



# Synthesis, photoluminescent and electrochemical properties of diacetoxyboron derivatives for bis- $\beta$ -diketone linked thienothiophene

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## ABSTRACT

Six novel diacetoxyboron complexes of bis- $\beta$ -diketones linked thienothiophene moiety were synthesized from acetoacetone by cyclization, Claisen condensation and chelation reaction. The obtained complexes were confirmed by means of  $^1\text{H}$  NMR, FTIR, MS and elemental analysis and their electrochemical and photoluminescent properties were investigated by cyclic voltammetry, UV–vis absorption and fluorescence spectroscopy. The results showed that these diacetoxyboron complexes yielded a blue emission in DMF solution and emitted a greenish-yellow emission in powders and PMMA films. Especially, diacetoxyboron bis- $\beta$ -diketonate with tert-butylphenyl thienothiophene exhibited the most intense photoluminescent intensity, highest quantum efficiency ( $\Phi_{\text{q}} = 0.95$ ) in solution and longest lifetime value ( $\tau = 38.42 \mu\text{s}$ ) in PMMA film among these complexes. In addition, these diacetoxyboron complexes showed the low-lying LUMO energy levels (2.71–2.75 eV), which was suitable for electron transfer.

## 1. Introduction

Over the past few decades,  $\beta$ -diketones and the related complexes of main group and transition metals have attracted a considerable attention to the chemists due to their wide-spread applications, such as metal extractions, chemical vapor deposition, catalyst precursors, photoluminescent and electroluminescent materials, etc [1–4]. Recently, many researchers reported the synthesis, photophysical and photochemical properties of some new difluoroboron  $\beta$ -diketonate complexes [5–8]. Because these difluoroboron complexes possess large molar extinction coefficients, high luminescence quantum efficiencies, second-order nonlinear optical properties, and ion sensing ability, they have been widely explored as light-emitting diodes, two-photon materials, photochromic materials, and fluorescent probes [9–12]. In addition, our group also reported some novel boron difluoride  $\beta$ -diketonates and investigated their spectroscopic and photoluminescent properties [13–15].

But until now the diacetoxyboron compounds of  $\beta$ -diketones have been little studied [16]. As a continuation of our previous work, herein we designed and synthesized some novel diacetoxyboron derivatives of bis- $\beta$ -diketones linked thienothiophene moiety. The fused thiophene, especially thienothiophene is a remarkable and significant chemical moiety in the design of opto-electronic materials with improved air-stability and good transport performance [17,18], as well as for their

ease of structural modification [19]. Many thienothiophene-based materials were synthesized and used in organic thin-film transistors, organic solar cells and liquid-crystalline semiconductors [20–22]. Obviously, the thienothiophene-based compounds possess a planar and stable heterocyclic system, which can form a fully conjugated pathway to preserve the close  $\pi$ – $\pi$  intermolecular distances necessary for high charge carrier mobility. Hence the diacetoxyboron  $\beta$ -diketonate photochromes with thienothiophene moieties should be able to further develop their fluorescence properties. In addition, the diacetoxyboron bis- $\beta$ -diketonates have a much better solubility in organic solvents compared with the difluoroboron compounds, which is due to the acetoxy instead of fluoro groups on photochromic molecules. In this study, the electrochemical and photoluminescent behavior of these new diacetoxyboron complexes were investigated in solution, powders and PMMA films in detail.

## 2. Experimental

### 2.1. Materials and measurements

Potassium tert-butoxide was prepared by our team according to the literature [13]. Tetrabutylammonium hexafluorophosphate, boric acid, acetic anhydride, acetoacetone, quinine sulfate and poly (methyl-methacrylate) were purchased from J&K Scientific Ltd. Other chemicals

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(potassium carbonate, hydrochloric acid, carbon disulfide, chloroacetone, chloroform, benzene, dichloromethane, dimethylformamide and aromatic esters) were of analytical grade.

Melting points were determined by X-4 digital melting-point apparatus. Elemental analysis was performed with a 2400CHN elemental analyzer (Perkin–Elmer).  $^1\text{H}$  NMR spectra were measured on an Avance 300 MHz NMR spectrometer (Bruker) in  $\text{CDCl}_3$  solution with TMS as an internal reference. The ultraviolet–visible spectra were recorded with U-3010 spectrophotometer (Hitachi). IR spectra were obtained from KBr pellets on a FTIR 5700 spectrophotometer (Nicolet). ESI–MS measurements were performed on a LCQ Advantage Max spectrometer (Finnigan). The PMMA films were prepared with a KW-4A spin coater (Xiamen Chemmat).

Cyclic voltammograms were recorded on an electrochemistry workstation (CHI 660E, USA) in a three-electrode cell with a platinum disk electrode as the working electrode, a platinum wire as the counter electrode and an  $\text{AgCl/Ag}$  electrode as the reference electrode in  $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$  solution at  $0.05 \text{ V/s}$ . The emission spectra were obtained on a fluorescence spectrometer (Varian Cary Eclipse). The fluorescence decay curves were recorded with same setup using a 500 ns multichannel scaler excited with a xenon flash lamp ( $\lambda_{\text{ex}} = 369 \text{ nm}$ ). The fluorescence quantum efficiencies ( $\Phi$ ) were measured with quinine sulfate in  $0.1 \text{ mol L}^{-1}$  sulfuric acid ( $\Phi_s = 0.55$ ,  $\lambda_{\text{ex}} = 366 \text{ nm}$ ) as a standard at room temperature [23].

## 2.2. General procedure for synthesis of bis- $\beta$ -diketones (2a–2f)

To a solution of acetoacetone (5.13 mL, 0.05 mol) in DMF (35 mL), anhydrous potassium carbonate (13.82 g, 0.10 mol) was added under stirring vigorously, and carbon disulfide (4.53 mL, 0.075 mol) was also added and kept for stirring at room temperature for 30 min. The reaction mixture was cooled to  $0^\circ\text{C}$  in ice bath, chloroacetone (9.95 mL, 0.125 mol) was added dropwise slowly and the mixture was stirred for 1 h at room temperature. The resulting reaction mixture was poured into 50 mL water and the solid product was obtained by filtration. The crude product was recrystallized from chloroform to obtain 2,5-diacetyl-3,4-dimethyl-thieno [2,3-*b*] thiophene (1) as a white crystal.

To a solution of 2,5-diacetyl-3,4-dimethyl-thieno [2,3-*b*] thiophene (1) (1.26 g, 5 mmol) in 30 mL dry benzene, potassium tert-butoxide (4.50 g, 40 mmol) was added and heated to  $80^\circ\text{C}$ . Then the aromatic esters (50 mmol) in benzene (10 mL) was added dropwise and refluxed for 10 h. The resulting mixture was poured into 100 mL ice-water and the organic layer was adjusted to  $\text{pH} = 6$ . The yellow products were precipitated and filtered. The resulting products were recrystallized from chloroform to give bis- $\beta$ -diketones 2a–2f. The synthetic compounds were confirmed by elemental analysis, FTIR,  $^1\text{H}$  NMR, and mass spectroscopy (The data are in the Supporting Information).

## 2.3. Synthesis of diacetoxyboron complexes (3a–3f)

Boric acid (0.06 g, 1 mmol) was dissolved in acetic anhydride (8 mL) and heated to reflux for 30 min. Then boron acetate in acetic anhydride was obtained as a light yellow solution. The bis- $\beta$ -diketones 2a–2f (0.25 mmol) was dissolved in benzene (20 mL) under refluxing. To this solution, the above synthetic solution of boron acetate (1 mmol) was added dropwise slowly and the mixture was refluxing for 4 h. The formed yellow precipitates were filtered off and recrystallized from  $\text{CH}_2\text{Cl}_2$  to give diacetoxyboron complexes 3a–3f.

### 2.3.1. Diacetoxyboron 3,3'-(3,4-dimethylthieno[2,3-*b*]thiophene-2,5-diyl) bis(1-phenyl) propane-1,3-dionate (3a)

Yellow powder, yield 70%, mp  $> 300^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d, 4H,  $J = 7.5 \text{ Hz}$ , Ar–H), 7.59 (t, 2H,  $J = 7.4 \text{ Hz}$ , Ar–H), 7.45 (t, 4H,  $J = 7.8 \text{ Hz}$ , Ar–H), 6.91 (s, 2H, C=C–H), 2.93 (s, 6H,  $\text{CH}_3$ ), 2.05 (s, 12H,  $\text{COCH}_3$ ) ppm; IR (KBr):  $\nu$  3065 (w), 2933 (w), 1721 (s), 1598 (s), 1532 (m), 1483 (s), 1418 (m), 1364 (s), 1268 (s),

1067 (s), 999 (s), 926 (m), 761 (m), 698 (m)  $\text{cm}^{-1}$ ; ESI–MS  $m/z$ : 739.03  $[\text{M} + \text{Na}]^+$ ; Anal. calcd. for  $\text{C}_{34}\text{H}_{30}\text{B}_2\text{O}_{12}\text{S}_2$ : C 57.01, H 4.22; found C 57.46, H 4.19.

### 2.3.2. Diacetoxyboron 3,3'-(3,4-dimethylthieno[2,3-*b*]thiophene-2,5-diyl) bis(1-(*p*-tolyl) propane-1,3-dionate) (3b)

Light yellow powder, yield 74%, mp  $> 300^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (d, 4H,  $J = 8.2 \text{ Hz}$ , Ar–H), 7.31 (d, 4H,  $J = 8.1 \text{ Hz}$ , Ar–H), 6.94 (s, 2H, C=C–H), 2.92 (s, 6H,  $\text{CH}_3$ ), 2.45 (s, 6H, Ar– $\text{CH}_3$ ), 2.11 (s, 12H,  $\text{COCH}_3$ ) ppm; IR (KBr):  $\nu$  3029 (w), 2929 (w), 1719 (s), 1600 (s), 1539 (m), 1501 (s), 1415 (m), 1363 (s), 1263 (s), 1064 (s), 1001 (m), 928 (m), 792 (m), 751 (m)  $\text{cm}^{-1}$ ; ESI–MS  $m/z$ : 767.12  $[\text{M} + \text{Na}]^+$ ; Anal. calcd. for  $\text{C}_{36}\text{H}_{34}\text{B}_2\text{O}_{12}\text{S}_2$ : C 58.09, H 4.60; found C 57.76, H 4.57.

### 2.3.3. Diacetoxyboron 3,3'-(3,4-dimethylthieno[2,3-*b*]thiophene-2,5-diyl) bis(1-(4-(*tert*-butyl)phenyl) propane-1,3-dionate) (3c)

Orange yellow powder, yield 73%, mp  $> 300^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01 (d, 4H,  $J = 8.5 \text{ Hz}$ , Ar–H), 7.54 (d, 4H,  $J = 8.1 \text{ Hz}$ , Ar–H), 6.98 (s, 2H, C=C–H), 2.94 (s, 6H,  $\text{CH}_3$ ), 2.13 (s, 12H,  $\text{COCH}_3$ ), 1.36 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ) ppm; IR (KBr):  $\nu$  3064 (w), 2961 (m), 2870 (w), 1721 (s), 1600 (s), 1532 (m), 1503 (s), 1415 (m), 1361 (s), 1264 (s), 1055 (s), 1001 (m), 852 (m), 799 (m), 697 (m)  $\text{cm}^{-1}$ ; ESI–MS  $m/z$ : 851.13  $[\text{M} + \text{Na}]^+$ ; Anal. calcd for  $\text{C}_{42}\text{H}_{46}\text{B}_2\text{O}_{12}\text{S}_2$ : C 60.88, H 5.60; found C 61.17, H 5.56.

### 2.3.4. Diacetoxyboron 3,3'-(3,4-dimethylthieno[2,3-*b*]thiophene-2,5-diyl) bis(1-(4-chloro phenyl)propane-1,3-dionate) (3d)

Yellow powder, yield 75%, mp  $> 300^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.04 (d,  $J = 8.2 \text{ Hz}$ , 4H, Ar–H), 7.45 (d,  $J = 8.3 \text{ Hz}$ , 4H, Ar–H), 6.95 (s, 2H, C=C–H), 2.89 (s, 6H,  $\text{CH}_3$ ), 2.06 (s, 12H,  $\text{COCH}_3$ ) ppm; IR (KBr):  $\nu$  3027 (w), 2932 (w), 1721 (s), 1599 (s), 1534 (m), 1496 (s), 1416 (m), 1356 (s), 1262 (s), 1064 (s), 998 (m), 776 (m)  $\text{cm}^{-1}$ ; ESI–MS  $m/z$ : 807.93  $[\text{M} + \text{Na}]^+$ ; Anal. calcd. for  $\text{C}_{34}\text{H}_{28}\text{B}_2\text{Cl}_2\text{O}_{12}\text{S}_2$ : C 52.01, H 3.59; found C 52.39, H 3.62.

### 2.3.5. Diacetoxyboron 3,3'-(3,4-dimethylthieno[2,3-*b*]thiophene-2,5-diyl) bis(1-(4-fluoro phenyl)propane-1,3-dionate) (3e)

Yellow powder, yield 70%, mp  $> 300^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.07 (dd, 4H,  $J = 5.2, 8.7 \text{ Hz}$ , Ar–H), 7.18 (t, 4H,  $J = 8.5 \text{ Hz}$ , Ar–H), 6.92 (s, 2H, C=C–H), 2.92 (s, 6H,  $\text{CH}_3$ ), 2.11 (s, 12H,  $\text{COCH}_3$ ) ppm; IR (KBr):  $\nu$  3074 (w), 2935 (w), 1718 (s), 1602 (s), 1546 (m), 1499 (s), 1412 (m), 1365 (s), 1269 (s), 1236 (s), 1065 (s), 1002 (m), 867 (m), 796 (m)  $\text{cm}^{-1}$ ; EI–MS  $m/z$ : 755.02  $[\text{M} + \text{Na}]^+$ ; Anal. calcd. for  $\text{C}_{34}\text{H}_{28}\text{B}_2\text{F}_2\text{O}_{12}\text{S}_2$ : C 54.28, H 3.75; found C 54.63, H 3.71.

### 2.3.6. Diacetoxyboron 3,3'-(3,4-dimethylthieno[2,3-*b*]thiophene-2,5-diyl) bis(1-(furan-2-yl)propane-1,3-dionate) (3f)

Light yellow powder, yield 68%, mp  $> 300^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (s, 2H, Furan–H), 7.48 (d, 2H,  $J = 3.5 \text{ Hz}$ , Furan–H), 6.89 (s, 2H, C=C–H), 6.68 (dd, 2H,  $J = 1.6, 3.6 \text{ Hz}$ , Furan–H), 2.91 (s, 6H,  $\text{CH}_3$ ), 2.10 (s, 12H,  $\text{COCH}_3$ ) ppm; IR (KBr):  $\nu$  3136 (w), 2928 (w), 1720 (s), 1592 (s), 1491 (s), 1411 (m), 1363 (s), 1263 (s), 1070 (s), 792 (m)  $\text{cm}^{-1}$ ; ESI–MS  $m/z$ : 718.96  $[\text{M} + \text{Na}]^+$ ; Anal. calcd. for  $\text{C}_{30}\text{H}_{26}\text{B}_2\text{O}_{14}\text{S}_2$ : C 51.75, H 3.76; found C 51.47, H 3.72.

## 2.4. Preparation for PMMA films of diacetoxyboron complexes

PMMA powder (28.5 mg) was dissolved in chloroform (1 mL) under refluxing to obtain a PMMA solution. To this solution, the diacetoxyboron complexes (3a–3f) (1.5 mg) solution in chloroform (1 mL) was added and the mixture was stirring for 30 min to form a transparent solution at room temperature. Thin films of complex -doped PMMA were spin-coated on quartz glass surfaces (20 mm  $\times$  20 mm  $\times$  1 mm) at 1000 rpm for 20 s. These films of doped polymers were baked at

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