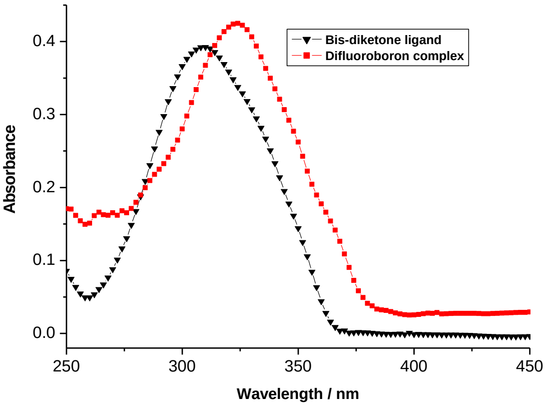


Fig. 1. UV-vis spectra for the free ligand and the boron complex in DMSO solution (1×10^{-5} mol/L).

Photoluminescence behavior

The photoluminescence properties of the difluoroboron bis-β-diketonate complex **2** were investigated in DMSO solution (1.0×10^{-5} mol·L^{-1}) and solid state. The emission spectra were shown in Fig. 2. In DMSO solution, difluoroboron complex showed fluorescence emission at 422nm when excited 312 nm, which can be attributed to π–π^* transition. Meanwhile it exhibited strong fluorescence intensity and high quantum yield ($\Phi_u = 0.90$) relative to quinine sulfate ($\Phi_s = 0.55$). In the solid state, boron complex revealed the stronger fluorescence emission at 554nm when excited 312 nm, and its emission maximum peak was red-shifted 132 nm in comparison with that in solution, which due to the intermolecular interactions in the solid state. This result is in accordance with the literatures [7,20]. Additionally, Luminescence decay curve for its emission at 554nm in the powder was measured at room temperature (Fig. 3). Its luminescence decay can be analyzed as sum of the single exponential that yields decay time 12.44 μs. These results indicated that the difluoroboron complex formed the effective π-conjugation between the pyridine ring and the two BF_2-chelating moieties.

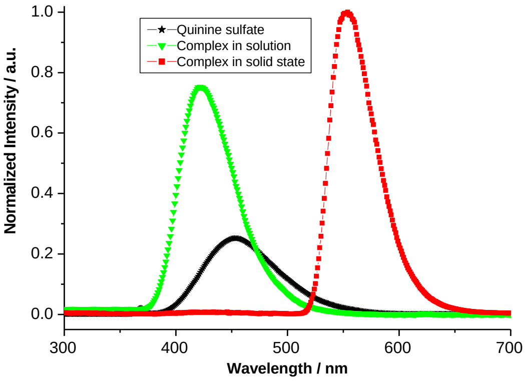


Fig. 2. Normalized photoluminescence spectra for quinine sulfate and the boron complex in solution and solid state.

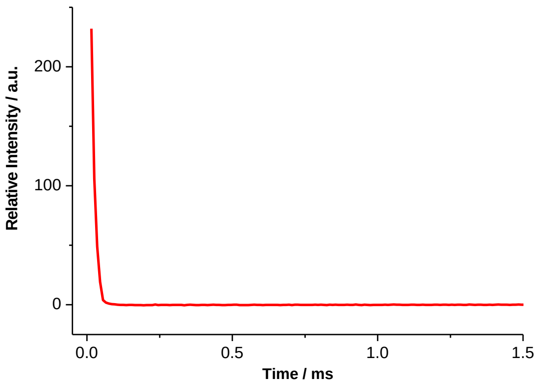


Fig. 3. Luminescence decay curve for the boron complex in the powder monitored at 554 nm at room temperature.

4. Conclusions

In conclusion, we synthesized a difluoroboron bis-β-diketonate complex and investigated its photoluminescence behaviors as a new light-emitting material in the solution and solid state. This complex displayed fluorescence emission in the visible with high quantum yield ($\Phi_u = 0.90$) in DMSO solution. It also exhibited the strong photoluminescence intensity in the solid state, and its emission color was red-shifted 132 nm in comparison with that in solution. Additionally, its luminescence decay curve conforms to the single exponential function and the lifetime value (τ) is 12.44 μs in the powder. These results indicated that the difluoroboron bis-β-diketonate complex has the excellent photoluminescence properties. Therefore, we are currently working on the design and synthesis of related high intense fluorescent difluoroboron complex applicable to fluorescent probes of chemical sensors and OEL devices.

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