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Synthesis, photophysical and solvatochromic properties of

diacetoxyboron complexes with curcumin derivatives

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Abstract: Five novel diacetoxyboron complexes of β -diketones incorporated curcumin moiety were designed and synthesized. Their photophysical behaviors were investigated by UV-vis absorption and fluorescence spectroscopy in different solvents and solid state. It was observed that their fluorescence spectra yielded a blue to yellow-green emission in solution and emitted a yellow to red emission in solid state. Especially, the complex **3b** displayed the strongest emission and the highest quantum efficiency ($\Phi_u = 0.98$) in toluene among these complexes. The CIE coordinate of the complex 3b in solid state was positioned in an ideal red region of the chromaticity diagram. The maximal emission of these complexes exhibited a large wavelength shift and Stokes shift increased with the increase of the solvent polarity. Their dipole moment differences between the ground and excited states were also estimated by using the Lippert-Mataga equation. Meanwhile, their HOMO, LUMO energy levels and energy band gaps were calculated by cyclic voltammetry. Keywords: Diacetoxyboron complex, curcumin derivative, photophysical properties, solvatochromic effect, electrochemical properties

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1. Introduction

For more than two decades, the synthesis and design of tetracoordinate organoboron compounds have caused tremendous attention because of their impressive photophysical properties with application in semiconductors [1], organic light-emitting diodes [2,3], chemical sensors [4], fluorescent probes [5,6], and two-photon materials [7]. In recent years, many new functional difluoroboron β -diketonates were synthesized and their photophysical and photochemical properties were investigated in detail [8–12]. These difluoroboron complexes showed the large Stokes shifts, intense fluorescence emission, high quantum yields, high molar absorption coefficients and second-order nonlinear optical properties. Similarly, Curcumin and its analogues possess two conjugated α,β -unsaturated β -diketone moieties, which can also form a keto-enol tautomerism [13-15]. Therefore, the researchers presented the curcumin boron complexes as a near-infrared imaging fluorescent probe [16] and a chemical sensor [17]. Meanwhile, some novel difluoroboron complexes with curcumin analogues were reported and their photophysical properties were also studied [18-20].

However, there is no report on the diacetoxyboron complexes with curcumin analogues so far. Recently, we reported the synthesis and photophysical behaviors of some new diacetoxyboron derivatives with bis- β -diketone [21]. In this work, we designed and synthesized several novel diacetoxyboron derivatives of β -diketones incorporated curcumin moiety and their structures were confirmed by ¹H NMR, ¹³C NMR, IR, ESI–MS spectroscopy and elemental analysis. The photophysical

properties of these diacetoxyboron complexes in solution and solid state were described in detail. Meanwhile, the spectroscopic behaviors of these complexes were investigated in different solvents at room temperature and their dipole moment differences between the ground and excited states were estimated by using the Lippert–Mataga equation.

2. Experimental

2.1. Chemicals and methods

Acetylacetone, benzaldehyde, 4-methoxybenzaldehyde, 4-methylbenzaldehyde, 1-naphthaldehyde, cinnamaldehyde, boron trioxide, tributyl borate, acetic anhydride, n-butylamine, tetrabutylammonium hexafluorophosphate, and boric acid were purchased from Shanghai Sun Chemical Technology Co., Ltd.. Other reagents (quinine sulfate, dichloromethane, chloroform, ethyl acetate, toluene, tetrahydrofuran, acetone and acetonitrile, petroleum ether, dimethyl sulfoxide, ethanol, benzene and hydrochloric acid) were analytically pure.

Elemental analyses were taken with Perkin–Elmer 2400CHN elemental analyzer. Melting points were measured on Beijing Tech X-4 digital melting-point apparatus. ¹H and ¹³C NMR spectra were recorded with Bruker Avance IIITM 300 MHz NMR spectrometer in CDCl₃ solution. FT-IR spectra were performed with Nicolet FTIR 5700 spectrophotometer in KBr disks. Mass spectra were determined by Finnigan LCQ Advantage Max spectrometer. UV-vis absorption spectra were carried out on Hitachi U-3010 spectrophotometer. The emission spectra were recorded with Varian Cary Eclipse fluorescence spectrometer and fluorescence lifetimes were performed

on an Edinburgh FS5 spectrofluorometer by the time-correlated single-proton counting (TCSPC) (picoseconds pulsed diode laser EPL-450, $\lambda_{ex} = 450$ nm). Quantum yields (Φ) were measured relative to quinine sulfate in 0.1M sulfuric acid ($\Phi_s = 0.55$, $\lambda_{ex} = 366$ nm) at room temperature by the standard method [22]. Cyclic voltammetry (CV) measurements were recorded on a CHI 660E electrochemistry workstation with a three-electrode cell (a platinum disk electrode as the working electrode, a platinum wire as the counter electrode and an AgCl/Ag electrode as the reference electrode) in a 0.1 mol L⁻¹ n-Bu₄NPF₆ solution in CH₂Cl₂ at a scanning rate of 50 mV s⁻¹.

2.2. Synthesis of curcumin derivatives (1a-5a)

In a round bottom flask, boron trioxide (0.49 g, 7.0 mmol) and acetylacetone (1.0 mL, 1.0 mmol) was dissolved in ethyl acetate (10 mL) and refluxed for 1h under stirring. To this solution, the aromatic aldehyde (20 mmol) and tributyl borate (4.8 mL, 20 mmol) were added and kept for stirring to a yellow-green solution. Then n-butylamine (2.0 mL, 20 mmol) were added and stirred for 4h at room temperature. Then 5% hydrochloric acid (15 mL) was added dropwise to the reaction mixture and adjusted to pH = 2. The organic layer was separated and aqueous layer was extracted with ethyl acetate. The organic phase was dried over anhydrous MgSO₄ and distilled by rotary evaporator. The residues were cooled to give crystal products and recrystallized from chloroform to obtain the curcumin derivatives (1a–5a) in 26–51% yields.

1,7-Diphenylhepta-1,6-diene-3,5-dione (1a): Yellow green powder, yield 35%, m.p.

144–145 °C; ¹H NMR (300 MHz, CDCl₃): δ 15.91 (s, 1H, enol OH), 7.67 (d, 2H, J = 15.9 Hz, C=C–H), 7.58–7.55 (m, 4H, Ar–H), 7.41–7.39 (m, 6H, Ar–H), 6.64 (d, 2H, J = 15.8 Hz, C=C–H), 5.86 (s, 1H, enol C=C–H) ppm; IR (KBr): v 3441 (m), 3067 (m), 2955 (w), 2869 (w), 1631 (s), 1588 (s), 1400 (s), 1351 (m), 1138 (m), 976 (m), 755 (s), 682 (m) cm⁻¹; ESI–MS *m/z*: 277.16 [M+H]⁺; Anal. calcd. for C₁₉H₁₆O₂: C 82.58, H 5.84; found C 82.85, H 5.88.

1,7-*Di-p-tolylhepta-1,6-diene-3,5-dione* (**2***a*): Yellow green powder, yield 43%, m.p. 213–214 °C; ¹H NMR (300 MHz, CDCl₃): δ 16.00 (s, 1H, enol OH), 7.64 (d, 2H, J = 15.9 Hz, C=C–H), 7.46 (d, 4H, J = 8.0 Hz, Ar–H), 7.20 (d, 4H, J = 7.9 Hz, Ar–H), 6.59 (d, 2H, J = 15.8 Hz, C=C–H), 5.82 (s, 1H, enol C=C–H), 2.38 (s, 6H, Ar–CH₃) ppm; IR (KBr): v 3441 (m), 3065 (m), 2949 (w), 2856 (w), 1631 (s), 1592 (s), 1400 (s), 1351 (m), 1141 (m), 977 (m), 819 (m) cm⁻¹; ESI–MS *m/z*: 305.18 [M+H]⁺; Anal. calcd. for C₂₁H₂₀O₂: C 82.86, H 6.62; found C 82.57, H 6.56.

1,7-Bis(*4-methoxyphenyl*)*hepta-1,6-diene-3,5-dione* (*3a*): Orange powder, yield 51%; m.p. 167–168 °C; ¹H NMR (300 MHz, CDCl₃): δ 16.10 (s, 1H, enol OH), 7.62 (d, 2H, *J* = 15.8 Hz, C=C–H), 7.51 (d, 4H, *J* = 8.6 Hz, Ar–H), 6.91 (d, 4H, *J* = 8.6 Hz, Ar–H), 6.50 (d, 2H, *J* = 15.8 Hz, C=C–H), 5.79 (s, 1H, enol C=C–H), 3.84 (s, 6H, OCH₃) ppm; IR (KBr): v 3440 (m), 3046 (m), 2963 (w), 2867 (w), 1631 (s), 1600 (s), 1512 (m), 1400 (s), 1350 (m), 1250 (m), 1177 (m), 1143 (m), 977 (m), 826 (s), 733 (s) cm⁻¹; ESI–MS *m/z*: 337.07 [M+H]⁺; Anal. calcd. for C₂₁H₂₀O₄: C 74.98, H 5.99; found C 75.66, H 6.03.

1,7-Di(naphthalen-1-yl)hepta-1,6-diene-3,5-dione (4a): Orange powder, yield:

45%; m.p. 190–191 °C; ¹H NMR (300 MHz, CDCl₃): δ 16.08 (s, 1H, enol OH), 8.55 (d, 2H, J = 15.6 Hz, C=C–H), 8.28 (d, 2H, J = 8.2 Hz, Ar–H), 7.92–7.82 (m, 6H, Ar–H), 7.63–7.49 (m, 6H, Ar–H), 6.77 (d, 2H, J = 15.5 Hz, C=C–H), 5.96 (s, 1H, enol C=C–H) ppm; IR (KBr): v 3431(m), 3057 (m), 2951 (w), 2864 (w), 1630 (s), 1589 (s), 1399 (s), 1347 (m), 1138 (m), 966 (m), 798 (m), 765 (s) cm⁻¹; ESI–MS *m/z*: 377.23 [M+H]⁺; Anal. calcd. for C₂₇H₂₀O₂: C 86.15, H 5.35; found C 86.43, H 5.31.

1,11-Diphenyl-undeca-1,3,8,10-tetraene-5,7-dione (*5a*): Orange powder, yield 26%; m.p. 214–215 °C; ¹H NMR (300 MHz, CDCl₃): δ 15.86 (s, 1H, enol OH), 7.49–7.31 (m, 12H, Ar–H or C=C–H), 6.92 (d, 4H, *J* = 5.4 Hz, Ar–H), 6.18 (d, 2H, *J* = 15.1 Hz, C=C–H), 5.70 (s, 1H, enol C=C–H) ppm; IR (KBr): v 3440 (m), 3086 (m), 3045 (m), 2949 (w), 2853 (w), 1631 (s), 1591 (s), 1400 (s), 1351 (m), 1119 (m), 995 (m), 748 (m), 687 (m) cm⁻¹; ESI–MS *m/z*: 658.13 [2M+H]⁺; Anal. calcd. for C₂₃H₂₀O₂: C 84.12, H 6.14; found C 84.41, H 6.18.

2.3. Synthesis of diacetoxyboron complexes (1b–5b)

In a round bottom flask, acetic anhydride (8 mL) and boric acid (0.06 g, 1 mmol) was added and refluxed for 30 min to give a light yellow solution. The curcumin derivatives **1a–5a** (0.5 mmol) were dissolved in benzene (20 mL) and heated to reflux in a three-necked round bottom flask. Then the above solution of boron acetate (1 mmol) in acetic anhydride was added dropwise slowly into the mixture over 30 min. The reaction mixture was kept refluxing for 5 h and complexes were precipitated out. The precipitates were filtered off and recrystallized from chloroform to obtain diacetoxyboron complexes (**1b–5b**) in 57–71% yields.

Diacetoxyboron 1,7-*diphenylhepta-1*,6-*diene-3*,5-*dionate* (**1b**): Yellow powder, yield 57 %, m.p. 217–218 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.93 (d, 2H, J = 15.7 Hz, C=C–H), 7.59–7.57 (m, 4H, Ar–H), 7.43–7.41 (m, 6H, Ar–H), 6.74 (d, 2H, J = 15.7 Hz, C=C–H), 6.25 (s, 1H, enol C=C–H), 2.11 (s, 6H, COCH₃) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 179.4, 172.4, 146.6, 134.2, 131.5, 129.1, 128.1, 120.9, 103.2, 23.2 ppm; IR (KBr): v 3064 (m), 2956 (w), 2866 (w), 1717 (s), 1602 (s), 1564 (s), 1404 (s), 1371 (s), 1270 (s), 1181 (m), 1045 (s), 979 (m), 768 (m), 688 (m) cm⁻¹; ESI–MS *m/z*: 426.80 [M+Na]⁺; Anal. calcd. for C₂₃H₂₁BO₆: C 68.34, H 5.24; found C 68.62, H 5.29.

Diacetoxyboron 1,7-*di-p-tolylhepta-1,6-diene-3,5-dionate* (**2b**): Orange powder, yield 61 %, m.p. 240–241 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.87 (d, 2H, *J* = 15.5 Hz, C=C–H), 7.44 (d, 4H, *J* = 7.4 Hz, Ar–H), 7.19 (d, 4H, *J* = 7.4 Hz, Ar–H), 6.67 (d, 2H, *J* = 15.6 Hz, C=C–H), 6.22 (s, 1H, enol C=C–H), 2.38 (s, 6H, Ar–CH₃), 2.11 (s, 6H, COCH₃) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 179.2, 172.3, 146.4, 142.3, 131.7, 129.8, 129.1, 120.0, 102.9, 23.2, 21.6 ppm; IR (KBr): v 3061 (m), 2953 (w), 2849 (w), 1726 (s), 1603 (s), 1555 (s), 1401 (s), 1371 (s), 1258 (s), 1169 (m), 1049 (s), 950 (m), 818 (m) cm⁻¹; ESI–MS m/z: 454.89 [M+Na]⁺; Anal. calcd. for C₂₅H₂₅BO₆: C 69.46, H 5.83; found C 69.75, H 4.77.

Diacetoxyboron 1,7-*Bis*(4-*methoxyphenyl*)*hepta*-1,6-*diene*-3,5-*dionate* (**3b**): Orange-red powder, yield 63 %, m.p. 229–230 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.85 (d, 2H, *J* = 15.5 Hz, C=C–H), 7.51 (d, 4H, *J* = 8.5 Hz, Ar–H), 6.89 (d, 4H, *J* = 8.5 Hz, Ar–H), 6.57 (d, 2H, *J* = 15.5 Hz, C=C–H), 6.17 (s, 1H, enol C=C–H), 3.85 (s,

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6H, OCH₃), 2.11 (s, 6H, COCH₃) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 178.7, 172.3, 162.4, 145.9, 131.0, 127.2, 118.5, 114.5, 102.7, 55.4, 23.2 ppm; IR (KBr): v 3045 (m), 2959 (w), 2865 (w), 1717 (s), 1601 (s), 1543 (s), 1398 (s), 1368 (s), 1263 (s), 1173 (m), 1039 (s), 975 (m), 828 (s) cm⁻¹; ESI–MS m/z: 486.80 [M+Na]⁺; Anal. calcd. for C₂₅H₂₅BO₈: C 64.68, H 5.43; found C 64.37, H 5.48.

Diacetoxyboron 1,7-*Di*(*naphthalen-1-yl*)*hepta-1,6-diene-3,5-dionate* (**4b**): Red powder, yield 71 %, m.p. 241–242 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.79 (d, 2H, *J* = 15.4 Hz, C=C–H), 8.24 (d, 2H, *J* = 8.3 Hz, Ar–H), 7.95–7.87 (m, 6H, Ar–H), 7.65–7.48 (m, 6H, Ar–H), 6.90 (d, 2H, *J* = 15.4 Hz, C=C–H), 6.39 (s, 1H, enol C=C–H), 2.18 (s, 6H, COCH₃) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 179.3, 172.4, 142.8, 133.8, 132.1, 131.7, 131.3, 128.9, 127.4, 126.5, 126.1, 125.4, 123.3, 123.0, 103.6, 23.3 ppm; IR (KBr): v 3052 (m), 2954 (w), 2858 (w), 1722 (s), 1606 (s), 1555 (s), 1398 (s), 1372 (s), 1273 (s), 1055 (s), 953 (m), 857 (m), 773 (s) cm⁻¹; ESI–MS m/z: 526.88 [M+Na]⁺; Anal. calcd. for C₃₁H₂₅BO₆: C 73.83, H 5.00; found C 73.56, H 5.05.

Diacetoxyboron 1,11-*Diphenyl-undeca-1,3,8,10-tetraene-5,7-dionate* (5*b*): Purple-red powder, yield 68 %, m.p. 211–212 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.68 (dd, 2H, J = 14.8, 10.7Hz, C=C–H), 7.48 (d, 4H, J = 5.9 Hz, Ar–H), 7.38–7.35 (m, 6H, Ar–H or C=C–H), 7.07–6.89 (m, 4H, Ar–H), 6.26 (d, 2H, J = 14.9 Hz, C=C–H), 6.07 (s, 1H, enol C=C–H), 2.10 (s, 6H, COCH₃) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 178.6, 172.3, 146.6, 144.2, 135.8, 129.9, 128.9, 127.7, 126.7, 124.5, 103.1, 23.2 ppm; IR (KBr): v 3081 (m), 3039 (m), 2952 (w), 2848 (w), 1712 (s), 1603 (s),

1543 (s), 1399 (s), 1370 (s), 1274 (s), 1143 (m), 1048 (s), 995 (m), 757 (m), 688 (m) cm⁻¹; EI–MS m/z: 478.82 [M+Na]⁺; Anal. calcd. for C₂₇H₂₅BO₆: C 71.07, H 5.52; found C 71.38, H 5.47.

3. Results and discussion

3.1. Chemistry

The synthetic route of diacetoxyboron complexes with curcumin derivatives was illustrated in Scheme 1. The curcumin derivatives (1a–5a) were synthesized by condensation reaction of the corresponding aromatic aldehydes with acetylacetone in the presence of boron trioxide, tributyl borate and n-butylamine in ethyl acetate according to literatures [13]. Then, the curcumin derivatives were converted to diacetoxyboron complexes by the chelation reaction with boron acetate in benzene. The products were recrystallized from chloroform to obtain the pure diacetoxyboron complexes (1b–5b).

< Scheme 1>

The structure elucidation of these diacetoxyboron complexes was based on the IR, ¹H NMR, ¹³C NMR, ESI–MS spectroscopy and elemental analysis. The IR spectra of these diacetoxyboron complexes (**1b–5b**) showed the C=O and enolic C=C stretching vibrations at 1606–1601 cm⁻¹ and 1564–1543 cm⁻¹ were red-shifted 24–30 cm⁻¹ and 24–57 cm⁻¹ compared to the curcumin derivatives, respectively [23,24], and the disappearance of corresponding O–H vibration bands at 3441–3431 cm⁻¹ which

existed in the curcumin derivative ligands due to their keto-enol tautomerism. Meanwhile, the new strong C=O stretching vibrations at 1726-1712 cm⁻¹ were assigned to the acetoxy moieties of diacetoxyboron complexes. The strong absorption bands at 1372–1368 cm⁻¹ and 1055–1039 cm⁻¹ were attributed to the B–O stretching vibrations [23, 25] and the strong C–O stretching vibrations at 1274–1258 cm⁻¹ were due to the acetoxy moieties. Obviously, the curcumin derivatives have no strong absorption bands in these ranges. In ¹H NMR spectra of the diacetoxyboron complexes (1b–5b), the enolic proton signals at $\delta = 16.10-15.86$ ppm disappeared completely and the new methyl proton signals of the acetoxy moieties at $\delta =$ 2.18–2.10 ppm were observed in comparison with the curcumin derivatives. The methylene proton signals at $\delta = 6.39-6.07$ ppm of the keto-enol tautomerism were shifted 0.37–0.43 ppm to lower field with respect to the corresponding curcumin derivatives [23,24], which was due to the strong coordination of the $B(OAc)_2$ fragments. However, other chemical proton signals have no significant changes.

3.2. UV-vis absorption properties

These diacetoxyboron complexes were the D–A–D electronic structure dyes, which possessed electron donor groups at both ends of the conjugated π –system with an electron acceptor group in the middle of the molecules. They exhibited high absorption coefficients at 400–550 nm (Fig. 1 and Table 1) in dichloromethane solution (1.0 ×10⁻⁵ mol L⁻¹), which were very suitable for photosensitizer and fluorescent dyes. From Fig. 1, it was observed that these diacetoxyboron complexes displayed the weaker absorption peaks at 240–280 nm, which were corresponding to

the terminal aromatic moieties, and the stronger absorption peaks at 424–474 nm with a shoulder at 450–502 nm except complex **4b**, which were due to π – π * transition of the conjugated B(OAc)₂-chelating system. As can also be seen, the electron donating abilities of the terminal aromatic moieties have a great influence on the spectroscopic behavior of these diacetoxyboron complexes. For instance, the maximum absorption wavelength of complexes **3b**, **4b** and **5b** revealed a considerable bathochromic shift (> 50 nm) in comparison with that of the complex **1b**, which was assignable to the introduction of the strong electron-donating methoxyl moiety or the large π -conjugated aromatic moieties. Meanwhile, these diacetoxyboron complexes (**1b–5b**) showed the much higher extinction coefficients (loge_{max} = 4.51–4.70).

<Figure 1>

<Table 1>

3.3. Fluorescence properties

The fluorescence behaviors of diacetoxyboron complexes (**1b–5b**) were determined in dichloromethane solution ($1.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$). Their fluorescence spectra are presented in Fig. 2 and the fluorescence data are listed in Table 1. From Fig. 2A, their excitation spectra showed a broad band at 350–500 nm, which were similar to their UV-vis absorption spectra, but excitation band of complexes **3b** was much broader and more intensive in these diacetoxyboron complexes. From Fig. 2B, their emission

spectra displayed the strong fluorescence ranging from blue to yellow-green at 473–554 nm in dichloromethane solution. The terminal aromatic moieties of these complexes exhibited a significant impact on their fluorescence behaviors. Compared to complex 1b, the emission bands of complexes 3b, 4b and 5b showed the much larger bathochromic shift (62-81 nm), which were due to the stronger electron-donating or the larger π -conjugated terminal aromatic moieties in the $B(OAc)_2$ -chelating system. Especially, the diacetoxyboron complex **3b** exhibited the strongest emission intensity in these complexes, which was in agreement with its excitation spectra. Furthermore, the quantum yields (Φ_u) of these diacetoxyboron complexes were also measured relative to quinine sulfate ($\Phi_s = 0.55$). From Table 2, it can be pointed out that these complexes had high quantum yields ($\Phi_u = 0.45 - 0.92$) in dichloromethane solution, especially the complex 3b exhibited the highest quantum efficiency ($\Phi_u = 0.92$) in these complexes, which was probably due to the introduction of the strong electron donor methoxyl in the terminal aromatic moieties. Meanwhile, the fluorescence lifetimes (τ) of complexes **1b–5b** in dichloromethane solution were studied by time-resolved fluorescence spectroscopy. Their fluorescence decays were fitted to a monoexponential function (Fig. 3) and the data were presented in Table 1. It was found that the complex 4b had much longer lifetime values ($\tau =$ 5.99 ns) in dichloromethane among these complexes, which was probably due to the introduction of the rigid naphthalene ring in the conjugated system. However, the complex 2b exhibited much shorter lifetime values ($\tau = 1.26$ ns) in these complexes, mainly assigned to the methyl moieties containing high-energy oscillator C–H groups

in the conjugated system, which led to an increase in the non-radiative decay.

<Figure 2>

< Figure 3>

The fluorescence behaviors of diacetoxyboron complexes (1b-5b) were also investigated in solid state at room temperature (Fig. 4 and Table 2). The excitation spectra of these complexes were much broader than in solution and red-shifted remarkably, which was attributed to the aggregation effect in solid state. Their emission spectra showed that these complexes emitted a yellow to red emission at 535-643 nm, which were red-shifted 62-94 nm in comparison with those of the corresponding complexes in dichloromethane solution. Meanwhile, the Stokes shifts of complexes (1b–5b) in solid state were much larger than in solution. For example, the complex 3b bore a Stokes shift of 115 nm. These fluorescence properties could probably be assigned to their molecular conformation and intermolecular interactions in solid state [26,27]. From Fig. 3B, the complex 3b revealed the strongest emission intensity and largest Stokes shift in solid state. However, the complex 5b exhibited the negligible emission intensities in solid state, which was much weaker than that recorded in solution. It was probably because of the consecutive and strong intermolecular $\pi - \pi$ interactions between neighbouring dye molecules resulting in fluorescence quenching in solid state [28]. In addition, the CIE color coordinates of

complexes **1b–5b** in solid state was determined from their emission spectra (Fig. 5 and Table 2). The results showed that the chromaticity coordinate for the complex **3b** was CIE (x = 0.641, y = 0.358), which was very close to the ideal red CIE (x = 0.64, y = 0.34) [29]. It indicated that the diacetoxyboron complex **3b** was promising for applications in optoelectronic materials.

<Figure 4>

<Figure 5>

<Table 2>

3.4. Solvatochromic effect

The effect of the solvent on UV-vis absorption and fluorescence behaviors of diacetoxyboron complexes (1b–5b) was investigated at room temperature. The UV-vis absorption and fluorescence spectra of these complexes in seven different solvents (such as toluene, tetrahydrofuran, chloroform, dichloromethane, acetone, acetonitrile and dimethyl sulfoxide) were shown in Figs. 6 and S1–S4. The changes in their photophysical properties depending on solvent polarity were listed in Table 3. From Table 3, the type of these solvents had a negligible effect on the UV-vis absorption behaviors of these diacetoxyboron complexes, which indicated a small difference in the dipole moments between the Franck–Condon excited state and the

ground state [30]. In contrast to UV-vis absorption spectra, these complexes showed a pronounced positive emission solvatochromism. The normalized fluorescence spectra of diacetoxyboron complexes in various solvents were shown in Figs. 7A and S5–S8. It was found that their fluorescence maxima caused a remarkable bathochromic shift (10–45 nm) and the Stokes shift values (562–1329 cm^{-1}) were significantly enlarged with the increase in solvent polarity. For instance, the complex 3b exhibited a large red-shift of 38 nm in emission peaks from 510 nm in low-polar toluene to 548 nm in high-polar DMSO. A notable change from green to yellow could obviously be observed when the solutions of the complex 3b were placed under 365 nm UV illumination (Fig. 7B). These data suggested that the energy of the excited state was more influenced by increasing the solvent polarity in comparison with the energy of the ground state [31]. It also revealed that there was a significant difference between the excited and ground state charge distribution in these diacetoxyboron molecules, which was due to the stronger intermolecular interaction with polar solvents in the excited state [32]. The fluorescence quantum yields of diacetoxyboron complexes (1b–5b) in seven different solvents were also determined using quinine sulfate ($\Phi_s =$ 0.55) as standard and presented in Table 3. It was found that these complexes exhibited the much higher quantum yields in toluene, which meant that the diacetoxyboron complexes were strong emissive in non-polar solvents and their quantum yields were decreased with the increase of the solvent polarity. This was because that the radiative decay process was decreased with increasing the solvent polarity [9]. In addition, the fluorescence decay behaviors of complexes 1b–5b were

measured using time-resolved fluorescence spectroscopy in seven different solvents (Figs. 8 and S9–S12) and lifetime values (τ) were summarized in Table 3. The results showed that all the fluorescence decays of diacetoxyboron complexes in solutions were well-fitted with a monoexponential function at their emission peak wavelength and their lifetime values (τ) also changed depending on solvent polarity. From Table 3, the fluorescence lifetimes (τ) of these complexes displayed a downward trend as a whole with the increase of the solvent polarity, which could be explained by the increase of the non-radiative decay in polar solvent resulted from these processes such as quenching, energy transfer, and solvent-solute interaction.



In order to gain further insight on solvatochromic behaviors of these diacetoxyboron complexes, the correlation of the Stokes shift value ($\Delta v = v_{abs} - v_{flu}$) with the solvent polarity parameter ($E_T(30)$) was investigated (the solvent parameters are in Table S1). We plotted the fluorescence Stokes shift to the solvent $E_T(30)$

parameter in Figs. 9 and S13–S17. Their linear variations were obtained and the plots were linear with correlation coefficients r = 0.94-0.97. The linear relationship of their plots implied that the dipole–dipole interaction between the solute and solvent was responsible for the larger solvent-dependent fluorescence shift in diacetoxyboron complexes.

<Figure 9>

According to the Lippert–Mataga equation (Eq.1) [33], the difference in dipole moments between the excited and ground states ($\Delta \mu$) can be calculated from the slope of a plot of the Stokes shift (Δv) versus Δf :

$$\Delta v = v_{abs} - v_{flu} = \frac{2\Delta\mu^2}{hca^3}\Delta f + \text{constant}$$
(1)

where Δv is the Stokes shift in wavenumber (cm⁻¹), v_{abs} and v_{flu} are the wavenumbers of the absorption and fluorescence maxima, respectively, *h* is the Planck's constant, *c* is the velocity of light, *a* is the cavity radius, and Δf is the orientation polarizability of the solvent, defined as follows (Eq. 2):

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$
(2)

Where ε is the solvent dielectric constant and *n* is the solvent refractive index. The Lippert–Mataga plots of diacetoxyboron complexes (**1b–5b**) in different solvents were shown in Figs. 10 and S18–S22. It was observed that these plots revealed the better linearity with correlation coefficients r = 0.94-0.96. The positive slope

indicated the dipole moments of these complexes in the excited state were larger than the corresponding dipole moments in the ground state [34]. Additionally, the dipole moment difference between the ground and excited states ($\Delta\mu$) of complexes (**1b–5b**) can be estimated by the slope of these lines from the Lippert–Mataga equation. The cavity radii (*a*) of complexes **1b–5b** were calculated as 5.43, 5.56, 5.69, 5.85 and 5.66 Å, respectively, by using Eq. (3) [35].

$$a = \left(\frac{3M}{4N\pi d}\right)^{1/3} \tag{3}$$

where *M* is the molecular weight of the solute, *N* is the Avogadro constant, and *d* is an assumed molecular density of 1g/cm³. The estimated dipole moment differences $(\Delta \mu)$ were 17.15, 18.12, 23.21, 29.30 and 23.41 D (debye) for complexes **1b–5b**, respectively. These large dipole moment differences suggested the occurrence of intramolecular charge-transfer induced by the solvent after excitation [36]. Especially, complexes **3b–5b** exhibited the higher $\Delta \mu$ values, indicating a stronger increase in the excited state dipole moment and a more noticeable fluorescence solvatochromic effects.

<Figure 10>

3.5. Electrochemical properties

Electrochemical behaviors of diacetoxyboron complexes **1b–5b** were determined by cyclic voltammetry (CV) in CH₂Cl₂ solutions ($5.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$) using the ferrocenium/ferrocene (Fc⁺/Fc) couple as the reference potential standard

(Fig. 11), and electrochemical data were summarized in Table 4. These complexes all exhibited the irreversible oxidation ($E_{ox}^{onset} = +1.11, +1.01, +0.81, +1.13, +1.16$ V vs. Fc⁺/Fc for complexes **1b–5b**, respectively) and reduction process ($E_{\rm red}^{\rm onset} = -0.93$, -0.96, -1.14, -1.10, -0.95 V vs. Fc⁺/Fc for complexes **1b**-**5b**, respectively) in the cyclic voltammograms. It was found that complex **1b** displayed the smaller oxidation and reduction potentials in these complexes, which was due to the electron-donating methoxy substituents in the conjugated B(OAc)2-chelating unit. From the onset potentials of the oxidation and reduction potentials, the HOMO and LUMO energy levels can be estimated from the empirical formula [37] : E_{HOMO} (eV) = $-(E_{\text{ox}}^{\text{onset}} +$ 4.8) and E_{LUMO} (eV) = $-(E_{\text{red}}^{\text{onset}} + 4.8)$. The obtained HOMO energy levels were -5.91, -5.81, -5.61, -5.93, -5.96 eV for complexes 1b-5b, respectively, and the LUMO energy levels were -3.87, -3.84, -3.66, -3.70, -3.85 eV for complexes 1b-5b, respectively (Table 4). The electrochemical HOMO-LUMO gaps can be obtained from the formula: $E_{gap} = E_{LUMO} - E_{HOMO}$, and the $E_g^{electrochem}$ of complexes **1b–5b** were 2.04, 1.97, 1.95, 2.23, 2.11 eV, respectively (Table 4). It was observed that the HOMO-LUMO gaps of complexes 2b and 3b were smaller in these complexes, which was probably due to the introduction of the electron donor moieties in the conjugated system [38]. Meanwhile, the optical band gaps of these complexes can also be calculated using Tauc relation [39] from the UV-vis absorption spectra (Table 4). Their values of E_g^{opt} were 2.67, 2.58, 2.43, 2.38, 2.36 eV for complexes 1b–5b, respectively, which was in agreement with their electrochemical band gaps.

<Figure 11>

<Table 4>

4 Conclusions

In conclusion, several novel diacetoxyboron complexes of β -diketones incorporated curcumin moiety were synthesized and characterized by FTIR, ¹H NMR, MS and elemental analysis. Their photophysical properties were studied by UV-vis absorption and fluorescence spectroscopy in detail. It was found that their fluorescence spectra yielded a blue to yellow-green emission at 473-554 nm in dichloromethane solution and emitted a yellow to red emission at 535-643 nm in solid state. The terminal aromatic moieties of these complexes exhibited a significant impact on their fluorescence behaviors. Especially, the complex 3b displayed the strongest emission intensity and the highest quantum efficiency ($\Phi_u = 0.98$) in toluene among these complexes. The CIE coordinate of the complex 3b [CIExy (0.641, 0.358)] in solid state was positioned in an ideal red region of the chromaticity diagram. Meanwhile, the effect of different solvents on absorption and fluorescence properties of these complexes was also studied and the solvent dependence of their spectral behaviors was discussed by using the solvent polarity parameter approach and Lippert-Mataga plot. The results showed that these complexes exhibited a pronounced positive fluorescence solvatochromism and the large dipole moment

differences between the ground and excited states. It implied a strong increase in the excited state dipole moment and the charge-transfer character of the excited state. In addition, the HOMO, LUMO energy levels and energy band gaps of these complexes were calculated according to the onset oxidation and reduction potentials of the cyclic voltammograms. These results indicated that these D–A–D electronic structure boron complexes might be used as excellent photoelectric functional materials and fluorescent molecular probes.

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Tables:

Table 1

Photophysical data of diacetoxyboron complexes 1b–5b in dichloromethane solution.

Complexes	λ_{max} (nm)	$\log\epsilon_{max}$	λ_{ex} (nm)	λ_{em} (nm)	au (ns)	$arPsi_{ m u}$	$\Delta v_{stokes} (cm^{-1})$
1b	424, 450(sh)	4.51	428	473	3.63	0.67	2443
2b	440, 466(sh)	4.64	442	492	1.26	0.56	2402
3b	464, 490(sh)	4.66	468	535	2.63	0.92	2860
4b	472	4.65	470	554	5.99	0.64	3136
5b	474, 502(sh)	4.70	478	545	1.84	0.45	2748

Table 2

Photophysical data for diacetoxyboron complexes 1b–5b in solid state.

Complexes	$\lambda_{\rm ex}$ (nm)	λ_{em} (nm)	$\Delta\lambda_{stokes} \ (cm^{-1})$	CIE_x	CIE _y
1b	473	535	2450	0.366	0.602
2b	482	566	3079	0.492	0.502
3 b	513	628	3570	0.641	0.358
4 b	537	643	3070	0.661	0.338
5b	550	639	2532	0.599	0.397

Table 3

Spectroscopic and photophysical properties of complexes 1b–5b in various solvents.

Complexes	Solvents	λ_{max} (nm)	$\log \epsilon_{max}$	λ_{em} (nm)	$\Delta v_{\text{stokes}} (\text{cm}^{-1})$	au (ns)	$arPsi_{ m u}$
1b	Toluene	424	4.61	466	2126	3.58	0.72
	THF	422	4.56	468	2329	3.49	0.73
	CHCl ₃	426	4.54	472	2288	3.60	0.66
	CH_2Cl_2	424	4.51	473	2443	3.63	0.67
	Acetone	422	4.61	473	2555	3.43	0.57
	CH ₃ CN	422	4.55	476	2688	3.24	0.64
	DMSO	428	4.68	480	2531	3.13	0.52
2 h	Toluene	136	1 58	/81	2146	1 3/	0.88
20	THE	430 /3/	4.50 1.61	-01 /18/	2380	1.34	0.88
	CHCL	440	4.0 4 1.59	/01	2360	1.52	0.75
		0 ///0	4.57 1.61	402	2300	1.25	0.05
		43A	4.61	489	2592	1.20	0.50
	CH ₂ CN	434	4 66	493	2352	1.17	0.50
	DMSO	442	4.69	499	2584	1.23	0.55
	Diffe	1.2	1.05		2301	1.27	0.01
3 b	Toluene	456	4.72	510	2322	2.45	0.98
	THF	456	4.69	518	2625	2.38	0.95
	CHCl ₃	464	4.64	529	2648	2.52	0.91
	CH_2Cl_2	464	4.66	535	2860	2.63	0.92
	Acetone	458	4.70	531	3002	2.29	0.88
	CH ₃ CN	462	4.69	541	3161	2.09	0.85
	DMSO	468	4.74	548	3120	2.26	0.83
4h	Toluene	468	4 56	529	2464	5 13	0.84
40	THE	464	4 54	539	2999	5 75	0.01
	CHCh	474	4 60	551	2948	5 73	0.73
	CH ₂ Cl ₂	472	4 65	554	3136	5 99	0.75
	Acetone	464	4.59	553	3469	4.67	0.58
	CH ₂ CN	468	4.58	569	3793	4.50	0.43
	DMSO	478	4.62	574	3499	4.24	0.38
5h	Tohumo	470	4 70	522	2156	2 57	0.74
30		470	4.70	525	2130	2.37	0.74
		400 171	4.07 170	5/2	2333	2.30 1.02	0.01
		4/4 171	4.70 170	545 575	2001	1.75	0.47
	$\Delta cetone$	4/4 /68	4.70 176	545 577	∠/40 2085	1.04	0.45
	CH.CN	400 /77	4.70 177	550	2905	1.//	0.41
		+12 178	+.// /\Q1	558	3003	2 03	0.33
	DNDO	4/0	4.01	550	3000	2.05	0.30

Complexes	$E_{\rm ox}^{\rm onset}(V)$	$E_{\rm red}^{\rm onset}$ (V)	HOMO(eV)	LUMO(eV)	$E_{\rm g}^{\rm electrochem}$ (eV)	$E_{\rm g}^{\rm opt}$ (eV)
1b	+1.11	-0.93	-5.91	-3.87	2.04	2.67
2b	+1.01	-0.96	-5.81	-3.84	1.97	2.58
3b	+0.81	-1.14	-5.61	-3.66	1.95	2.43
4 b	+1.13	-1.10	-5.93	-3.70	2.23	2.38
5b	+1.16	-0.95	-5.96	-3.85	2.11	2.36

Table 4 Electrochemical properties of diacetoxyboron complexes 1b–5b.

Schemes:



Scheme 1 Synthesis of diacetoxyboron complexes 1b–5b

Figure Captions:

Fig. 1 UV-vis spectra for diacetoxyboron complexes (1b–5b) in dichloromethane solution $(1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1})$.

Fig. 2 The excitation (A) and emission (B) spectra for diacetoxyboron complexes (1b–5b) in dichloromethane solution $(1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1})$.

Fig. 3 Fluorescence lifetime decay for complexes 1b–5b in dichloromethane (1.0 × 10^{-5} mol·L⁻¹), monitored at 473, 492, 535, 554 and 545 nm, respectively.

Fig. 4 The excitation (A) and emission (B) spectra for diacetoxyboron complexes (**1b–5b**) in solid state at room temperature.

Fig. 5 The CIE chromaticity diagram of diacetoxyboron complexes 1b–5b in solid state.

Fig. 6 The absorption (A) and emission (B) spectra for diacetoxyboron complex **3b** in different solvents $(1.0 \times 10^{-5} \text{ mol·L}^{-1})$.

Fig. 7 Normalized emission spectra (A) in different solvents $(1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1})$ and photographs under 365 nm UV illumination (B) for diacetoxyboron complex **3b**.

Fig. 8 Fluorescence lifetime decay for complex **3b** in different solvents $(1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1})$, monitored at 510, 518, 529, 535, 531, 541 and 548 nm, respectively.

Fig. 9 The plots of Stokes shift versus the solvent polarity parameter $E_T(30)$ of diacetoxyboron complexes 1b–5b.

Fig. 10 The plots of Stokes shift versus the orientation polarizability function (Δf) of diacetoxyboron complexes **1b–5b**.

Fig. 11 Cyclic voltammograms of diacetoxyboron complexes 1b-5b in

dichloromethane $(5.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1})$.

Figures:

Fig.1



Fig. 3



Fig. 5













Fig.9



Fig. 10



Fig. 11



Graphical Abstract



Highlights

- ► Synthesis of diacetoxyboron complexes with curcumin derivatives.
- ▶ Photophysical behaviors of diacetoxyboron complexes in solution and solid state.
- Solvatochromic effect for diacetoxyboron complexes in different solvents.
- Electrochemical behaviors for diacetoxyboron complexes.







Figure 3













Figure 9



Figure 10



Figure 11