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Article

Molecular Structure, Luminescent and DFT Computational Studies of Two Novel Eu (III) β-diketonate Complexes

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Abstract: In this paper, the synthesis of two novel luminescent Eu^{3+} ion complexes [$Eu(TFT)_3(phen)$ (**1**) and $Eu(TFT)_3(bpy)\cdot Hex$ (**2**)] based on the combination of 2-(2,2,2-trifluoroethyl)-1-tetralone (TFT), containing n-donor ligands (1,10-phenanthroline or 2,2'-Bipyridine) and Eu^{3+} ion is reported herein, and their structural features are discussed on the basis of X-ray crystallographic and thermal analyses. We observed that the ligands transfer energy effectively to the metal center by fluorescence, IR and UV spectrograms studies. The structures and properties of complexes **1**-**2** were optimized by the DFT theoretical calculation, and the calculation results were consistent with the experimental X-ray structure data and spectral analysis.

Keywords: TFT; complexes; luminescent; synthesis; Density functional theory (DFT)-computation

1. Introduction

As is known to all, lanthanide ions play a significant role on the basis of their peculiar luminescent properties in the field of optical research [1]. However, Ln^{3+} ions are unable to generate efficient luminescence emission under direct excitation because the 4f–4f transitions of lanthanide ions are spin forbidden [2], which results in free lanthanide ions have a weak luminescence merely. For this point, the design of lanthanide coordination compounds have attracted particular attention in order to improve luminescent properties of lanthanide ions. In this context, scientists consistently synthesize new molecular structures in order to study finely fluorescence system in recent years. In particular, lanthanide organic complexes [3], such as β-diketonate Ln^{3+} complexes [4], have great potential application in amplifiers for fluorescent materials [5], biological probes [6], and analytical sensors [7] in virtue of sharp fluorescence emissions and high quantum efficiencies. In our preliminary work, we designed a β-diketonate-type Ligand, 2-(2,2,2-trifluoroethyl)-1-tetralone (TFT) act as organic chelating agents of the trivalent Eu^{3+} ion, which formed a tris-β-diketonate (Eu^{3+}) salt in the end. Then, the tris-β-diketonate (Eu^{3+}) salts combined with 1,10-phenanthroline (phen) or 2,2'-Bipyridine (bpy) on the basis of coordination chemistry principle, respectively, which may increase the light absorption cross-section of metal complex via ligands transfer energy to the central Ln^{3+} ion. Furthermore, there are two key reasons for our designing scheme. On one hand, TFT is able to compose firm coordination compound with Eu^{3+} ions , and enhance the luminescence intensity due to the effect of its $\pi-\pi^*$ transition [8]. The presence of fluorinated groups also enhances luminescent property and stable performance of complexes effectively because of its strong

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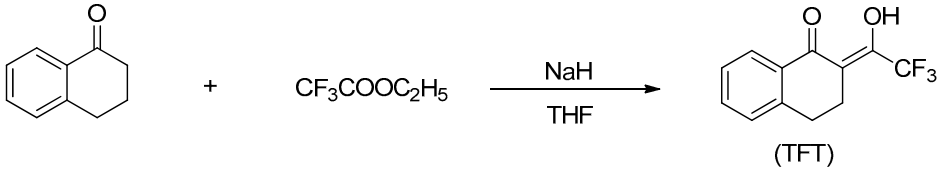
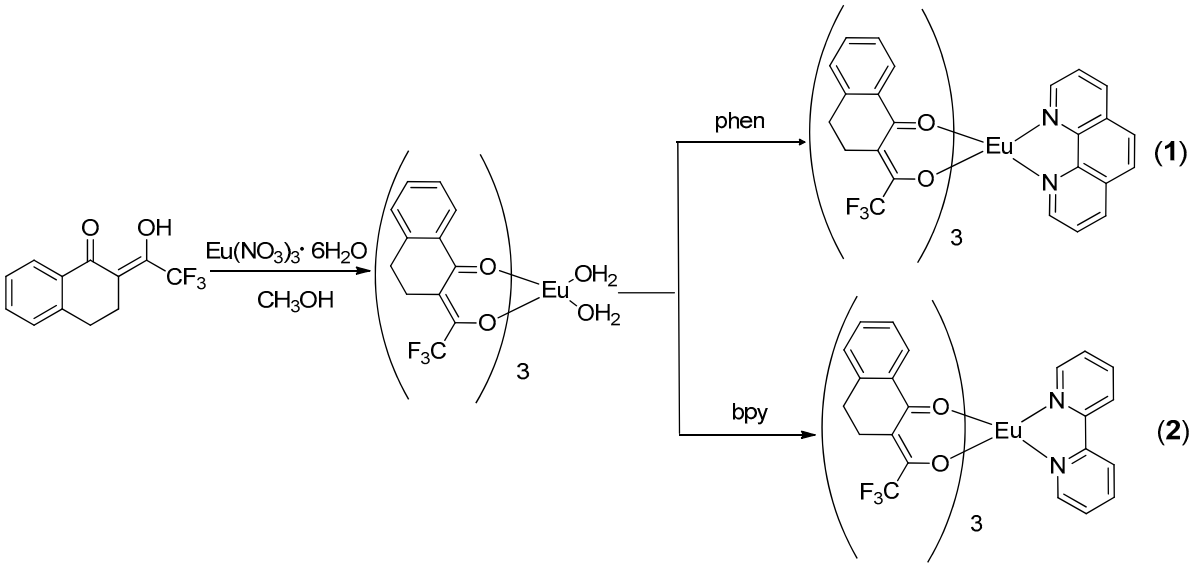
electron-withdrawing function and oxidative stability, respectively [9]. On the other hand, the auxiliary ligands ， such as phen and bpy play an important role in increasing luminous emission intensity and inhibiting the fluorescence quenching by an intramolecular energy transfer process from ancillary ligands to central metal ion ， the so-called ‘‘synergistic effect’’ [10]. The structure and property analysis of complexes are described in more detail below.

2. Results and Discussion

As shown in Scheme **I**, the ligand 2-(2,2,2-trifluoroethyl)-1-tetralone has been synthesized by classical Claisen condensation of 1-tetralone with ethyl trifluoroacetate in the THF containing NaH. According to the synthetic method of relevant literature [11], we synthesized the target compound with excellent yield. The reaction conditions would be described in detail in a follow-up Experimental Section. Here, we designed the tris-β-diketonate (Eu^{3+}) salt, $Eu(TFT)_3(H_2O)_2$ [TFT = 2-(2,2,2-trifluoroethyl)-1-tetralone]. In order to seek target complexes with outstanding luminescent properties, we focused on attractive 1,10-phenanthroline or 2,2'-Bipyridine as ancillary ligand, reacted with $Eu(TFT)_3(H_2O)_2$ to generate complexes **1**-**2** in methanol (Scheme **II**). Herein, we report the successful assembly of two new tris-β-diketonate Eu(III) complexes, namely Eu[2-(2,2,2-trifluoroethyl)-1-tetralone]$_3$phenanthroline and Eu[2-(2,2,2-trifluoroethyl)-1-tetralone]$_3$bipyridine, and reveal the crystal structures of them. The crystal datas and refinement details are summarized in Table 1.



Scheme I. Synthesis of the TFT.



Scheme II. Synthesis of complexes **1**-**2.**

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Table 1. Crystal Data and Structure Refinement for Complex **1-2**

Parameter	Complex 1	Complex 2
empirical formula	C48 H30 Eu F9 N2 O6	C49 H39 Eu F9 N2 O6
formula weight	1053.70	1074.78
temperature/K	296(2)	296(2)
Color	Buff	Buff
crystal system	monoclinic	monoclinic
space group	P21/n	P21/n
a/Å	21.005(2)	12.0336(16)
b/Å	9.6340(9)	21.134(3)
c/Å	22.989(2)	19.0963(17)
α (deg)	90.000	90.000
β (deg)	105.1550(10)	110.757(6)
γ (deg)	90.000	90.000
V (Å3)	4490.3(7)	4541.3(10)
Z	4	4
ϱ (g cm^3)	1.559	1.572
μ (mm^{-1})	1.485	1.470
F (000)	2096.0	2156.0
R1, [I > 2σ (I)]	0.0524	0.0430
wR2, [I > 2σ (I)]	0.1174	0.0961
R1, (all data)	0.1240	0.0828
wR2, (all date)	0.1475	0.1134
CCDC	1484014	1524434

*2.1. Molecular Structure of the Complex **1***

The molecular structure of complex **1** [Eu(TFT)$_3$(phen)] is revealed by Single crystal X-ray diffraction studies, which crystallizes in the the monoclinic crystal system with a space group of P21/n. The asymmetric unit of complex **1** is composed of one independent Eu^{3+} ion, three deprotonated ligands (TFT), and one phen. The ligand (TFT) and phen serve as two bidentate ligands and chelate the Eu^{3+} ion on coordination chemistry principle (Figure 1a, Figure S1). Each Eu^{3+} ion centre adopts a distorted hexahedron, coordinated by six oxygen atoms from three carbonyl groups (O_1, O_3, O5), three methoxy groups (O_2, O_4, O_6) of three ligands (TFT) and two nitrogen atoms (N_1, N_2) from one phen (Figure 1b). The selected bond lengths for complex **1** are shown in Table 2, and the selected bond angles (°) are in Table S1. The average bond length of the Eu−O (TFT oxygen atoms) and Eu−N (phen nitrogen atoms) is 2.347 Å and 2.588 Å，respectively. The average length of the Eu-N bond (2.588 Å) with the nitrogen atoms from phen is substantial longer indicating a weak interaction. In other words, the TFT ligand is more stable binding to the central metal ion, which is due to the strong interaction of Eu^{3+} ion and oxygen atoms.

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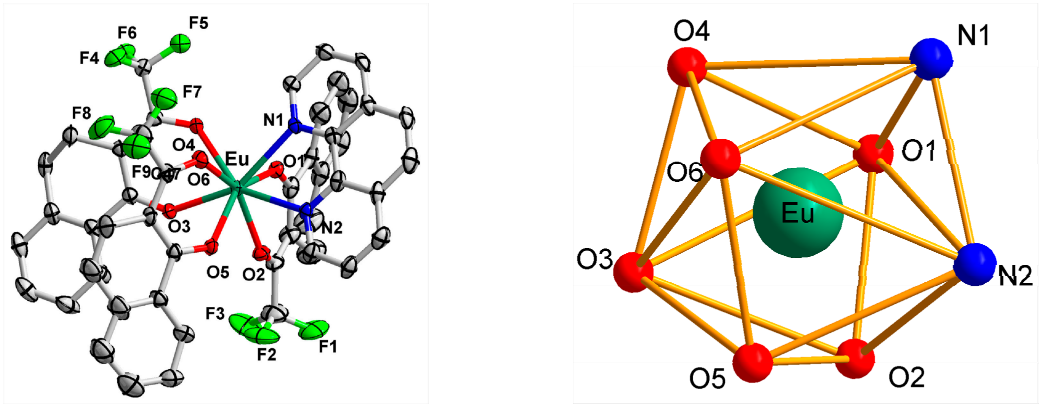

(a) (b)

Figure 1. Molecular structure for $Eu(TFT)_3(phen)$, the ORTEP drawing (15% probability level) (a); and simplified stick exhibition (b).

Table 2. Selected bond lengths (Å) in $Eu(TFT)_3(phen)$

Bond Lengths	
Eu(1) -O1	2.347(4)
Eu(1)-O2	2.351(5)
Eu(1)-O3	2.324(4)
Eu(1)-O4	2.347(4)
Eu(1)-O5	2.354(4)
Eu(1)-O6	2.358(4)
Eu(1)-N1	2.590(5)
Eu(1)-N2	2.586(5)

Each asymmetric unit of complex **1** can form a more stable structure via several hydrogen bonds interaction between the atoms, as shown in Figure 2. These hydrogen bonds (C-H...F, C-H...O) are composed of F, O and H atoms from TFT and phen ligands, which is an important factor in enhancing the thermal stability and stabilizing the crystal structure for the complex **1** [12]. Within these hydrogen bonds, the F(4) and F(6) atoms are interconnected with a same atom H(33B), which form the C(33)-H(33B)...F(4) and C(33)-H(33B)...F(6), respectively. It's worth mentioning that hydrogen bonds C(1)-H(1)...O(4) and C(12)-H(12)...O(5) are composed of [O(4), O(5)] from TFT and [H(1), H(12)] from phen. The ligands TFT and phen are interconnected via weak hydrogen bonds C(1)-H(1)...O(4) and C(12)-H(12)...O(5) contacts enhancing stability of crystal structure. In this context, The success ratio of cultivation of single crystal is also significantly higher than β-diketonate (Eu^{3+}) salt $[Eu(TFT)_3(H_2O)_2]$ during the practical tests. The length and angle of hydrogen bonds are listed in Table S2.

2.2. Molecular Structure of the Complex **2**

The molecular structure of the complex **2** is exhibited in Figure 3. Single crystal X-ray diffraction studies reveal that complex **2** crystallizes in the monoclinic space group P21/n with Z = 4 and consists of neutral and mononuclear $[Eu(TFT)_3bpy]$ units and solvent n-hexane. In analogy to complex **1**, the complex **2** introduces bpy instead of phen as ancillary ligand. The average bond length of the Eu−O (TFT oxygen atoms) and Eu−N (bpy nitrogen atoms) is 2.357 Å and 2.583 Å, which reduced 0.01 (Eu−O) and 0.005 (Eu−N) in contrast to complex **1,** respectively. The selected bond lengths for complex **2** are shown in Table 3, and the selected bond angles (°) are in Table S3. Besides that, the π−π stacking interaction which is same as hydrogen bonding (Table S4) also has a

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great significance to the stabilization of crystal structure. The molecules of complex **2** formed a 1D chained structure via the π–π stacking interaction, as shown in Figure 4. The result of the π–π bond measured was 3.898 Å.

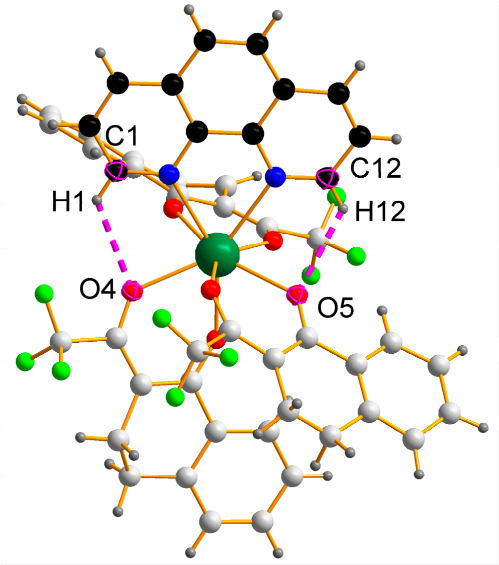

Figure 2. Intramolecular hydrogen bonding of Eu(TFT)$_3$(phen).

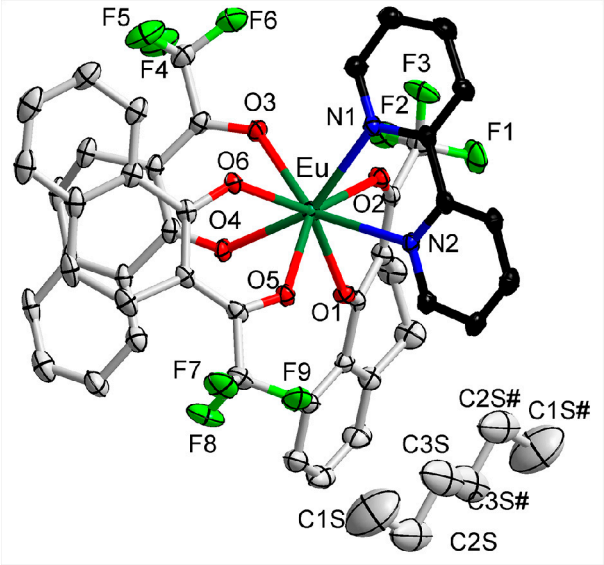

Figure 3. Molecular structure for Eu(TFT)$_3$(bpy)·Hex, the ORTEP drawing (15% probability level), Symmetry operator (1 − x, 1 − y,1 − z) generates equivalent atoms that are marked with "#".

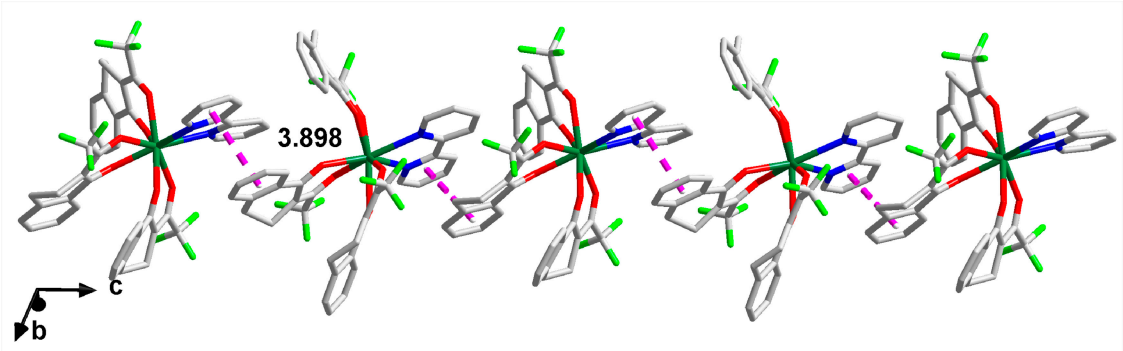

Figure 4. Complex **2** formed 1D chained structure by the π–π stacking interaction.

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Table 3. Selected bond lengths (Å) in $Eu(TFT)_3(bpy)\cdot Hex$

Bond Lengths			
Eu(1)-O1	2.341(3)	C(3S)-C(2S)	1.41(3)
Eu(1)-O2	2.368(3)	C(3S)-C(3S)#1	1.46(4)
Eu(1)-O3	2.356(3)	C(1S)-C(2S)	1.542(9)
Eu(1)-O4	2.347(3)		
Eu(1)-O5	2.351(3)		
Eu(1)-O6	2.379(3)		
Eu(1)-N1	2.576(3)		
Eu(1)-N2	2.590(8)		

2.3. UV–Vis spectral analysis

The ultraviolet absorption spectrum of TFT, and complexes **1-2** are shown in CH_3CN solution (1×10^{-5} mo·L^{-1}). According to spectral (Figure 5), the absorption broad band appeared slight blue-shift from 363 nm for the TFT to 362 nm for the Na(TFT) because of β-diketonate proton transfer happened. In addition, the absorption maximum observed around 263 and 272 nm in phen and bpy respectively are due to the singlet–singlet π–π* absorption of the ancillary ligand .As for the lanthanide(III)-cored complexes **1-2**, two sets of typical UV–Vis absorption peaks 353 and 359 nm are observed with a higher absorption intensity, which are blue-shifted compared to ligand TFT (max = 363 nm), respectively, duing to the influence of TFT complexation with Eu^{3+} ion. In addition, the molar absorption coefficient values of complexes **1-2** is about 0.9×10^5·L^{-1} mol^{-1} cm^{-1} around 350-360 nm, which is three times higher than that for the ligand TFT base on each of the complexes consisting of three ligands.

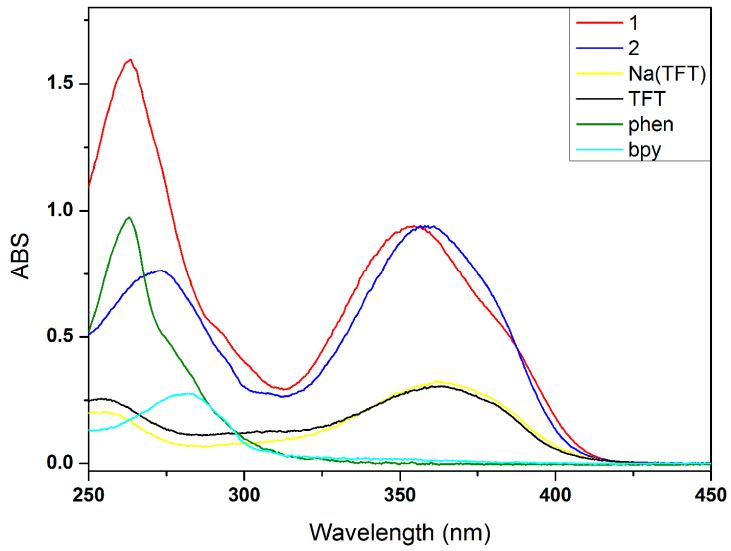

Figure 5. UV-vis absorption spectra of TFT, Na(TFT), phen , bpy and complexes **1-2** in CH_3CN solution ($c = 1 \times 10^{-5}$ M).

2.4. Thermal stability analysis

The thermal stabilities of the β-diketonate (Eu^{3+}) salt $[Eu(TFT)_3(H_2O)_2]$ and complexes **1-2** are analyzed with thermogarvimetric analysis (TGA) in a temperature range from 50 to 720 °C at a rate

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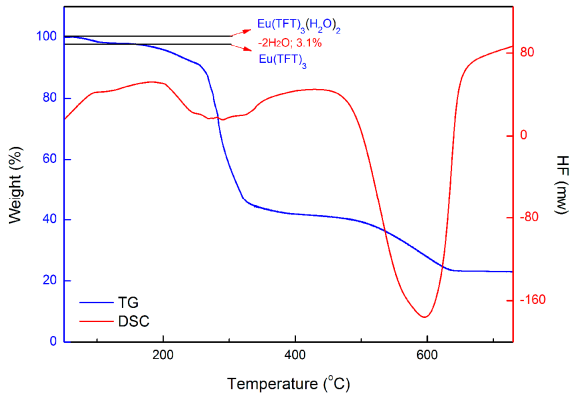
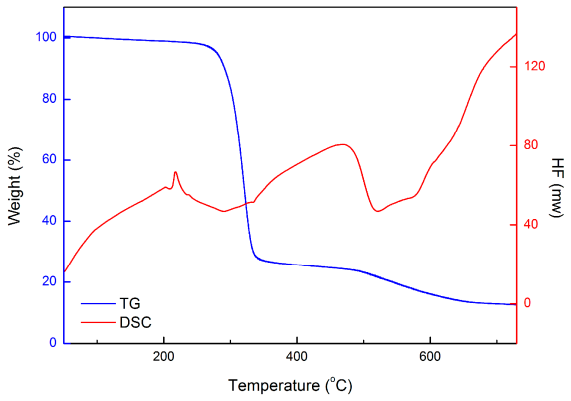
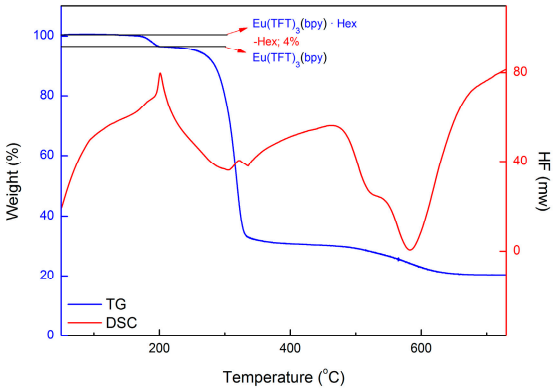
of 10 °C·min^{-1} under nitrogen gas atmosphere. As shown in Figure 6a, the TGA curve of [Eu(TFT)$_3$(H$_2$O)$_2$] shows a weight loss of 3.4% in the temperature range 50–120 °C, corresponds to the coordinated water molecules (calcd 3.4%) lost gradually, a weight loss of 74.2% in the temperature range 180–650 °C, corresponds to the TFT ligands (calcd 73.8%) decomposes gradually. The TGA curve of complex **1** shows a weight loss of 85.9% in the temperature range 250–650 °C (Figure 6b), corresponds to the TFT and phen ligands (calcd 86.1%) decomposes gradually, while the TGA curve of complex **2** shows a weight loss of 4% in the temperature range 190–210 °C (Figure 6c), corresponds to the solvent n-hexane (calcd 4%) decomposes gradually, a weight loss of 76.2% in the temperature range 250–650 °C, corresponds to the TFT and bpy ligands (calcd 76.8%) decomposes gradually. The final mass residues of complexes **1**-**2** were europium oxide. The weight-loss temperature of TFT will transfer from 180 °C to 250 °C when the auxiliary ligands bonded in metal ion. This result is consistent with the conclusion of hydrogen bonds analysis, the TFT ligands are interconnected with phen or bpy via weak hydrogen bonds or π–π stacking enhancing stability of crystal structure.



(**a**)



(**b**)



(**c**)

Figure 6. TGA and DSC of Eu(TFT)$_3$(H$_2$O)$_2$ (a), Eu(TFT)$_3$(phen) (b), Eu(TFT)$_3$(bpy)·Hex (c). Heating rate 10 °C·min^{-1}.

2.5. Photoluminescent properties

The fluorescence spectrum of TFT and complexes **1**-**2** are shown in Figure 7. As can be seen in the emission spectra of complexes **1**-**2**, the several characteristic narrow emission bands the of Eu^{3+} ion are formed upon excitation at 390-410 nm (Figure 7a), and corresponding to the transitions from the metal-centered $^5D_0$ excited state to the ^7F_J (J = 0–4) ground state multiple, there are $^5D_0 \rightarrow {}^7F_0$

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(around 580 nm), $^5D_0 \rightarrow {}^7F_1$ (around 595 nm), $^5D_0 \rightarrow {}^7F_2$ (around 611 nm), $^5D_0 \rightarrow {}^7F_3$ (around 650 nm), and $^5D_0 \rightarrow {}^7F_4$ (around 700 nm) (Figure 7b), respectively [13]. Among them, the $^5D_0 \rightarrow {}^7F_2$ transition around λ = 611 nm is the highest intensity emission, which belongs to an induced electric dipole transition, thus indicating that the Eu^{3+} ion is not situated in a location with inversion center symmetry [14].

As is known, Eu(III) complexes are the most intense emitters among the lanthanide series [15] , and emit red light at 605-700 nm. The blue light appeared at 450-480 nm. As can be seen in Figure 7c, the broad emission band of organic ligands (λem = 468 nm) can not be observed in field of complexes **1**-**2**, which indicates that the ligand transfers the absorbed energy effectively to the emitting level of the Eu3+ ion [16]. Meanwhile we discover that the emission peak of complex **1** is far stronger than complex **2**, which is due to phen has a more high efficiency of light absorption (λ = 264 nm, ε = 33 900 M^{-1} cm^{-1}) than bpy (λ = 282 nm, ε = 22 900 M^{-1} cm^{-1}), the energy of its triplet excited state (22 100 cm^{-1}) is higher than the lowest emitting level of the Eu(III) (17 500 cm^{-1}) [17]. In addition to these research, luminescent lifetime study also has a great significance. This study consequence declares that luminescence decay time of complex **1** and **2** are 27.38 and 30.73 μs. Luminescence decay profiles been demonstrated in Figure 4(S3a, S3b).

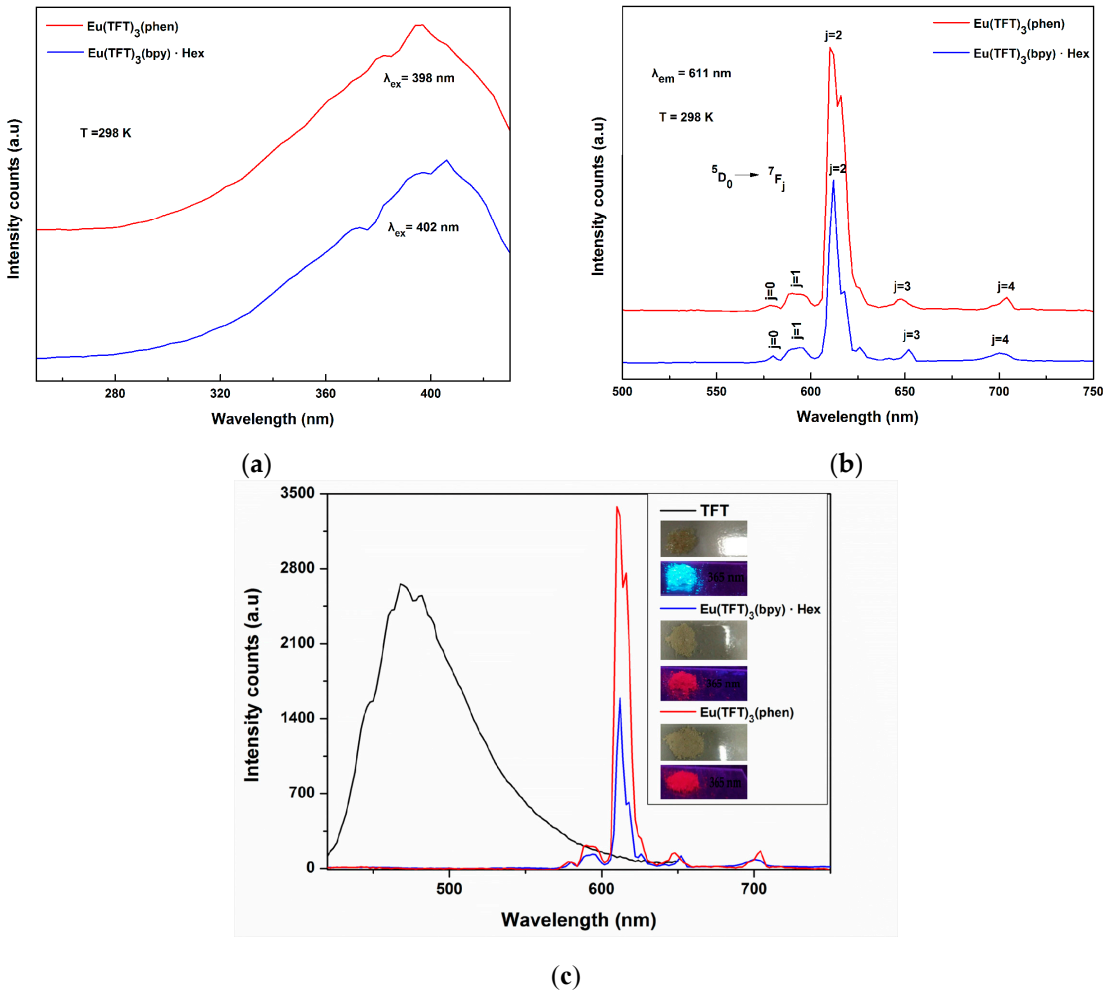

Figure 7. Excitation spectra of $Eu(TFT)_3(phen)$ and $Eu(TFT)_3(bpy)\cdot Hex$ in the solid state (a); Emission spectra of $Eu(TFT)_3(phen)$ and $Eu(TFT)_3(bpy)\cdot Hex$ in the solid state (b); Emission spectra of $Eu(TFT)_3(phen)$, $Eu(TFT)_3(bpy)\cdot Hex$ and TFT in the solid state (c).

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2.6. Computational Studies

The results of theoretical calculations for absorption properties of the complex **1** [Eu(TFT)$_3$(phen)] were shown in Figure 8 and Table 4. The HOMO and LUMO levels for the ground and singlet excited state of Eu^{3+} complex were -0.21 eV and -0.08 eV, -0.30 eV and 0.05 eV, respectively. The electronic cloud distribution of HOMO in singlet excited state localizes at three TFT ligands, while the one of LUMO localizes at 1,10-phenanthroline. As shown in Table 4，the lowest excitation energy of Eu^{3+} complex calculated by TD-DFT is 4.47 eV. The absorption transition is mainly due to the intraligand charge transfer (ILCT or $\pi \rightarrow \pi^*$), ligand-to-metal charger transfer(LMCT), metal-to-ligand charger transfer (MLCT) and metal centered (MC) transitions. The calculating data of S4 and S5 can explain the reason why the absorption intensity of the complex **2** is about three times as great as the ligand in the UV-vis spectra quite well.

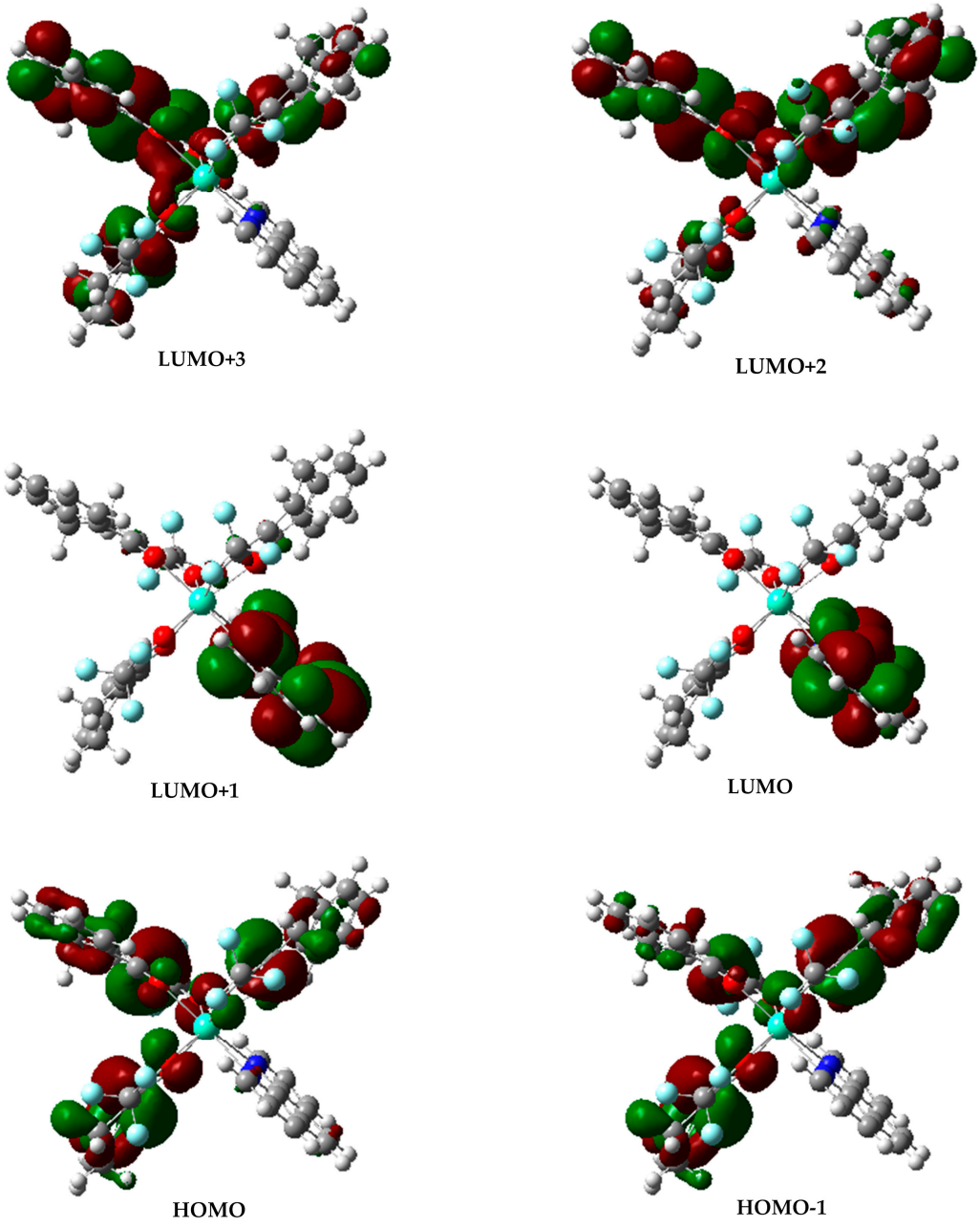

Figure 8. Spatial plots of the selected frontier molecular orbits of excited states of complex **1.**

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Table 4. Absorptions of Eu complex Calculated with the TDDFT Method

complex	Sn	Confign	CI codff	E/nm (eV)	oscillator	assignt
1	S1	H→L+2	0.2898	277.23(4.47)	0.1533	ILCT/LMCT/MLCT/MC
	S2	H→L+3	0.3316	275.69(4.49)	0.3093	ILCT
	S3	H-1→L+2	0.1572	266.16(4.66)	0.4822	ILCT/LMCT/MLCT/MC
	S4	H→L+1	0.1091	254.70(4.87)	0.0279	LMCT/MLCT/MC
	S5	H→L	0.1363	249.71(4.97)	0.0024	LMCT/MLCT/MC

3. Materials and Methods

All chemicals were purchased from Beijing Fine Chemical Co. (Beijing,China). ^{1}H NMR spectra were measured with a Bruker Avance III 400 MHz spectrometer in $CDCl_3$ solution. Fourier transform infrared (FT-IR) spectra were obtained with KBr disks in the range 4000−450 cm^{-1}. UV-Vis spectra were recorded with a Perkin-Elmer Lambda 25 spectrometer. Excitation and emission spectra were measured with an Edinburgh FLS 920 fluorescence spectrophotometer. Thermal analyses were conducted on a Perkin-Elmer STA 6000 with a heating rate of 10 °C·min^{-1} in a temperature range from 50 to 720 °C. Single crystal diffraction intensity data were collected with a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 296(2) K. The structures were solved by direct methods and refined on F2 by full-matrix least squares using the SHELXTL-97 program [18].

3.1. Ligand 2-(2,2,2-trifluoroethyl)-1-tetralone Syntheses

First, to a solution of 1-tetralone (0.73 g, 5.00 mmol) in THF (20 mL) was added a THF solution (10 mL) of ethyl trifluoroacetate (1.42 g, 10.00 mmol). The mixed solution was allowed to stir for 20 min. Later, NaH (0.30 g, 7.5 mmol) solids were added with vigorous stirring, and the combined solution was stirred at room temperature for 24 h in an inert atmosphere. The resulting solution was simply dumped into the distilled water and successively acidified to pH 2−3 with 6M hydrochloric acid aqueous solution. The mixed solution was extracted twice using dichloromethane (40 mL). The organic layer was separated from the water and dried overnight with anhydrous sodium sulfate. After the solvent removed by reduced pressure distillation, the oily solid is obtained. The buff solid product was isolated by column chromatography using hexane. Yellow crystal. Yield: 0.98 g (81%). m.p. 50 °C. Calculated for $C_{12}H_9F_3O_2$ (242.20 g·mol^{-1}): C 59.51; H 3.75; F 23.53; O 13.21. Found: C 59.30; H 3.81;F 23.48; O 13.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.66 (s, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.50 (td, J = 7.5, 1.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.28 – 7.25 (m, 1H), 3.49 (s, 1H), 2.94 – 2.87 (m, 1H), 2.77 (t, J = 6.8 Hz, 1H) (Figure S5). IR (KBr) νmax: 2947 cm^{-1} (s, ν_{O-H}), 1600 cm^{-1} (s, $\nu_{C=O}$), 1303 cm^{-1} (s), 1246 cm^{-1} (s), 1139 cm^{-1} (s, ν_{C-F}), 753 cm^{-1} (m, ν_{CF3}) (Figure S6).

3.2. Complex Eu(2-(2,2,2-trifluoroethyl)-1-tetralone)$_3$phenanthroline Syntheses

A mixture of 2-(2,2,2-trifluoroethyl)-1-tetralone (0.5 g, 2.06 mmol) and NaOH (0.125 g, 2.06 mmol) in an methanol solvent (15 ml) was stirred for 0.5 h. Another methanol solution (10 ml) of $Eu(NO_3)_3{\cdot}6H_2O$ (0.31 g, 0.69 mmol) was added dropwise under stirring. To this solution，the 1,10-phenanthroline (0.125 g, 0.69 mmol) was added and allowed to stir for 12 h at room temperature. After removing part of the solvent by reduced pressure distillation, the precipitate formed and filtered off, washed with hexane, and recrystallized with the dichloromethane–hexane.

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Single crystals of complex suitable for single-crystal X-ray diffraction study were obtained in about three weeks. Yellow crystal. Yield: 1.73 g (80%). IR (KBr) νmax: 1595 cm^{-1} (s, $\nu_{C=O}$), 1305 cm^{-1} (s), 1233 cm^{-1} (s), 1126 cm^{-1} (s, ν_{C-F}), 755 cm^{-1} (m, ν_{CF3}).

3.3. Complex Eu(2-(2,2,2-trifluoroethyl)-1-tetralone)$_3$(Bipyridine)·Hex Syntheses

A methanol solution (10 ml) of $Eu(NO_3)_3{\cdot}6H_2O$ (0.31 g, 0.69 mmol) was added to another mixture methanol solution (15 ml) of 2-(2,2,2-trifluoroethyl)-1-tetralone (0.5 g, 2.06 mmol) and NaOH (0.125 g, 2.06 mmol) under stirring. To this solution， the 2,2'-Bipyridine (0.125 g, 0.69 mmol) was added and allowed to stir for 12 h at room temperature. After removing part of the solvent by reduced pressure distillation, the precipitate formed and filtered off, washed with hexane, and recrystallized with the dichloromethane–hexane. Single crystals of complex suitable for single-crystal X-ray diffraction study were obtained in about three weeks. Yellow crystal. Yield: 0.58 g (75%). IR (KBr) νmax: 1596 cm^{-1} (s, $\nu_{C=O}$), 1307 cm^{-1} (s), 1231 cm^{-1} (s), 1123 cm^{-1} (s, ν_{C-F}), 755 cm^{-1} (m, ν_{CF3}).

3.4. Theoretical Calculations

The DFT-B3LYP method [19] and Time-dependent density functional theory (TDDFT) in the Gaussian 03 software [20] were used to optimize the structure obtained from the X-ray single crystal structure analysis and calculate the absorption properties on the basis of the optimized geometry structures in the excited states. The ECP52MWB basis sets with the effective core potentials (ECPs) [21-22] were used for Eu atoms and 6-31G(d) basis sets for other atoms. No negative frequencies were obtained in frequency calculations of the optimized structures demonstrated that the optimized structures are the energy minimum on the potential energy surfaces.

4. Conclusions

In summary, we reported that two novel eight-coordinated Eu(III) complexes, Eu(2-(2,2,2-trifluoroethyl)-1-tetralone)$_3$phenanthroline and Eu(2-(2,2,2-trifluoroethyl)-1-tetralone)$_3$(Bipyridine)·Hex, which were synthesized by the reaction of 2-(2,2,2-trifluoroethyl)-1-tetralone, containing n-donor ligands (1,10-phenanthroline or 2,2'-Bipyridine) and $Eu(NO_3)_3{\cdot}6H_2O$ in ethanol solution at room temperature. The structure and propertiy of complexes **1-2** were characterized by thermal stability analysis, X-ray single crystal diffraction analysis, IR, UV and fluorescence spectrums study. Structural analysis shows that the tris-β-diketonate Eu^{3+} complexes, each eight-coordinated center Eu^{3+} is chelated with three β-diketonate-type ligands (TFT) and one bidentate containing n-donor ligand (phen or bpy). Luminescence studies revealed that the TFT ligand is an effective sensitizer on luminescence of Eu^{3+} ions due to the ligand transfers the absorbed energy effectively to the emitting level of the center metal ion, and the phen and bpy, acts as a ancillary bidentate nitrogen ligands enhance not only the luminescence property but also thermal stability effectively. The experimental data can be explained with the DFT calculated transitions quite well.

Supplementary Materials: The following are available online at www.mdpi.com/link, Figure S1: Crystal structure of complex **1**, Table S1: Selected bond lengths/Å for complex **1**, Table S2: Hydrogen bond lengths/Å and bond angles/°for complex **1**, Figure S2: Crystal structure of complex **2**, Table S3: Selected bond lengths/Å for complex **2**, Table S4: Hydrogen bond lengths/Å and bond angles/°for complex **1**, Figure S3: Schematic energy level diagram for complex **1** (S, excited singlet state; T, excited triplet state), Figure S4: Luminescence

decay profiles for complex **1** (a) and **2** (b) in solid-state were measured at 298K, Figure S5: ^{1}H NMR analysis of 2-(2,2,2-trifluoroethyl)-1-tetralone, Figure S6: FT-IR spectra of TFT and complexes **1-2.**

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