

# Synthesis, Crystal Structure and Photoluminescence of a Cyclometalated Iridium(III) Coumarin Complex

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**Abstract** In this paper a new cyclometalated iridium(III) coumarin complex, Ir(III)bis(3-(2-benzothiazolyl)coumarinato N, C<sup>4</sup>)(acetylacetonate) (Ir(L)<sub>2</sub>(acac)), was synthesized and characterized. X-ray crystallography demonstrated that the iridium(III) ion is hexacoordinated by two C atoms and two N atoms from 3-(2-benzothiazolyl)coumarinato ligands and two O atoms from acac ligand, displaying distorted octahedral coordination geometry. The Ir(L)<sub>2</sub>(acac) complex has good thermal stability with less than 2 % weight-reduction occurring at 300 °C, and exhibits strong reddish orange emission. The results shown that Ir(L)<sub>2</sub>(acac) is useful for fabrication organic light-emitting diodes.

**Keywords** Iridium(III) complex · Coumarin derivative · Crystal structure · Photoluminescence

## Introduction

Research on organic light-emitting diodes (OLEDs) has attracted tremendous interest in the last two decades due to their potential applications in low-cost, full-color, flat-panel displays and portable electronic devices [1–4]. Phosphorescent organic light-emitting devices (PhOLEDs) based on transition metal complexes have attracted considerable attentions because they can harvest singlet and triplet excitons, enabling internal quantum efficiencies approaching

100 % [5–7]. Of these transition metal complexes, cyclometalated iridium complexes are particularly important due to their relatively short excited-state lifetime, high photoluminescence efficiencies and excellent color tuning [8–12]. The color of the emission from cyclometalated Ir(III) complexes can be tuned through the design and synthesis of novel cyclometalating ligands [11, 13]. Increasing the  $\pi$ -conjugation length or introducing fused heteroaromatic rings into the cyclometalating ligand caused a red shift in the emission [14, 15], whereas lowering the highest occupied molecular orbital (HOMO) by adding an the electron-withdrawing group or raising the triplet state energy by use of a ligand with a strong ligand strength resulted in a blue shift in the emission [16, 17].

Coumarin derivatives have super thermal stability and outstanding optical properties including an extended spectral response, high quantum yields, superior photostability, which are commonly used as efficient laser dyes fluorescing in the blue-green spectral region [18, 19]. Coumarin derivatives can realize easy tuning of energy gaps of the corresponding Ir(III) complexes due to the synthetic possibilities of a large variety of coumarin derivatives, the class of coumarin ligands could be a promising candidate for the preparation of iridium(III) complexes for a variety of photonic applications, such as optical sensing technology [20, 21] and OLED technology [22–24]. Cyclometalated iridium(III) coumarin complexes represent new type of phosphorescence materials for organic lighting emitting diodes (OLEDs), which possess efficient visible absorption, higher quantum yields and higher brightnesses.

In recent years, we have been interested in the synthesis and photoluminescent and electroluminescent study of some new coumarin derivatives [25–27] and some coumarin-based iridium(III) complexes [28, 29]. In this work, a new cyclometalated iridium(III) coumarin complex, Ir(III) bis(3-(2-benzothiazolyl)coumarinato N,C<sup>4</sup>)(acetylacetonate)

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(Ir(L)<sub>2</sub>(acac)), was synthesized and characterized. The X-ray crystal structure, the UV–vis absorption and luminescent properties and the thermal stability of Ir(L)<sub>2</sub>(acac) were also investigated.

## Experimental

### Materials and Methods

Salicylaldehyde, *o*-aminothiophenol, ethyl cyanoacetate and benzoic acid were purchased from AstaTech (Chengdu) Pharmaceutical Co., Ltd. (China). IrCl<sub>3</sub>·nH<sub>2</sub>O (iridium content > 60.0 %) was bought from Shanxi Kaida Chemical Co. Ltd. (China) and used without further purification. Acetylacetone was purchased from Shanghai Jingchun Reagent Co. Ltd. (China). All other chemicals were analytical grade reagent.

IR spectra (400 – 4,000 cm<sup>-1</sup>) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. <sup>1</sup>H NMR spectra were obtained on Unity Varian-500 MHz. C, H, and N analyses were obtained using an Elemental Vario-EL automatic elemental analysis instrument. Melting points were determined on an X-4 microscopic melting point apparatus (Beijing Taike Instrument Limited Company). UV–vis absorption and photoluminescent spectra were recorded on a Shimadzu UV-2550 spectrometer and on a Perkin-Elmer LS-55 spectrometer, respectively. The thermogravimetry analysis ((TGA) was recorded on a Shimadzu DT-40 thermal analysis instrument.

### Synthesis and Characterization of Ir(III) Complex (Ir(L)<sub>2</sub>(acac))

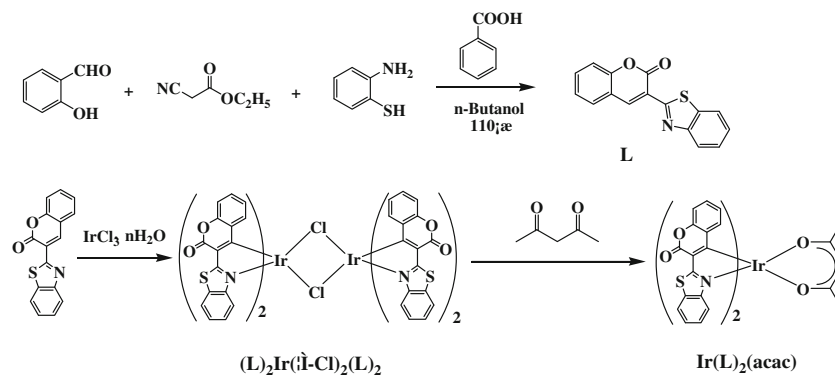
The synthetic routes were shown in Scheme 1.

*3-(benzothiazol-2-yl)coumarin (L)* Under nitrogen atmosphere, a mixture of salicylaldehyde (2.93 g, 24 mmol), ethyl cyanoacetate (2.72 g, 24 mmol), *o*-aminothiophenol (3.00 g, 24 mmol) and benzoic acid (1.465 g, 12 mmol) was

dissolved in 1-butanol (50 mL). The mixture solution was refluxed for 24 h. After the reaction mixture was cooled to room temperature, the yellow solid was filtered, and washed with water. Monitoring by TLC, a large amount of blue fluorescent product and a less amount of green fluorescent product appeared in TLC. The crude was purified by chromatography on silica gel using ethyl acetate/petroleum ether (1:8, v/v) as the eluent to obtain the blue fluorescent product. Yield 58 %; m.p.: 213–215 °C (Lit: 216–217 °C) [30]. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 9.09 (s, 1H), 8.11 (d, *J*=8.0 Hz, 1H), 7.98 (d, *J*=8.0 Hz, 1H), 7.74 (dd, *J*=8.0 Hz, *J*=2.4 Hz, 1H), 7.66 (td, *J*=8.0 Hz, *J*=1.4 Hz, 1H), 7.54 (td, *J*=8.0 Hz, *J*=1.4 Hz, 1H), 7.46–7.38 (m, 3H). IR (KBr, cm<sup>-1</sup>): 3048, 1716 (C = O), 1607, 1557 (C = N). Anal. Calcd. For C<sub>16</sub>H<sub>9</sub>NO<sub>2</sub>S: C, 68.80, H, 3.25, N, 5.01. Found: 68.85, H, 3.22, N, 5.04.

*Ir(L)<sub>2</sub>(acac)* The cyclometalated Ir (III) μ-chloro-bridged dimer of (L)<sub>2</sub>Ir(μ-Cl)<sub>2</sub>Ir(L)<sub>2</sub> was synthesized by refluxing IrCl<sub>3</sub>·nH<sub>2</sub>O (1.00 g, 3.12 mmol) with 2.5 equiv. of 3-(benzothiazol-2-yl)coumarin (2.179 g, 7.80 mmol) in a 3:1 mixture of 2-ethoxyethanol and water (30 mL) under nitrogen at 135 °C for 24 h. The mixture was cooled to room temperature, and 100 mL of water was added. The rufous precipitate was collected by filtration, and washed twice with water and then methanol/water mixture (1:2, v/v). The solid was pumped dry to give the crude (L)<sub>2</sub>Ir(μ-Cl)<sub>2</sub>Ir(L)<sub>2</sub>. The crude dimer was directly used for subsequent preparation of Ir(L)<sub>2</sub>(acac). The chloro-bridged dimer (0.4 g, 0.255 mmol), acetylacetone (0.230 g, 2.297 mmol) and sodium carbonate (0.244 g, 2.297 mmol) were refluxed in dichloroethane under nitrogen atmosphere for 12 h. After cooling, a small quantity of water was added. The mixture was extracted with dichloromethane (50 mL × 3). The organic phase was washed with water (2 × 50 mL) and dried over anhydrous MgSO<sub>4</sub>. After filtering, the filtrate was evaporated to dryness under reduced pressure. The crude was purified by chromatography on silica gel using ethyl acetate/petroleum ether (1:6, v/v) as the eluent to give red powdery Ir(L)<sub>2</sub>(acac) in 65.5 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.96 (d, 2H, *J*=7.6 Hz, Aryl-H), 7.57 (d, 2H, *J*=8.8 Hz,

**Scheme 1** Synthetic routes to the ligand L and iridium(III) complex Ir(L)<sub>2</sub>(acac)



Aryl-H), 7.40 (t, 2H,  $J=7.2$  Hz, Aryl-H), 7.28–7.20 (m, 6H, Aryl-H), 6.55 (t, 2H,  $J=6.8$  Hz, Aryl-H), 6.22 (d, 2H,  $J=8.4$  Hz, Aryl-H), 5.30 (s, 1H,  $-\text{CH}=\text{C}-$ ), 1.69 (s, 6H,  $-\text{CH}_3$ ). Anal. Calcd. For  $\text{C}_{37}\text{H}_{23}\text{N}_2\text{O}_6\text{S}_2\text{Ir}$ : C, 52.41, H, 2.73, N, 3.30. Found: 52.73, H, 2.80, N, 3.26.

### Crystallography

Suitable single crystal of the complex was obtained by slow evaporation of the chloroform solution at room temperature. The diffraction data were collected with a Bruker Smart Apex CCD area detector with graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda=0.71073$  Å) at 295(2) K. The structure was solved by using the program SHELXL and Fourier difference techniques, and refined by full-matrix least-squares method on  $F^2$ . All hydrogen atoms were added theoretically. The crystal and experimental data of  $\text{Ir}(\text{L})_2(\text{acac})$  are shown in Table 1. The selected bond lengths and bond angles of  $\text{Ir}(\text{L})_2(\text{acac})$  are listed in Table 2.

### Quantum Chemical Calculation

The structure of the complex  $\text{Ir}(\text{L})_2(\text{acac})$  was optimized by density functional theory (DFT) using a B3LYP/6-31 G(d)

**Table 1** Crystallographic and experimental data for  $\text{Ir}(\text{L})_2(\text{acac})\cdot\text{CHCl}_3$

Empirical formula	$\text{C}_{38}\text{H}_{24}\text{Cl}_3\text{IrN}_2\text{O}_6\text{S}_2$
Formula weight	967.26
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	$a=9.2606(4)$ Å $\alpha=85.5540(10)^\circ$ $b=13.2592(6)$ Å $\beta=75.5800(10)^\circ$ $c=15.0875(7)$ Å $\gamma=88.1350(10)^\circ$
Volume (Å <sup>3</sup> ), Z	1788.64(14), 2
Calculated density (g/cm <sup>3</sup> )	1.796
Absorption coefficient (mm <sup>-1</sup> )	4.124
F(000)	948
Crystal size (mm)	0.29 × 0.21 × 0.13
$\theta$ range for data collection (°)	1.54 to 26.02
Limiting indices	$-10 \leq h \leq 11$ , $-16 \leq k \leq 16$ , $-18 \leq l \leq 16$
Reflections collected/unique	9703/6880 ( $R_{\text{int}}=0.0141$ )
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6162 and 0.3809
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	6880/0/471
Goodness-of-fit on $F^2$	1.025
Final R indices [ $I > 2\sigma(I)$ ]	$R_1=0.0322$ , $wR_2=0.0811$
R indices (all data)	$R_1=0.0353$ , $wR_2=0.0832$
Largest diff. peak and hole (e <sup>Å</sup> <sup>-3</sup> )	2.678 and $-1.744$

**Table 2** Selected bond distances (Å) and angles (°) for  $\text{Ir}(\text{L})_2(\text{acac})$ .

Bond distances (Å)			
Ir(1)–C(16)	1.987(4)	Ir(1)–C(32)	1.999(4)
Ir(1)–N(1)	2.048(4)	Ir(1)–N(2)	2.057(4)
Ir(1)–O(5)	2.110(3)	Ir(1)–O(6)	2.111(3)
Angles (°)			
C(16)–Ir(1)–C(32)	98.68(17)	C(16)–Ir(1)–N(1)	80.43(16)
C(16)–Ir(1)–N(2)	100.71(16)	C(16)–Ir(1)–O(6)	85.52(15)
C(16)–Ir(1)–O(5)	172.18(14)	C(32)–Ir(1)–N(1)	101.53(16)
C(32)–Ir(1)–N(2)	80.56(17)	C(32)–Ir(1)–O(6)	174.24(15)
C(32)–Ir(1)–O(5)	87.50(15)	N(1)–Ir(1)–N(2)	177.49(14)
N(1)–Ir(1)–O(5)	93.71(13)	N(1)–Ir(1)–O(6)	83.01(13)
N(2)–Ir(1)–O(5)	84.96(13)	N(2)–Ir(1)–O(6)	94.82(14)
O(5)–Ir(1)–O(6)	88.66(13)		

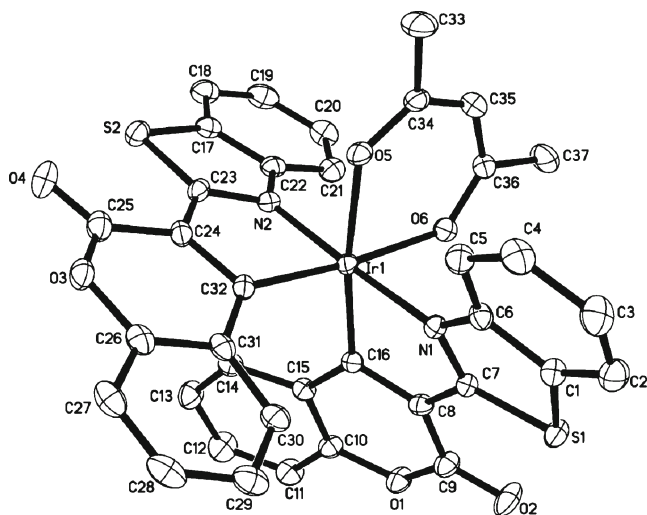
basis set. The structural energy of the complex  $\text{Ir}(\text{L})_2(\text{acac})$  was calculated at B3LYP/6-31 G(d) levels. The structure optimization and energy calculations were performed with the GAUSSIAN 98 program.

## Results and Discussion

### X-ray Crystal Structure of $\text{Ir}(\text{L})_2(\text{acac})$

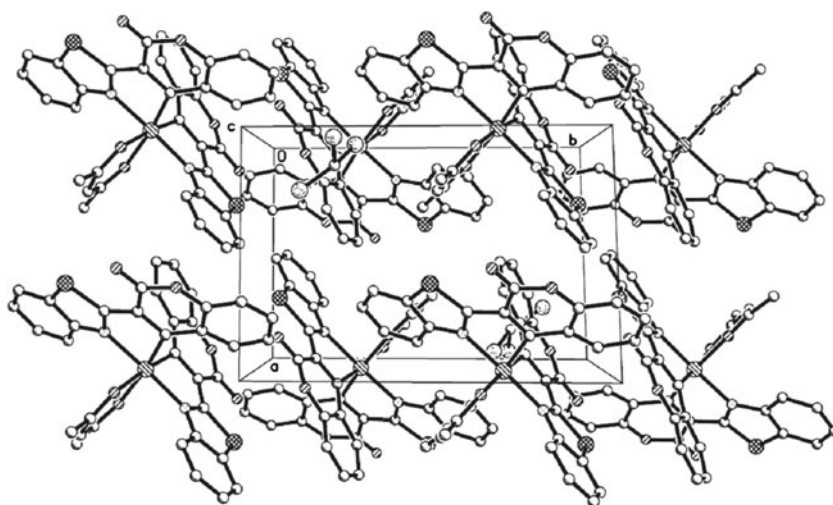
The crystal structure and packing diagram of  $\text{Ir}(\text{L})_2(\text{acac})$  are given in Figs. 1 and 2, respectively.

The structure of  $\text{Ir}(\text{L})_2(\text{acac})$  was measured by X-ray crystallography. The crystal structure of  $\text{Ir}(\text{L})_2(\text{acac})$  consists of one  $\text{Ir}(\text{L})_2(\text{acac})$  molecule and one crystallizing  $\text{CHCl}_3$  molecule. So the crystal structural formula of  $\text{Ir}(\text{L})_2(\text{acac})$  was described as  $\text{Ir}(\text{L})_2(\text{acac})\cdot\text{CHCl}_3$ . The



**Fig. 1** Crystal structure of  $\text{Ir}(\text{L})_2(\text{acac})$ . Hydrogen atoms and solvent molecule are removed for clarity

**Fig. 2** Packing diagram of  $\text{Ir(L)}_2(\text{acac})$  along  $b$ -axis.. Hydrogen atoms and solvent molecule are removed for clarity



crystal of  $\text{Ir(L)}_2(\text{acac})$  belongs to the triclinic space group P-1,  $a=9.2606(4)$  Å,  $b=13.2592(6)$  Å,  $c=15.0875(7)$  Å,  $\alpha=85.5540(10)^\circ$ ,  $\beta=75.5800(10)^\circ$ ,  $\gamma=88.1350(10)^\circ$ ,  $U=1788.64(14)$  Å<sup>3</sup>,  $Z=2$ ,  $D_c=1.796$  g/cm<sup>3</sup>,  $\mu=4.124$  mm<sup>-1</sup>.

As shown in Fig. 1, it is shown that the iridium(III) in  $\text{Ir(L)}_2(\text{acac})$  is hexacoordinated by two C atoms and two N atoms from 3-(benzothiazol-2-yl)coumarin ligands and two O atoms from acetylacetonate ligand, displaying a distorted octahedral coordination geometry. Two C atoms and two N atoms from 3-(benzothiazol-2-yl)coumarin ligands exhibit *cis*-C-C and *trans*-N,N chelate mode, and two O atoms from acetylacetonate ligand locate *cis*-O-O chelate disposition. The Ir-C bonds (1.987(4) and 1.999(4) Å) are shorter than the Ir-N bonds (2.048(4) and 2.057(4) Å). Two Ir-O bonds are nearly equal, they are 2.110(3) and 2.111(3) Å, respectively, indicating that the delocalized  $\pi$  bond formed when acetylacetonate ligand coordinated to Ir atom. And the Ir-O bonds are shorter than those of (ppy)Ir(acac) (2.146(4) Å) and (tpy)Ir(acac) (2.161(4) Å) [31]. In addition, the benzothiazolyl rings are not coplanar with the coumarin rings in two 3-(benzothiazol-2-yl)coumarin ligands, the dihedral angles are 14.06° and 18.05°, respectively.

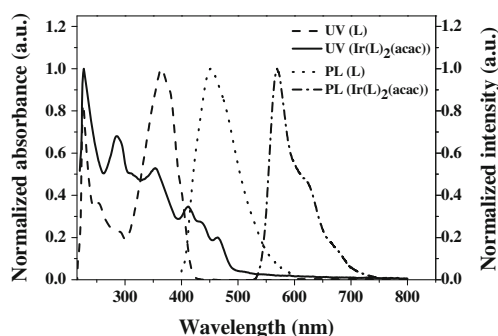
The packing diagram for unit cell of  $\text{Ir(L)}_2(\text{acac})$  along  $b$ -axis was shown in Fig. 2, it was found that the  $\pi$ - $\pi$  interaction of two adjacent  $\text{Ir(L)}_2(\text{acac})$  molecules through respective 3-(benzothiazol-2-yl)coumarin ligands favors to stack along  $b$ -axis.

#### UV-vis Absorption and Photoluminescence Spectra

The UV-vis absorption and photoluminescence spectra of the ligand L and the complex  $\text{Ir(L)}_2(\text{acac})$  were measured in diluted dichloromethane solutions, as shown in Fig. 3. The

ligand L exhibits two intense absorption bands at 227 and 365 nm, and one weak absorption band at 253 nm. The absorption band at 365 nm can be attributed to the charge transfer type  $\pi$ - $\pi^*$  transition from the HOMO located at the electron-donating coumarin moiety to the LUMO located at electron-accepting benzothiazole moiety. The absorption bands at 227 and 253 nm should come from the locally excited  $\pi$ - $\pi^*$  transitions at the coumarin moiety [32, 33]. In UV-vis absorption spectrum of  $\text{Ir(L)}_2(\text{acac})$ , there are six obvious absorption bands at 227, 286, 354, 412, 436 and 464 nm, in which the absorption bands below 400 nm could be ascribed to spin-allowed  $\pi \rightarrow \pi^*$  transition of the ligands, and the bands at the longer wavelengths (412, 436 and 464 nm) can be assigned to both spin-orbit coupling enhanced  $^3(\pi \rightarrow \pi^*)$  and spin-forbidden  $^3\text{MLCT}$  transitions [34–36].

The ligand L is photoactive and exhibits bright blue emission with peak at 452 nm in dilute solution when excited at 365 nm (Fig. 3). The ligand L is a typical D-A molecule in which the coumarin ring acts as an electron-donor (D) and the benzothiazole moiety acts as an electron-



**Fig. 3** Normalized UV-vis absorption and photoluminescence spectra of ligand L and the complex  $\text{Ir(L)}_2(\text{acac})$  in diluted dichloromethane solutions. ( $C=1 \times 10^{-6}$  mol/L)

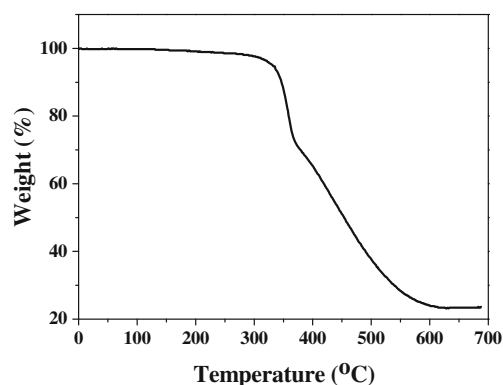
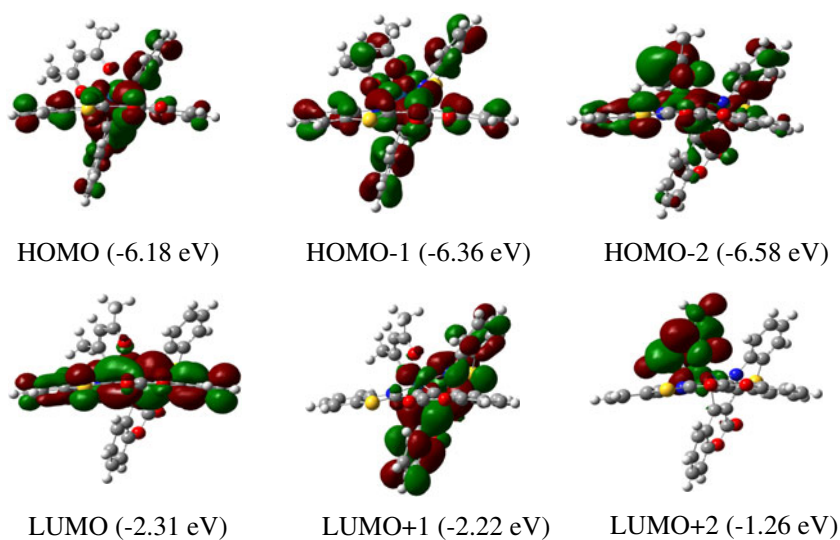
acceptor (A),  $\pi$ -conjugation through the donor to the acceptor forms a strong donor-acceptor system. Addition of a benzothiazole ring to coumarin ring at the C3 position caused a 22 nm red-shift in  $\lambda_{em}$  with respect to the emission of the unsubstituted parent coumarin [32]. As shown in Fig. 3, by excitation at 464 nm the complex  $\text{Ir(L)}_2(\text{acac})$  in dichloromethane solution exhibits reddish orange emission with a maximum main peak (569 nm) and a shoulder peak (623 nm), the Commission Internationale de L'Eclairage (CIE) coordinates is (0.53, 0.47).

#### Quantum Chemical Calculations

Frontier molecular orbitals play an important role in electric and optical properties for a materials [37]. Compared with the X-ray data of the complex  $\text{Ir(L)}_2(\text{acac})$ , its structure was optimized by density functional theory (DFT) using a B3LYP/6-31 G(d) basis set. It was shown that the DFT optimized structure is in good agreement with the X-ray crystal structure. The electronic distributions and energy levels of HOMO and LUMO orbitals for  $\text{Ir(L)}_2(\text{acac})$  obtained from time-dependent DFT (TD-DFT) calculation is shown in Fig. 4. It can be seen that the orbital energy levels of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of the complex are  $-6.18$  and  $-2.31$  eV, respectively. The energy gap between HOMO and LUMO is 3.87 eV.

From Fig. 4, the electron density in the HOMO of the complex resides significantly on the cyclometalating ligands as well as the core Ir(III) atom. The HOMO is followed, in order of decreasing energy, by two orbitals (HOMO-1 and HOMO-2) showing a increasing contribution from ancillary ligand acac except the contributions coming from the cyclometalating ligand L and the core Ir(III) atom. The electron

**Fig. 4** Frontier molecular orbitals of the complex  $\text{Ir(L)}_2(\text{acac})$



**Fig. 5** Thermogravimetric analysis (TGA) of the complex  $\text{Ir(L)}_2(\text{acac})$  in nitrogen atmosphere (heating rate  $10$  °C/min)

density in LUMO locates mainly on a cyclometalating ligand and the core Ir(III) atom, and the electron density in LUMO + 1 locates mainly on the core Ir(III) atom and another cyclometalating ligand. The LUMO + 2 is mainly a  $\pi^*$  bonding combination of the acac ligand with small metal character.

#### Thermal Property of the Complex

Thermogravimetric analysis (TGA) measurement was performed in flowing drying nitrogen atmosphere at the heating rate of  $10$  °C/min on approximately 3.484 mg sample. The result of TGA measurement of  $\text{Ir(L)}_2(\text{acac})$  is shown in Fig. 5. It shows good thermal stability of the complex up to  $300$  °C ( 2 % weight loss). At  $337$  and  $370$  °C, there are two sharp weight losses in the TGA curve, it shows that the complex undergoes two large-stage decomposition processes. The complex meets with the thermal stability requirement of fabrication of OLED luminescence application.

## Conclusion

A new iridium(III) complex containing coumarin derivative as a cyclometalated ligand, Ir(L)<sub>2</sub>(acac), was synthesized and confirmed by means of element analysis, <sup>1</sup>H NMR, and single crystal X-ray crystallography. The electronic distributions and energy levels of HOMO and LUMO orbitals for Ir(L)<sub>2</sub>(acac) obtained from time-dependent DFT (TD-DFT) calculation, and the energy gap between HOMO and LUMO is 3.87 eV. The complex has high thermal stability, and exhibits bright reddish orange emission with a maximum main peak (569 nm) and a shoulder peak (623 nm), which is suggested to be a phosphorescent material for OLEDs.

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### Supplementary material

The crystallographic data (excluding structure factors) of Ir(L)<sub>2</sub>(pic) had been deposited with the Cambridge Crystallographic Center as supplementary publication no. CCDC 917825.