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ARTICLE

A high-efficient blue-light excitable red phosphor: intramolecular π−stacking interactions in one dinuclear europium(III) complex

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A series of ternary dinuclear europium(III) complexes [Eu_2(2,7-BTFDBC)$_{3-n}$(DBM)$_{2n}$(Phen)$_2$] (n = 0, 1, or 2) are synthesized by using 2,7-bis(4'4'4'-trifluoro-1,3-dioxobutyl)-(9-ethyl-9*H*-carbazole) (2,7-BTFDBC), dibenzoylmethane (DBM), 1,10-phenanthroline (Phen) and europium(III) ions. All these complexes display broad excitation band in blue region and high intensity emission with high colour purity. The intensity of emission significantly increases with the increase of DBM in [Eu_2(2,7-BTFDBC)$_{3-n}$(DBM)$_{2n}$(Phen)$_2$] (n = 0, 1, or 2). The theoretical predictions of molecular geometry and electronic absorption spectrum of [Eu_2(2,7-BTFDBC)(DBM)$_4$(Phen)$_2$] confirm that the pendant phenyl domains engage in multiple T-shaped and parallel-dispalced π−stacking interactions with the coordination sphere of two europium(III) centers. Using [Eu_2(2,7-BTFDBC)(DBM)$_4$(Phen)$_2$] as red phosphor, the single red LED has been obtained with a ~460 nm-emitting GaN chip.

Introduction

Light-emitting diodes (LEDs) have been widely used in solid-state illumination, due to their many advantages, such as high efficiency, long service life, low energy consumption, and environment-friendly.[1-4] The warm white LEDs with low correlated colour temperature and high colour rendering index for indoor lighting can be obtained by combining a ~460 nm blue-emitting GaN LED chip with commercial $Y_3Al_5O_{12}:Ce^{3+}$ (YAG) and a sharp red-emitting phosphor.[5-8] At present, red-emitting phosphors, which can be efficiently excited by blue-emitting GaN LED chip, are mainly inorganic phosphors, such as Eu^{2+} activated (oxy)nitrides and Mn^{4+} doped fluorides.[5-8] However, these Eu^{2+} activated (oxy)nitrides suffer from significant emission into the near infrared which result in warm WLEDs that have low luminous efficiency of radiation. In addition, harsh synthetic requirements of nitrides limit their practical application.[7] Mn^{4+} doped fluoride red phosphors also have several drawbacks:[9] 1) these fluorides red phosphors doped with Mn^{4+} could be susceptible to degradation under high temperature and humidity conditions. 2) Mn^{4+} ions are easy to hydrolyze into Mn oxides or hydroxides. 3) In order to synthesize high brightness phosphors, an excess of toxic HF is often employed during the preparation process. Relatively, Eu^{3+} β-diketonate complexes are a kind of promising red-emitting phosphors, because they show wide excitation band in the UV region, strong emission intensity, and high quantum yield.[10-12] For example, the complex [Eu(DBM)$_3$(phen)] is one of the famous red-emitting Eu^{3+}-based molecular phosphors with high quantum yield.[13-17] However, a major disadvantage of this kind of complex is their low photochemical stability under ultraviolet irradiation. Meanwhile, this kind of complex shows weaker absorption band in blue region, which is not suitable for blue-emitting GaN LED chip.

There are two traditional approaches to achieve visible light excitation. One is to introduce a 4*d*- or 5*d*- transition metal ion into the Eu(III) complex. Unfortunately, the photoluminescence efficiency of this kind of Eu(III) complexes is always very low. The other strategy is to synthesize Eu^{3+} organic complexes with a suitably expanded π−conjugated system in molecule so that the excitation wavelength shows red-shift. Some researchers have done some good jobs to expand π−conjugated system using the ligands Michler's ketone, phenalenone and tridentate in Eu(III) complexes.[18-21] Using the carbazole group, our group has synthesized a novel dinuclear Eu^{3+} organic complex with longer π−conjugated system.[22]

To the best of our knowledge, strong π−stacking interactions between aromatic ligands can produce a significant bathochromic-shift in fluorescent excitation and UV-vis spectra of the complexes.[23-27] And the intramolecular π−stacking structure has also been found in the lanthanide complexes.[28] Thus, the π−stacking interactions could be used to achieve visible light excitation for the Eu(III) complexes. In this work, three europium complexes with aromatic ligands were synthesized with 2,7-

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bis(4'4'4'-trifluoro-1,3-dioxobutyl)-(9-ethyl-9*H*-carbazole) (2,7-BTFDBC) and/or dibenzoylmethane (DBM) as the first ligand, and 1, 10-phenanthroline (Phen) as the second ligand. The broad excitation bands in blue region have been observed for the as-synthesized complexes. The thermal stability and photoluminescence (PL) properties of the synthetic complexes were also investigated. At last, the single red LED was fabricated by combination of the synthetic Eu(III) complex with a ~460 nm-emitting GaN chip.

Experimental

Materials and characterization. All reagents and chemicals are analytical grade, purchased from commercial sources, and used without further purification unless otherwise stated.

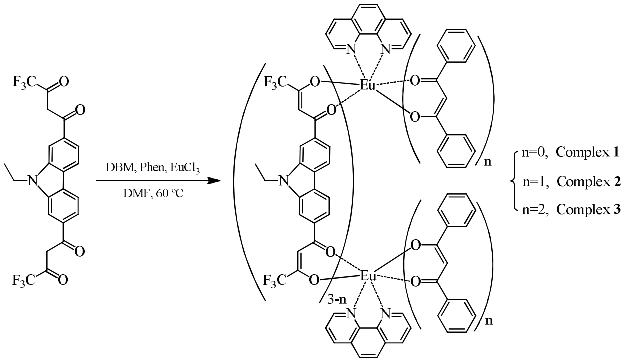
Elemental analyses (EA) for the synthesized Eu(III) complexes were carried out on Germany Vario EL III Elemental Analysis Instrument. Mass spectra (MS) were obtained on a Bruker amaZon SL liquid chromatography mass spectrometer (LC-MS) with an electrospray ionization (ESI) interface using methanol as matrix solvent. Ultraviolet-visible (UV-vis) absorption spectra were measured on an Agilent HP8453E spectrophotometer. Infrared spectra were recorded using a Fourier transform infrared spectrometer (IS10). The excitation and emission spectra of the phosphors were recorded on a JOBIN YVON FL3-21 spectrofluorometer at room temperature and a 450 W xenon lamp was used as excitation source. Thermogravimetric analysis (TGA) was carried out up to 700 °C in N_2 atmosphere with a heating speed of 10.0 K/min on a NETZSCH STA 449F3 thermogravimetric analyzer. The emission spectrum of the red LED was recorded on Labsphere Inc. LED-1100.

Synthesis of the organic ligand 2,7-BTFDBC and the Eu(III) complexes 1-3. The ligand 2,7-bis(4'4'4'-trifluoro-1,3-dioxobutyl)-(9-ethyl-9*H*-carbazole) (2,7-BTFDBC) was synthesized according to our previous work.[10] Scheme 1 depicts the structures and synthesis route of the Eu(III) complex **1**-**3**. For synthesis of the Eu(III) complexes, 2,7-BTFDBC and DBM were used as the first ligand, and Phen as the second ligand. The raw materials including 2,7-BTFDBC, DBM, Phen and $EuCl_3$ (the molar ratio of 3:0:2:2/2:2:2:2/1:4:2:2, respectively) were dissolved in N,N-dimethylformamide (DMF) solution. Then the pH value of the solution was carefully adjusted to 7.0–8.0 by dropping the concentrated triethylamine. Followed by stirring for 6 h at 60 °C, the solution was cooled to room temperature. Then, the products were collected from the solution on a vacuum filter by washing with water and ethanol alternately. At last, the yellow powder was obtained after the products at 60 °C in a vacuum drying oven for 24 h.

The complex $Eu_2(2,7\text{-BTFDBC})_3Phen_2$ (complex **1**) Yield 53.3%, FT-IR (KBr): υ= 1611; 1567; 1529; 1461; 1277; 1128 cm^{-1}; Element Anal, Calculated for $C_{90}H_{55}Eu_2F_{18}N_7O_{12}$(%): C, 52.15; H, 2.66; N, 4.73. Found(%): C, 52.44; H, 2.42; N, 4.88.

The complex $Eu_2(2,7\text{-BTFDBC})_2(DBM)_2Phen_2$ (complex **2**) Yield 77.45% FT-IR (KBr, cm^{-1}): υ= 1606; 1560; 1519; 1463; 1277; 1127; Element Anal, Calculated for $C_{98}H_{64}Eu_2F_{12}N_6O_{12}$(%): C, 57.42; H, 3.12; N, 4.10. Found(%): C, 57.24; H, 3.30; N, 4.38.

The complex $Eu_2(2,7\text{-BTFDBC})(DBM)_4Phen_2$ (complex **3**), Yield 65.40%. FT-IR (KBr,cm^{-1}): υ= 1603; 1530; 1517; 1464; 1271; 1126; Element Anal, Calculated for $C_{106}H_{73}Eu_2F_6N_5O_{12}$(%): C, 62.81; H, 3.60; N, 3.46. Found(%): C, 62.61; H, 3.90; N, 3.34.



Scheme 1. Structure and synthesis procedure of the Eu(III) complexes 1-3

Theoretical calculation. The ground state geometries of the Eu^{3+} complex **3** were calculated using both the density functional theory (DFT) and semiempirical method. The molecular coordinates of $[Eu_2(2,7\text{-BTFDBC})(DBM)_4(Phen)_2]$ from theoretical calculations are listed in ESI†**.** DFT calculations were performed using Gamess suite of program without symmetry restrict.[29] The large core effective core potential (LC-ECP) as well as the corresponding basis set suggested by Dolg et al. was used for europium.[30,31] For valence orbitals, the (7s6p5d)/ [5s4p3d] basis set was used.[32] All-electrron basis set 6-311+G(d, p) has been used for F, O, C, N and H.

The semiempirical calculations on the ground state geometries of the Eu(III) complex **3** were carried out using Sparkle/PM7 model implemented in MOPAC2012 program.[33] The MOPAC keywords used in the Sparkle/PM7 calculations were: PRECISE, GEO-OK, GNORM=0.25, SCFCRT=1.D-10 (in order to increase the SCF convergence criterion) and XYZ (the geometry optimizations were performed in Cartesian coordinates).

Using the intermediate neglect of differential overlap/spectroscopic-configuration interaction (INDO/S-CI) method[34.35] implemented in the ZINDO program,[36] we have calculated the electronic excited states and oscillator strengths of the Eu(III) complex **3** by the representation of Eu(III) with a point charge of +3e. The results were transformed via the SWizard program (Version 4.6)[37] into each UV spectrum using Gaussian functions with half-widths of 3000 cm^{-1}.

Fabrication of red LED devices. The LEDs devices were fabricated by combing GaN chips (~460 nm) with the mixture of as-synthesized complexes and epoxy resin (the ratio of mass is 1:15). Firstly, the mixtures of europium(III) complex and epoxy resin was coated on GaN chip and solidified. Then the device was packaged with epoxy resin and solidified at 150 °C for 1 h.

Results and discussion

UV-vis absorption spectra

UV-visible absorption spectra of the free ligands (2,7-BTFDBC, DBM, Phen), and their corresponding Eu(III) complexes in C_2H_5OH solution (1.0×10^{-5} mol·L^{-1}) are shown in Figure 1. The similar absorption peaks, located at 228, 264 and 350 nm, are observed after the coordination of the Eu(III). This indicates that the Eu(III)-coordination does not influent significantly on the π–π* transitions of the free ligands. On the other hand, the complex **3** exhibits the highest intensity, which are attributed to the increase of DBM. This suggests that DBM in complex **3** is a good alternative for the ancillary ligand.

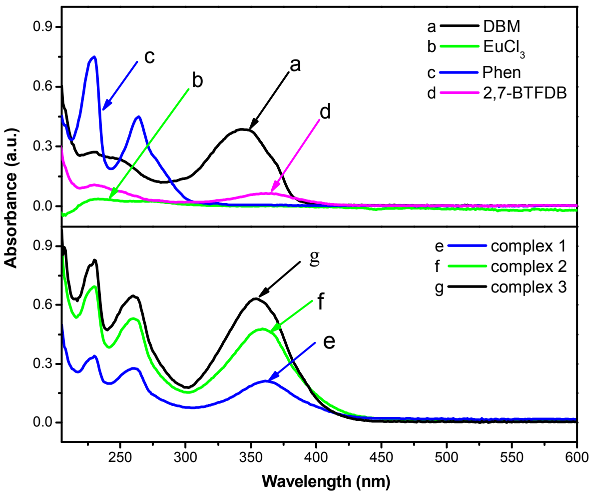


Fig.1 UV-visible absorption spectra of europium(III) complexes **1-3** , ligands (2,7-BTFDBC, DBM, Phen) and $EuCl_3$ in C_2H_5OH solution of 1.0×10^{-5} mol/L.

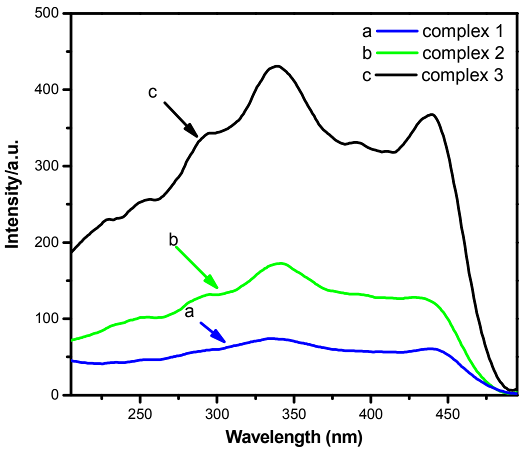


Fig.2 Excitation spectra of europium (III) complexes (**1-3)** powders by monitoring 612 nm emission.

Photoluminescence properties

To investigate the PL properties of the complexes **1-3**, their powders excitation spectra by monitoring 612 nm emissions are recorded as shown in Figure 2. All excitation spectra exhibit a broad band between 200 nm and 500 nm, which could be attributed to the large π–conjugated system.[11] Interestingly, the excitation intensity in the excited band has been remarkably enhanced after the ligand DBM was introduced, and reach highest intensity in complex **3**.

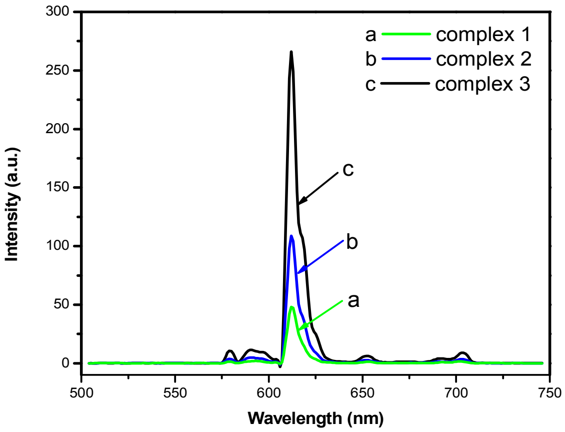


Fig.3 Emission spectra of europium(III) complexes powders excited by 440 nm light.

The emission spectra of the synthetic complexes **1**-**3** are also measured by fixing 440 nm as the excitation wavelength (Figure 3). The intensity of emission peaks in the vicinity of 612 nm is remarkably enhanced after the ligand DBM was introduced, and reach highest value in complex **3**. This enhanced intensity of the transition band ($^5D_0 \rightarrow {}^7F_2$) indicates that the double β-diketone ligands complex **3** can stimulate Eu^{3+} occurring the emission of bright red light.[38] The CIE coordinates according to the emission spectra of complex **3** is calculated to be (x = 0.666, y = 0.334), which is very close to the NTSC (National Television Standard Committee) standard values for red (x = 0.67, y = 0.33). This result suggests that complex **3** can be performed in the application of some special fields excited by long wavelength light, such as a red phosphor in blue light excited LEDs.

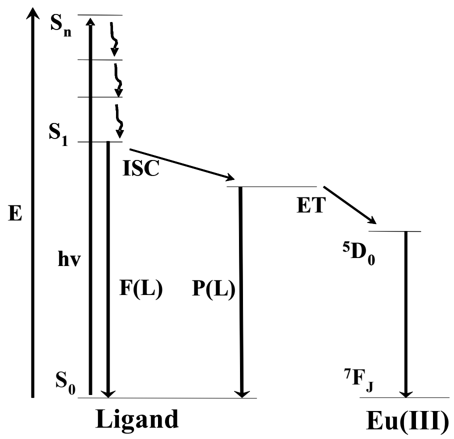


Fig. 4 Schematic representation of the photophysical process of the Eu(III) complexes.

Besides, Figure 3 also shows that all complexes have a similar emission spectra, and five characteristic emission peaks with different intensity can be observed in 578 nm, 591 nm, 612 nm, 652 nm, 704 nm, corresponding to the Eu^{3+} energy level transition of $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$, respectively. The photophysical process in the Eu(III) complex can be called a ligand-sensitized luminescence process (antenna effect), and is schematically represented in Figure 4.

Theoretical calculation

The molecular geometry and electronic absorption spectrum of the complex **3** have been calculated using theoretical calculation approaches. The DFT and semiempirical calculation (Sparkle/PM7) give the coincident predictions for the structure of the complex **3** (Figure 5). Each Eu(III) ion is coordinated with eight atoms, including six oxygen atoms (two of which are from the -biketonate ligand 2,7-BTFDBC, four of which are from two DBM ligands), and two nitrogen atoms from the ligand Phen. The coordination structure of the central Eu(III) can be best described as a distorted square antiprism. It is in line with the coordination chemistry of Eu(III) with eight coordinated structure.[39] The electronic absorption spectrum (red line), simulated by ZINDO/S based on the theoretical structure, is overlaid with the experimental result (black line) in Figure 6. The oscillator strengths and λ_{max} are close to the experimental data, indicating that the predicted molecular geometries of the complex **3** are reasonable.

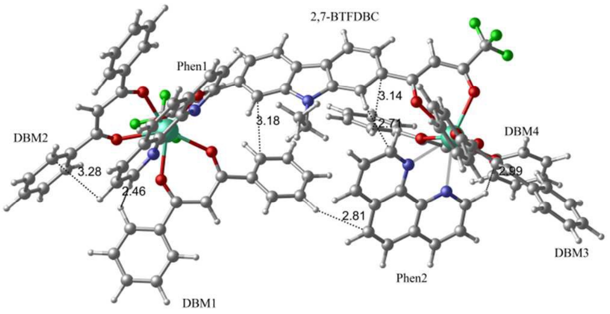


Fig. 5 The stacking interactions in global minimum energy structure observed from the theoretical calculations on the complex **3**. Color code: blue, N; gray, C; red, O; white, H.

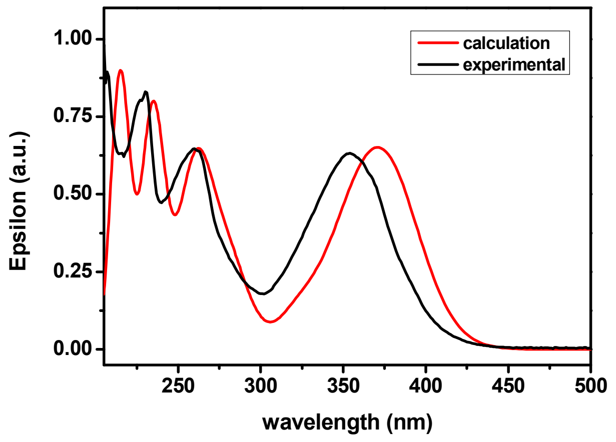


Fig. 6 The comparison of the absorption spectra of the complex **3** from theoretical calculation and experimental results

Meanwhile, the approximate distances among the ligands (Phen, DBM, and 2,7-BTFDBC) in complex **3** are the region between 2.57 and 3.89 Å (Table 1), which indicates that there are some kinds of π–stacking structures.[40] Furthermore, two types of π–stacking among these ligands can be observed in complex **3**: T-shaped and parallel dispalced.[40] Interestingly, the ligand Phen in the complex 3 formed obvious π–stacking structure with DBM and 2,7-BTFDBC: one parallel dispalced and two T-shaped. The π–stacking structures of Phen can effectly stablize the coordination structure, which can improves the thermal stability for the complex **3**. More importantly, the π–stacking effect can produce a significant spectral bathochromic-shift in fluorescent excitation spectra, due to the lowing effect for the energy of excited states. This bathochromic-shift effect has been observed in the Table 1. On the other hand, the remarkable enhancement intensity in excited and emission spectra can be understood by the modification of the electron density of the ligand 2,7-BTFDBC. Compared with the complex **1**, the π–stacking effect in complex **3** leads to increasing the electronic density in the carbazole ring, and thus increases the electron transition probability. Therefore, the excitation and emission intensity are enhanced coincidently.

Table 1. The approximate distance and types of π–stacking among the ligands of **3**

	Distance (Å)	Types of π–stacking
Phen1–DBM1	2.46	T-shaped
Phen1–DBM2	3.28	parallel dispalced
DBM1–2,7-BTFDBC	3.18	parallel dispalced
Phen2–DBM1	2.81	T-shaped
DBM4–2,7-BTFDBC	3.14	parallel dispalced
Phen2–DBM4	2.99	T-shaped
Phen2–2,7-BTFDBC	2.71	T-shaped

Thermal stability

High thermal stability is an important requirement for most applications, especially in the LEDs. Then the thermal stability of the complex **3** with the highest emission intensity was investigated by the thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) curves. The result in Figure 7 indicates that the decomposition temperature of the complex **3** is 363.5 °C, which is high enough for the luminescence application on GaN LEDs.

Fabrication and electro-luminescence of red LEDs

For the sake of further investigation the potential application of the ternary complex **1**-**3**, all the complexes were used as red phosphor for fabrication of red LEDs. The emission spectra and photographs of original ~460 nm LED without phosphors (a) and with the complex **1**-**3** (b-d) under 20 mA forward bias are shown in Figure 8. The peak at ~460 nm can be attributable to the emission of GaN chip, while the sharp and intense red-emission peak at 612 nm is due to the emission of the complex **1**-**3**. This result indicates that the blue light emitting from the

GaN chip has been efficiently absorbed and transferred to the central Eu^{3+} ions by the ligands in the complexes, so Eu^{3+} ion characteristic red light-emitting is observed. The most important observation is that the intensity of the emitting red-light increases remarkably with the increase of the ligand DBM in the synthetic Eu(III) complexes 1-3. Thus, the complex **3** ($[Eu_2(2,7\text{-BTFDBC})(DBM)_4(Phen)_2]$) can be used as a good component in the fabrication of white LEDs excited by ~460 nm LED chip.

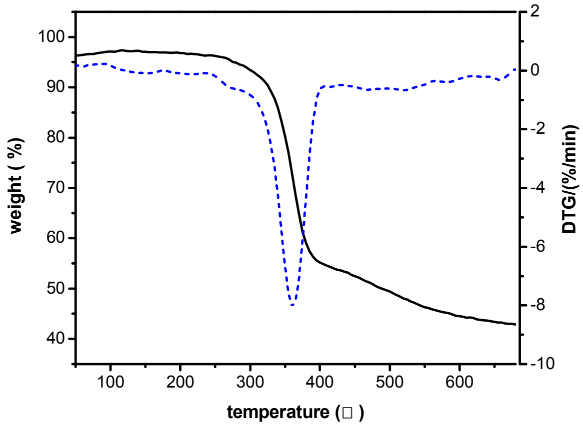


Fig. 7 TG and DTG curves of the complex **3** in N_2 atmosphere.

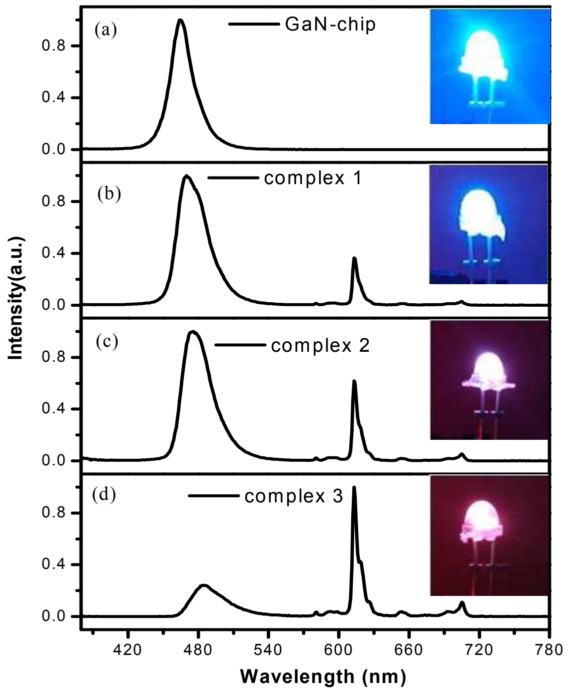


Fig. 8 Emission spectra and photographs (right) of the initial GaN-LED without phosphor (a) and LED with phosphors **1**-**3**, respectively (b-d).

Conclusions

We have synthesized a series of europium(III) complexes $[Eu_2(2,7\text{-BTFDBC})_{3-n}(DBM)_{2n}Phen_2]$ (n = 0, 1, or 2), in order to examine the effects of having intramolecular π−stacking interactions on the photoluminescence properties. The complex $[Eu_2(2,7\text{-BTFDBC})(DBM)_4(Phen)_2]$ exhibits the highest emission intensity with visible-light excitation. The theoretical calculation results confirm that the pendant phenyl domains in this complex engage in multiple π-stacking interactions, including T-shaped and parallel displaced stacking. Thus, the intramolecular π−stacking interactions can cause high emission intensity with visible-light excitation in europium(III) complexes, while will help to provide a new way to designed an efficiently red phosphor with the visible light excitation.

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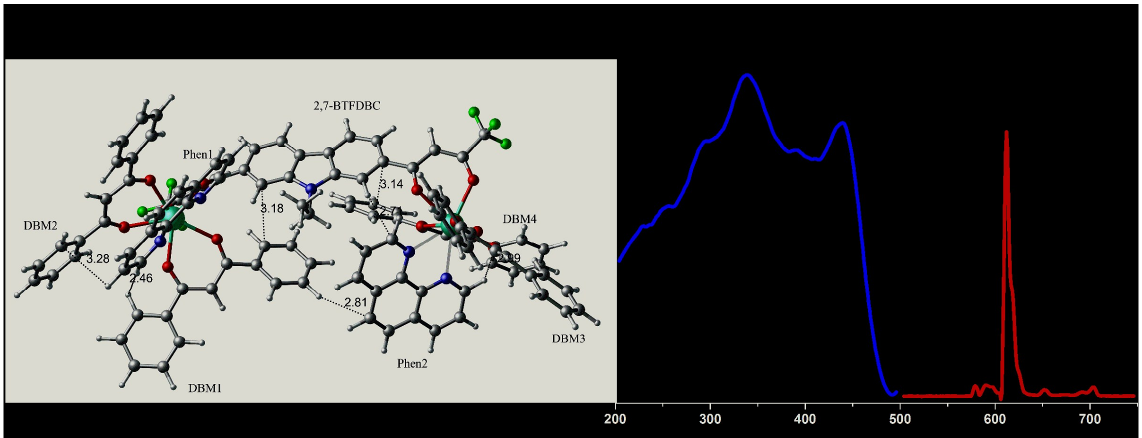
Graphical Abstract

The europium(III) complex [Eu_2(2,7-BTFDBC)$(DBM)_4(Phen)_2$] with multiple T-shaped and parallel-dispalced π–stacking interactions exhibits intense red emission under blue light excitation with high colour purity.



[Eu_2(2,7-BTFDBC)$(DBM)_4(Phen)_2$]