Research paper

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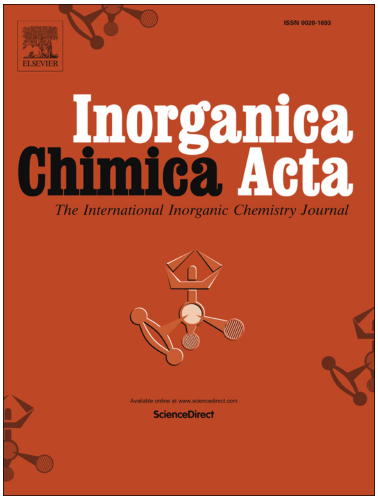

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A Green-Emitting Iridium Complex Used for Sensitizing Europium Ion with High Quantum Yield

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A green-emitting iridium(III) complex Ir(dfppy)$_2$(cbphen) (dfppy = 2-(4',6'-difluoro-phenyl)pyridine, cbphen = 4-carboxylate-phenanthroline) was synthesized and fully characterized. The single crystal data confirm its Ir(C^N)$_2$(N^N) structure with the carboxylate group on phenanthroline stretching freely which could be able to combine with europium(III) ion. The complex was reacted with $EuCl_3 \cdot 6H_2O$ and $Eu(TTA)_3 \cdot 2H_2O$ to provide bimetallic complexes. Through photophysical studies, characteristic emission from Eu^{III} ion was obtained, and meanwhile the green emission from iridium(III) center was almost quenched completely, suggesting this iridium(III) complex is a good sensitizer for ~~these~~ Eu^{III} ions. It is well worth noticing that by introducing the iridium(III) complex as a chromophore, the excitation wavelength of Eu^{III} ion has been extended to the visible range (470 nm). Besides, due to the efficient energy transfer, the quantum yield of ~~of~~ **Ir$_3$-Eu** was nearly equal to that of $Eu(TTA)_3 \cdot 2H_2O$.

Keywords: iridium(III) complex; europium(III) ion; bimetallic complex; visible light excitation; lanthanide; sensitize

1. Introduction

Lanthanide complexes as a brilliant group of luminescent materials due to their special f-f transition with narrow line-like emissions, and long luminescent lifetimes [1, 2], have received considerable attention due to their potential use in organic light-emitting diodes (OLED) [3-10], analytical probes [11-16], and biological sensing and imaging [17-24]. Because of the low absorption coefficient of lanthanides resulting from the f-f forbidden transitions, intense luminescence of lanthanide is usually achieved from indirect excitation of light harvesting chromophores (termed the ‘antenna effect’) [25-27]. Although abundant antennas have been reported for decades, new sensitizers are still craved for a deep understanding of the lanthanide photophysics [28]. The traditional antennas are usually pure organic molecules with absorption in the UV region, which does not match well with the lanthanide energy level, especially for the red-emitted Eu^{III} ions and near infrared lanthanide ions (Nd^{III}, Er^{III}, Yb^{III}). It does not only cause a waste in energy, but will also increase the damage to the organisms when the materials are applied in labeling. Many efforts are made to expand the excitation of lanthanide ions, such as Wang’s great improvement in the singlet pathway for the sensitization of europium(III) luminescence [29]. Another well-known way is introducing transition-metal-based ligands (Ir^{III}, Ru^{II}, Re^{I}, Pt^{II}, Pd^{II}, etc.) as antennas because these organometallic sensitizers usually have high triplet quantum yields as well as long-lived triplet excited state, which will promote energy transfer to the lanthanide centers [30-32]. Especially, cyclometalated iridium(III) complexes are intriguing in sensitizing Ln^{III} ions due to their tunable MLCT (metal-to-ligand charge-transfer) transitions and high quantum efficiency [33-35], which makes it not so difficult to achieve energy match between the donor and lanthanide acceptor. The first iridium(III) complexes used as an antenna was reported by De Cola and co-workers using 5-(2-pyridinyl)-1,2,4-triazole-3-carboxylic acid as a bridging ligand for sensitizing europium(III) ion

[36]. Due to the partial energy transfer, white emission was detected resulting from the mixture of the cyan emission (Ir^{III} center) and red emission (Eu^{III} ion).

Our group has made a lot of progress in studying Ir^{III}-Ln^{III} dyads, including Ir^{III}-Eu^{III} [37-40], and Ir^{III}-Ln^{III} (Ln=Nd, Er, Yb) [41-43] complexes. Among them, the most brilliant iridium(III) complex, Ir(dfppy)$_2$(phen5f), with 4,4,5,5,5-pentafluoro-1-(1′,10′-phenanthrolin-2′-yl)pentane-1,3-dione (Hphen5f) as the bridging ligand, was shown to achieve effective energy transfer from Ir^{III} complex to Eu^{III} center [37]. During our research, we found that for the cyclometalated iridium complex, the cyclometalating ligand (2,4-difluoro)phenylpyridine (dfppy) is more suitable for sensitizing Eu^{III} ions than ppy (1-phenylpyridine) [39]. The energy level of the Ir^{III} complex is considered to be the most important factor affecting the luminescence efficiency [43]. And complete energy transfer will occur only when the triplet energy level of the linking ligand was lower than the ^{3}MLCT energy level of the Ir^{III} moiety and higher than the ^5D_J level of Eu^{III} ion [38]. Furthermore, for Ir^{III}-Eu^{III} bimetallic complexes, the discrepancy in their quantum yields can be explained by the nonradiative relaxation of the excited energy of Eu^{III} ion [40].

However, among the lots of iridium(III) complexes reported for sensitizing europium(III) ion, few of them show both an obvious luminescence emission at room temperature and suitable energy levels to achieve total energy transfer, even for Ir(dfppy)$_2$(phen5f) [37] or its analogs Ir(dfppy)$_2$(phen3f), Ir(dfppy)$_2$(bpy5f), Ir(dfppy)$_2$(bpy3f) [40]. Luminescent iridium(III) complexes with suitable energy level to sensitize Eu^{III} ion are desirable because there will be an obviously visible change in luminescence outputs, which is particularly welcome in analytical probes field [44]. Therefore, with dfppy as the cyclometalating ligand, we modulated the ancillary ligand phen5f to cbphen (cbphen = 4-carboxylate-phenanthroline), to synthesize a novel iridium(III) complex, Ir(dfppy)$_2$(cbphen). The iridium(III) complex was characterized with well-defined X-ray structure~~ to sensitize the red luminescence of Eu^{III} ion~~. Photophysical results show that it has a suitable triplet energy level to match the excited states of Eu^{III} ion and intense red emission of the Ir^{III}-Eu^{III} bimetallic complexes was found with high quantum yield.

2. Experimental

2.1. Materials and methods

All reagents and solvents were analytical grade. 2-(4’,6’-Difluoro-phenyl)pyridine (dfppy) [45], phenanthroline-4-carboxylic acid (Hcbphen) [46] and Eu(TTA)$_3$·2H$_2$O [47] were prepared and purified according to previous literatures. Cyclometalated iridium(III) dimer (dfppy)$_2$Ir(μ-Cl)$_2$Ir(dfppy)$_2$ was synthesized through the Nomoyama route, by refluxing IrCl$_3$·3H$_2$O with 2.2 equiv of dfppy in 2-ethoxyethanol mixed with water (3:1) for 24 h [48].

The ^{1}H NMR spectra were measured on an ARX-400 NMR (Bruker) spectrometer. The chemical shift data of each compound were reported in ppm units with tetramethylsilane as the internal reference. Elemental analysis (C, H, N) was performed on an Elementar Vario MICRO CUBE. High-resolution mass spectra were measured on a Bruker Apex IV FTMS. The X-ray diffraction data were collected on a Rigaku MicroMax-007 CCD diffractometer using graphite-monochromated Mo/KR (λ = 0.71073 Å) radiation. Full crystallographic data are provided in CIF file as Supporting Information and are available from the Cambridge Crystallographic Data Centre (CCDC-764289). A Shimadzu UV-3100 spectrometer was used to detect the UV–vis absorption spectra. The photoluminescence (PL) spectra and lifetime data were obtained on an Edinburgh Analytical Instruments FLS920 spectrometer. The solvents employed in photophysical experiments were spectroscopic grade. Luminescence quantum yields (Φ) in different solvents were measured at room temperature with an aerated aqueous solution of [Ru(bpy)$_3$]Cl$_2$ (Φ_r =

0.028) as a standard [49].

2.2. Synthesis

Ir(dfppy)$_2$(cbphen) The suspension of phenanthroline-4-carboxylic acid (Hcbphen, 0.44 mmol) in CH_3OH (15 ml) was mixed with a solution of (dfppy)$_2$Ir(μ-Cl)$_2$Ir(dfppy)$_2$ (0.2 mmol) in CH_2Cl_2 (15 ml). Excessive Na_2CO_3 (1 mmol) was added to the reaction mixture which was then heated to reflux under stirring for 4 h. After cooled to room temperature, the solvent was removed under reduced pressure. The residue was then purified through a silica column with CH_2Cl_2/CH_3OH (1:1) for the elution and a green-yellow solid was collected as pure product with a yield of 81%. ^{1}H NMR (400MHz, $CDCl_3$): δ 9.11 (1H, d, *J* = 9.0 Hz), 8.78 (1H, d, *J* = 8.1 Hz), 8.30 (2H, d, *J* = 8.4 Hz), 8.23 (1H, d, *J* = 4.2 Hz), 8.19-8.14 (3H, m), 7.89-7.86 (1H, td, *J* = 3.1 Hz, *J* = 6.6 Hz, *J* = 13.2 Hz), 7.75 (2H, t, *J* = 7.9 Hz, *J* = 15.7 Hz), 7.36 (1H, d, *J* = 4.9 Hz), 7.19 (1H, d, *J* = 5.5 Hz), 6.93 (1H, t, *J* = 6.2 Hz, *J* = 12.4 Hz), 6.87 (1H, t, *J* = 6.2 Hz, *J* = 12.4 Hz), 6.63-6.57 (2H, m), 5.82-5.79 (1H, dd, *J* = 2.3 Hz, *J* = 8.2 Hz), 5.75-5.73 (1H, dd, *J* = 2.3 Hz, *J* = 8.2 Hz). Anal. Found for $C_{35}H_{19}IrF_4N_4O_2 \cdot H_2O$: C, 51.49; H, 2.69; N, 6.92. Calcd: C, 51.66; H, 2.60; N, 6.88. HRMS (ESI$^+$, CH_3OH) calcd for $C_{35}H_{20}IrF_4N_4O_2$, 797.1152 ($[M+H]^+$); found, 797.1145.

Ir(dfppy)$_2$(cbphen) was refluxed with $EuCl_3 \cdot 6H_2O$ (for **Ir$_3$-Eu**) or Eu(TTA)$_3 \cdot 2H_2O$ (for **Ir-Eu**) in EtOH for about 6 h. After cooled to room temperature, the solvent was removed under reduced pressure and the solid left was recrystallized with CH_2Cl_2/*n*-hexane to offer the final Ir^{III}-Eu^{III} bimetallic complexes.

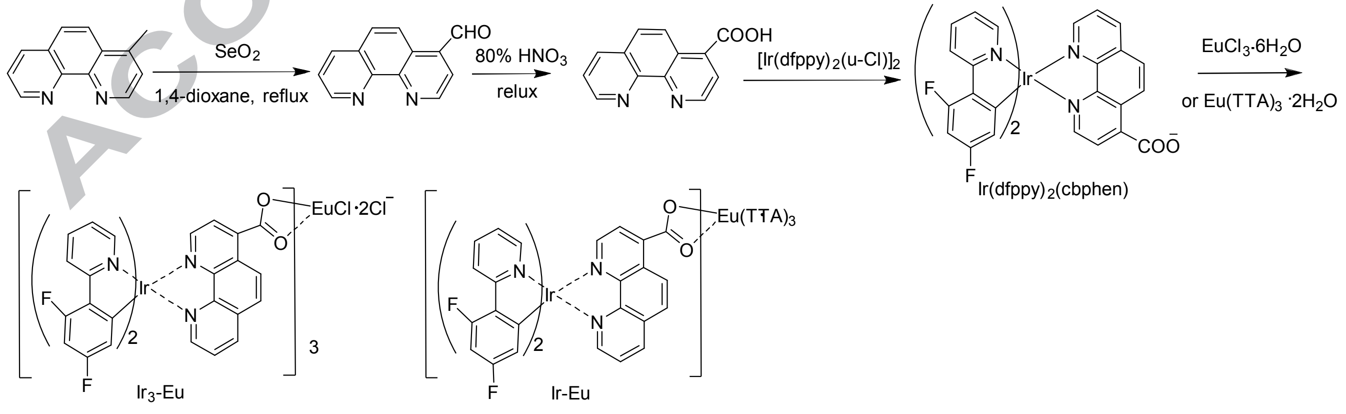
{[Ir(dfppy)$_2$(cbphen)]$_3$ClEu}Cl$_2$ (Ir$_3$-Eu) Yield 84%. Anal. Found for $C_{105}H_{57}Cl_3EuF_{12}Ir_3N_{12}O_6 \cdot 2H_2O$: C, 46.44; H, 2.92; N, 6.10. Calcd: C, 46.71; H, 2.35; N, 6.23. HRMS (ESI$^+$, CH_3OH) calcd for $C_{105}H_{57}Cl_2EuF_{12}Ir_3N_{12}O_6$, 2610.1820 ($[M-Cl]^+$); found, 2610.2421.

Ir(dfppy)$_2$(cbphen)Eu(TTA)$_3$ (Ir-Eu) Yield 90%. Anal. Found for $C_{59}H_{31}EuF_{13}IrN_4O_8S_3\cdot H_2O$: C, 43.44; H, 2.15; N, 3.60. Calcd: C, 43.49; H, 2.04; N, 3.44. HRMS (ESI$^+$, CH_3OH) calcd for $C_{51}H_{27}EuF_{10}IrN_4O_6S_2$, 1389.0031 ([M-TTA]$^+$); found, 1389.0047.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 shows the general synthesis route of the iridium(III) complex and Ir^{III}-Eu^{III} bimetallic complexes concerned in this work. The purchased 4-methyl-1,10-phenanthroline was oxidized by SeO_2 in a solvent of 1,4-dioxane mixed with water (96:4, v/v). The obtained 1,10-phenanthroline-4-carbaldehyde was further oxidized by 80% HNO_3 to form the ligand, 1,10-phenanthroline-4-carboxylic acid (Hcbphen). HNO_3 with a concentration of lower than 70% could seriously reduce the yield. The ligand Hcbphen was refluxed with the cyclometalated dimers (dfppy)$_2$Ir(μ-Cl)$_2$Ir(dfppy)$_2$ in a mixture of CH_3OH and CH_2Cl_2 (1:1, v/v) in the presence of excessive Na_2CO_3 to give the complex Ir(dfppy)$_2$(cbphen). The Ir^{III}-Eu^{III} bimetallic complexes were obtained by reacting Ir(dfppy)$_2$(cbphen) with corresponding $EuCl_3\cdot 6H_2O$ (for **Ir$_3$-Eu**) or Eu(TTA)$_3\cdot 2H_2O$ (for **Ir-Eu**) in EtOH. All the products were characterized through ^{1}H NMR, high-resolution mass spectrometry and elemental analysis.



Scheme 1 Synthetic procedure of the Ir(dfppy)$_2$(cbphen) and Ir^{III}-Eu^{III} bimetallic complexes

3.2. X-ray crystal structure of Ir(dfppy)$_2$(cbphen)

The single crystal of Ir(dfppy)$_2$(cbphen) was obtained by slowly evaporating solvent from a CH_2Cl_2/acetone/*n*-hexane solution of Ir(dfppy)$_2$(cbphen). X-ray crystallographic structure is shown in Fig. 1 and crystallographic data are listed in Table 1. Just as we expected, the two nitrogen atoms on Hcbphen coordinate well with the centered iridium(III) ion because of the strong affinity of Ir to N, while the carboxyl group unfolds freely. The hydrogen atom on the carboxyl is lost to meet the need of electroneutrality of the molecule. Due to the electronic delocalization, the two bond lengths of O(1)-C(35) (1.240 Å) and O(2)-C(35) (1.205 Å) are averaged, though the former is still a little longer because of the attraction of the H atom on C(27) to O(1). The bond lengths between Ir and N on cbphen group are about 2.151 Å and 2.144 Å for Ir(1)-N(3) and Ir(1)-N(4) respectively, while the bond lengths between Ir and N on dfppy are about 2.040 Å and 2.054 Å for Ir(1)-N(1) and Ir(1)-N(2) respectively. So the distance between Ir and cbphen is longer than that between Ir and dfppy because of the trans effect of the C donor in dfppy (bonds trans to C atoms are longer than bonds trans to N atoms due to the sigma donation of the carbons) [50, 51]. In the octahedral geometry of Ir center, N atoms from C^N ligands adopt trans-configuration which was popular in many studies of Ir(C^N)$_2$(LX) complexes. The angles for N(1)-Ir(1)-C(11), C(22)-Ir(1)-N(2) and N(4)-Ir(1)-N(3) all deviate from 90°, while those for C(11)-Ir(1)-N(3), C(22)-Ir(1)-N(4) and N(1)-Ir(1)-N(2) deviate from 180 °, meaning the Ir^{III} ion is centered at a distorted octahedron.

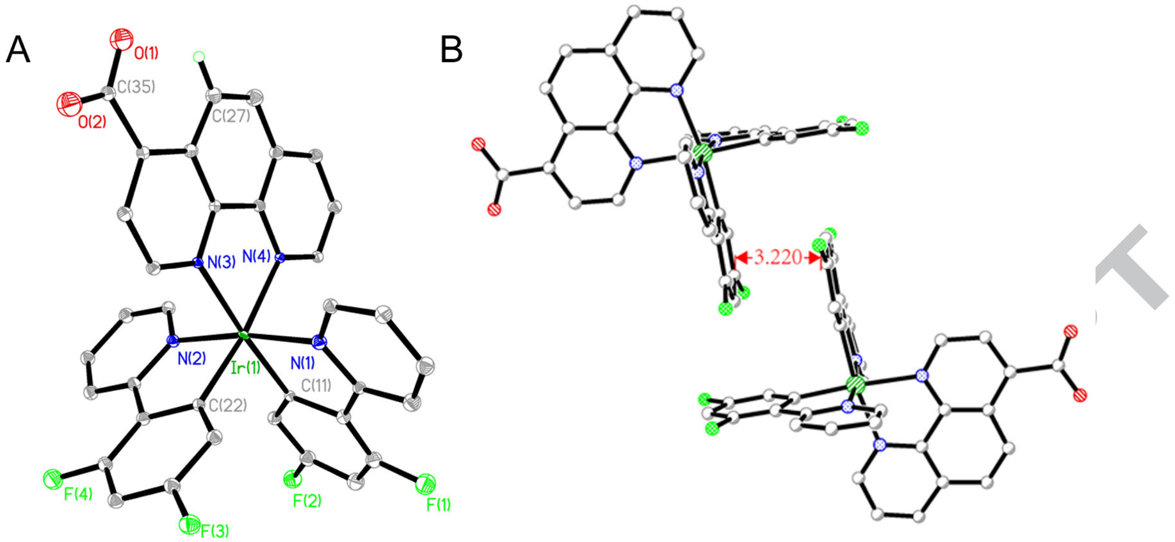


Fig. 1 (A) X-ray crystal structure and (B) molecule packing of Ir(dfppy)$_2$(cbphen), with thermal ellipsoids drawn at the 30% probability level. H atoms and solvent molecules were omitted for clarity.

Table 1 Crystal data and structure refinement for Ir(dfppy)$_2$(cbphen)

complex	Ir(dfppy)$_2$(cbphen)
empirical formula	$C_{35}H_{19}F_4IrN_4O_2$
crystal system	Triclinic
space group	P_1
a (Å)	8.6184(17)
b (Å)	10.262(2)
c (Å)	17.387(3)
α (deg)	104.93(3)
β (deg)	97.47(3)
γ (deg)	102.02(3)
V (Å^3)	1425.5(5)
Z	2
ρ (calcd) (g·cm^{-3})	1.854
F(000)	772
θ range (deg)	2.47-25.02
GOF on F^2	0.803
Final R indices [I>2sigma(I)]	R1 = 0.0576, wR2 = 0.1455
R indices (all data)	R1 = 0.0608, wR2 = 0.1487

Table 2 Selected bond lengths (Å) and angles (°) of Ir(dfppy)$_2$(cbphen)

Ir(1)-N(1)	2.040(8)	O(2)-C(35)	1.205(11)
Ir(1)-N(2)	2.054(7)	N(1)-Ir(1)-C(11)	80.5(3)
Ir(1)-N(3)	2.151(7)	C(22)-Ir(1)-N(2)	80.5(3)
Ir(1)-N(4)	2.144(7)	N(4)-Ir(1)-N(3)	77.0(3)
Ir(1)-C(11)	2.031(9)	C(11)-Ir(1)-N(3)	176.1(3)
Ir(1)-C(22)	2.023(9)	C(22)-Ir(1)-N(4)	172.2(3)
O(1)-C(35)	1.240(11)	N(1)-Ir(1)-N(2)	171.7(3)

3.3. Photophysical properties of Ir(dfppy)$_2$(cbphen)

The absorption and photoluminescence spectra of Ir(dfppy)$_2$(cbphen) in different solvents are shown in Fig. 2. The intense absorption below 310 nm is assigned to the spin-allowed π-π* transition of the organic ligands. From 310 to 390 nm, weak absorption bands were detected, attributed to the ^{1}MLCT (metal-to-ligand-charge-transfer) of the complex and ^{1}LLCT (ligand-to-ligand-charge-transfer) between different ligands. Furthermore, there is also absorption in the visible region (> 390 nm), which may be resulted from the ^{3}MLCT and ^{3}LLCT of the complex, suggesting a potential in the long-wave excitation [35, 51].

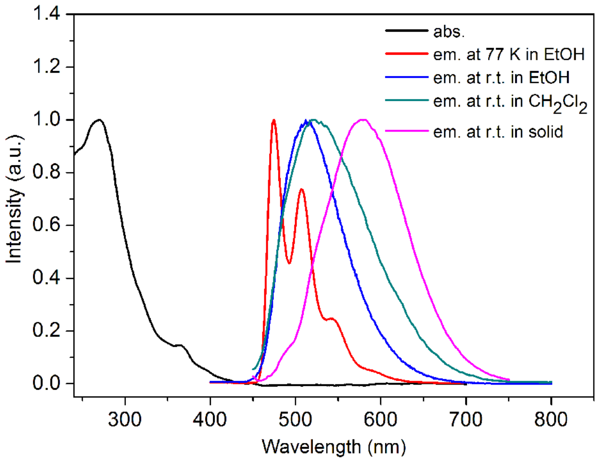


Fig. 2 UV-vis absorption and photoluminescence spectra of Ir(dfppy)$_2$(cbphen) in different solvents

The complex shows typical emission of cyclometalated Ir(dfppy)$_2$(L) in EtOH glass at 77 K [52].

Two intense emission bands at 474 nm and 507 nm indicate the triplet levels of the complex are $T_1 = 21097$ cm^{-1} (τ = 9.75 μs), T_2 =19724 cm^{-1}, respectively. This triplet energy is also similar to Ir(dfppy)$_2$(phen5f) as well as the Ir(dfppy)$^{2+}$ moiety [37], which is suitable for sensitizing Eu^{III} ion ($^5D_1$ = 19000 cm^{-1}, $^5D_0$ = 17500 cm^{-1}). When the temperature rose up to room temperature, a strongly broad band at 512 nm was observed. It is because at low temperature, the transition from T_1 to T_2 was partly restricted, both the emissions from the two states were detected; while at room temperature, the fast reorganization of solvent molecules enhanced the non-radiative transition from T_1 to T_2, so only the emission from the lower vibrational level of T_2 (512 nm) was observed [53, 54].

The emission of the complex at room temperature in CH_2Cl_2 centers at 520 nm, a little red shift to that in EtOH (512 nm), which is contrary to the previous studies that λ_{max} gets longer with the increase in polarity of solvents [53]. In order to explain such a phenomenon and study the excitation states of the complex, TD-DFT analysis was carried out with the result shown in Fig. 3. It suggests that the HOMO orbital mainly localizes on the –COO$^-$ group, and the LUMO is mainly on the phenanthroline of cbphen group. The abnormal distribution of HOMO from other Ir(C^N)$_2$(N^N) complexes may be caused by the strong electron-withdrawing ability of –COO$^-$ group and the electron-deficient phenanthroline, which facilitates the electron density flowing from Ir^{III} ion to –COO$^-$. Thus, the electron density on Ir is lowered to HOMO-3 and –COO$^-$ becomes to be the main distribution area of electrons.

In EtOH, the H atom on the EtOH will bind with –COO$^-$ to form H bond, which will slightly decrease the electron density of HOMO, then enlarging the energy gap. The luminescence lifetime in EtOH and CH_2Cl_2 are 339.2 ns and 392.2 ns, which also indicates the H bond quenches the emission a little more in EtOH. The submicrosecond lifetime reveals the phosphorescent property of the emissions. Furthermore, the red shift of the emission in solid state suggests an obvious π-π stacking in the solid state, which is also confirmed by the X-ray structure shown in Fig. 1B.

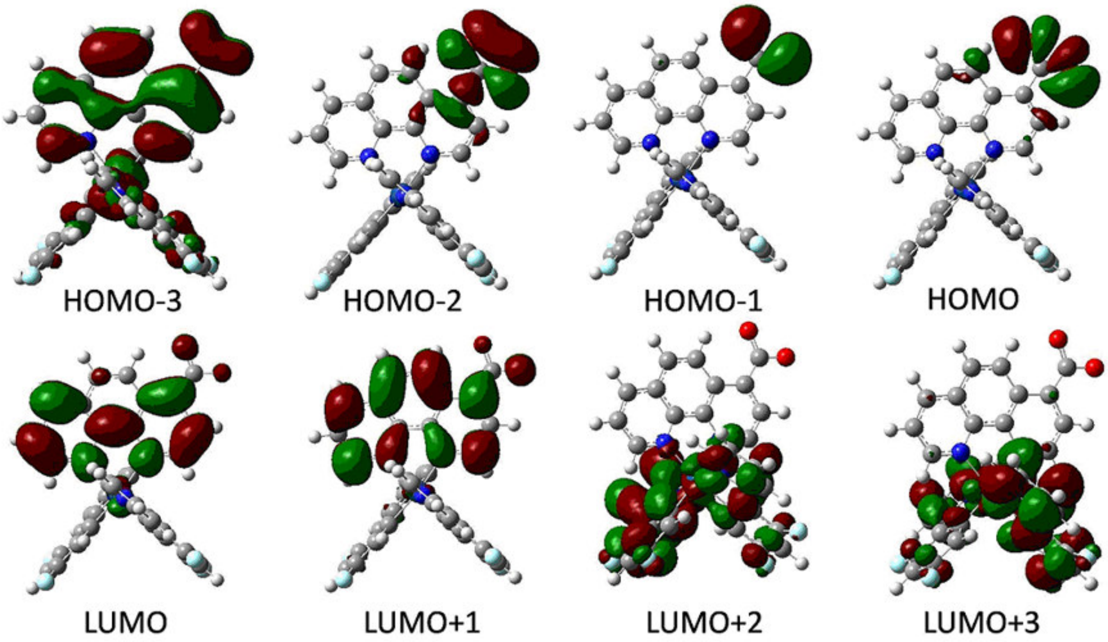


Fig. 3 HOMOs and LUMOs distributions for Ir(dfppy)$_2$(cbphen)

The calculated excitation states in the complex were listed in Table 3. We can see all the emissions in EtOH and CH_2Cl_2 at room temperature can be attributed to the ^{3}LLCT from –COO$^-$ to dfppy, while the higher energy emission at 77 K involves the ^{3}MLCT (Ir→phen) and π→π* transition of phen. That is to say, when the ancillary ligand was modulated from phen5f to cbphen, the enhanced ^{3}LLCT transition results in the strong luminescence of the Ir(dfppy)$_2$(cbphen). On the other hand, the shorter C chain of cbphen than phen5f and its analogs will effectively reduce the luminescence quenching caused by the fast vibration.

Table 3 The calculated excitation states in Ir(dfppy)$_2$(cbphen)

λ_{cal}, nm	E_{cal}, eV	Electron transition orbitals	Excitation state
514	2.41	HOMO-2→LUMO+2 (0.70)	^{3}LLCT
499	2.49	HOMO-2→LUMO+3 (0.70)	^{3}LLCT

453	2.73	HOMO-3→LUMO (0.47) HOMO-3→LUMO+1 (0.39)	^{3}MLCT+^{3}LC

3.4. Photophysical properties of Ir^{III}-Eu^{III} bimetallic complexes

In order to examine the sensitization performance that the iridium(III) complex played on Eu^{III} ion, the photophysical properties of Ir^{III}-Eu^{III} bimetallic complexes together with Ir(dfppy)$_2$(cbphen) and Eu(TTA)$_3$·2H$_2$O were studied in detail. From Fig. 4 it can be found that Eu(TTA)$_3$·2H$_2$O shows no absorption signal in the region > 400 nm. The ^{3}MLCT in Ir(dfppy)$_2$(cbphen) made the two bimetallic complexes with longer-wavelength absorption property. The absorption of **Ir-Eu** is nearly the overlay of Ir(dfppy)$_2$(cbphen) and Eu(TTA)$_3$·2H$_2$O. As to **Ir$_3$-Eu**, the shape of its absorption spectrum is similar to Ir(dfppy)$_2$(cbphen), meaning same transition bands exist in the two complexes; while the molar extinction coefficient (ε) of **Ir$_3$-Eu** is remarkably larger, since there are three Ir(dfppy)$_2$(cbphen) moieties in one **Ir$_3$-Eu** molecule.

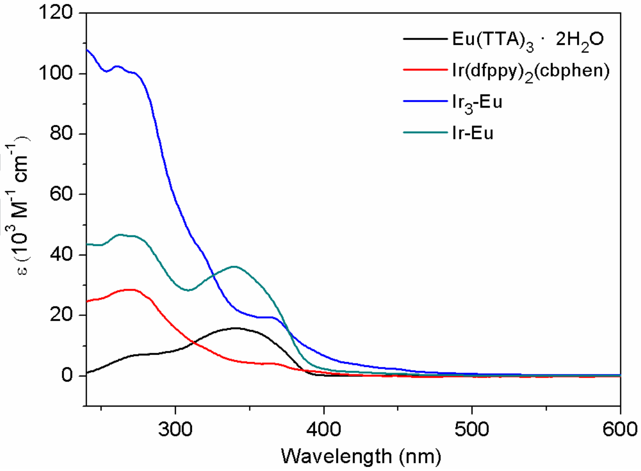


Fig. 4 UV-vis absorption spectra of the complexes in CH$_2$Cl$_2$ at room temperature.

Fig. 5 demonstrates that the excitatiocn spectra of Eu(TTA)$_3$·2H$_2$O and **Ir-Eu** are similar, but the latter shows obvious long-wavelength excitation property because of the introduction of Ir^{III} complex. For the both bimetallic complexes, the excitation window was expanded to about 470 nm.

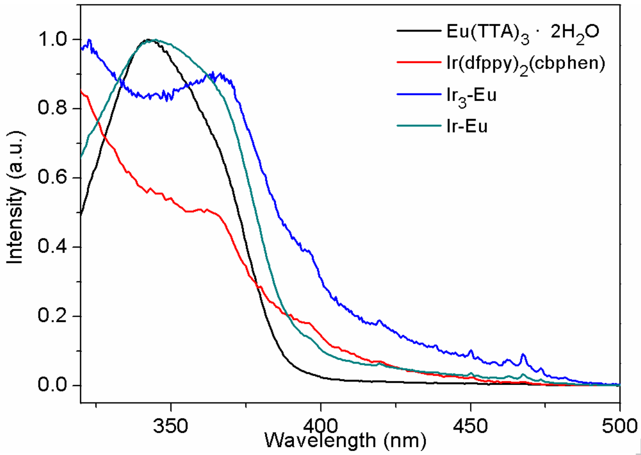


Fig. 5 Excitation spectra of the complexes in CH_2Cl_2 at room temperature.

Fig. 6 shows the luminescence titration spectra of $EuCl_3 \cdot 6H_2O$ into $Ir(dfppy)_2(cbphen)$ in EtOH. It is found that the green emission of $Ir(dfppy)_2(cbphen)$ quenched gradually as the addition of Eu^{III} ion, togerther with the emission of Eu^{III} ion at 615 nm ($^5D_0 \rightarrow {}^7F_2$) rising, indicating energy transfer from $Ir(dfppy)_2(cbphen)$ to Eu^{III} ion took place. However, the emission of Eu^{III} fell after a maximum value, with the 615 nm emission shape changed, implying a multi coordination type between Ir^{III} complex and Eu^{III}. At the beginning of the titration, enough Ir^{III} complexes can sensitize each Eu^{III} ion well, so the emission at 615 nm turned strong. As the amount of Eu^{III} ions increased, there are not enough Ir^{III} complexes to coordinate with every Eu^{III} ion, so after a maximum value the luminescence intensity fell due to the weak sensitization and quenching effect made by the water and EtOH molecules.

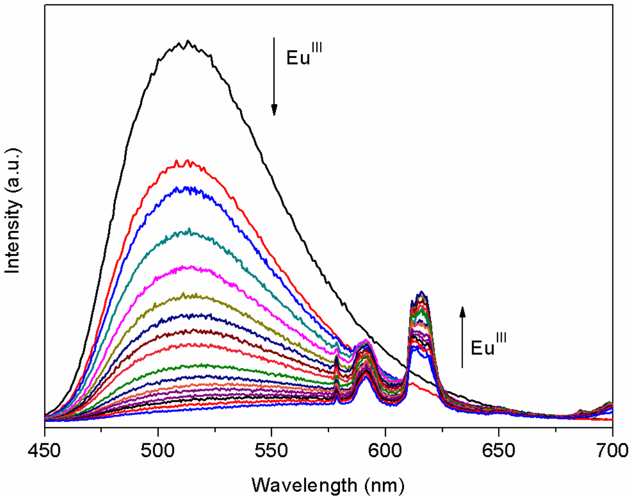


Fig. 6 Luminescence titration spectra of $EuCl_3 \cdot 6H_2O$ into $Ir(dfppy)_2(cbphen)$ in EtOH

When **Ir-Eu** and **Ir_3-Eu** were excited at 360 nm (Fig. 7A), both of them emitted strong red luminescence of Eu^{III}, while the green emission of $Ir(dfppy)_2(cbphen)$ was nearly quenched completely. That is to say, the energy transferred from iridium(III) complex to the Eu^{III} ion effectively. Moreover, longer-wavelength excitation of Eu^{III} was studied for the three Eu^{III} complexes with an excitation wavelength of 470 nm (Fig. 7B). The ratio of the intensity of the peak near 613 nm ($^5D_0 \rightarrow {}^7F_2$) for the three complexes is 12.9 : 33.0 : 1 (**Ir_3-Eu** : **Ir-Eu** : $Eu(TTA)_3 \cdot 2H_2O$). The measured quantum yield of **Ir_3-Eu** (10%) was nearly equal to that of $Eu(TTA)_3 \cdot 2H_2O$ (11%) (Table 4), suggesting the $Ir(dfppy)_2(cbphen)$ can sensitize Eu^{III} ion well; while **Ir-Eu** has a high quantum yield of 44%, quadruples that of $Eu(TTA)_3 \cdot 2H_2O$. Silva et al. measured the quantum yields of $Eu(TTA)_3 \cdot 2H_2O$ and $Eu(TTA)_3$phen (phen = 1,10-phenanthroline), which are 23% and 69% by experiment respectively [55]. It is clear that the introduction of both $Ir(dfppy)_2(cbphen)$ and phen can improve the luminescence intensity of Eu^{III} ion because of the removement of coordinated water. Nevertheless, the $Ir(dfppy)_2(cbphen)$ works better than phen, as phen is not good at sensitizing Eu^{III} ion with a triplet level of 16807 cm^{-1} [56], lower than the $^5D_0$ level of Eu^{III}. The energy transfer processes in these Eu^{III} complexes are summarized in Fig. 8.

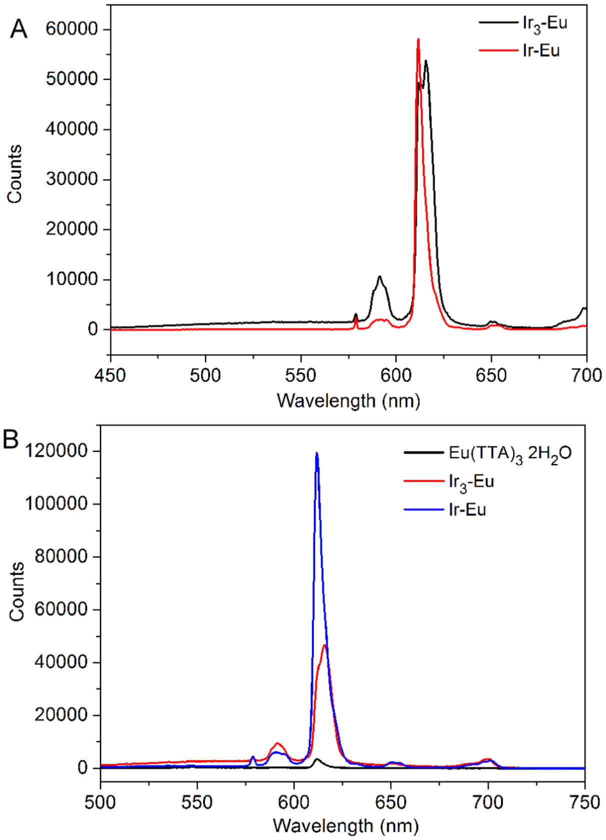


Fig. 7 (A) Emission spectra of Ir^{III}-Eu^{III} bimetallic complexes (λ_{ex} = 360 nm); (B) Emission spectra of Ir^{III}-Eu^{III} bimetallic complexes and Eu(TTA)$_3$·2H$_2$O (λ_{ex} = 470 nm)

For the three Eu^{III} complexes, the lifetime for the Eu^{III} emission is 344 μs for Eu(TTA)$_3$·2H$_2$O, 424 μs for **Ir$_3$-Eu** and 428 μs for **Ir-Eu** (Table 4), implying the larger iridium(III) complex is helpful to prevent the solvent molecule quenching the Eu^{III} emission. Fig. 9 exhibits the photographs of the solutions of mononuclear iridium(IIII) complexes and europium(IIII) compounds as well as Ir^{III}-Eu^{III} bimetallic complexes under excitation with a UV lamp at 365 nm, from which an obvious luminescence change can be observed.

Table 4 Luminescent intensity and lifetime for the Eu^{III} complexes

complex	quantum yield	Lifetime (μs)	Maximum emission intensity (λ_{ex} = 470 nm)
Eu(TTA)$_3$·2H$_2$O	0.11	344	1
Ir$_3$-Eu	0.10	424	11.6
Ir-Eu	0.44	428	33.3
Eu(TTA)$_3$·2H$_2$O*	0.23 (0.29)	-	-
Eu(TTA)$_3$phen*	0.69 (0.63)	-	-

* reported data in Ref [52]; the data in parenthesis are calculated values in the literature.

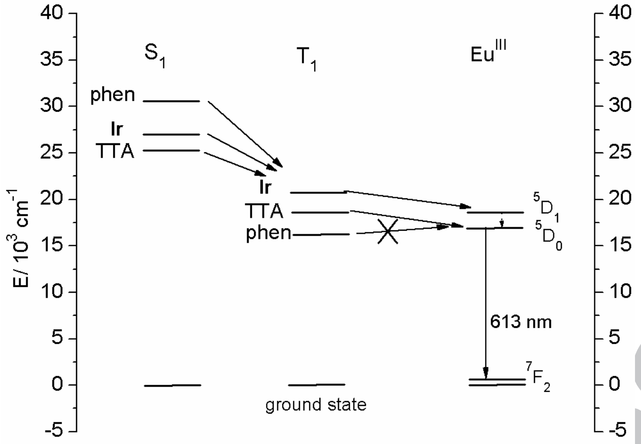


Fig. 8 The energy transfer process in Eu^{III} complexes (S_1: the lowest excited singlet state, T_1: the lowest excited triplet state)

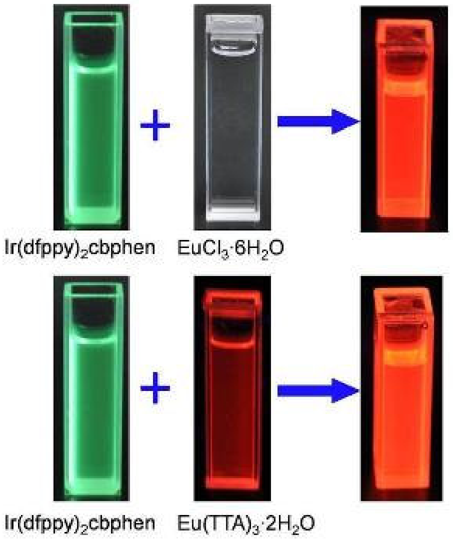


Fig. 9 The photographs of the solutions of Ir^{III} and Eu^{III} complexes under excitation with a UV lamp at 365 nm

4. Conclusions

We designed and synthesized a novel green-emitting iridium(III) complex Ir(dfppy)$_2$(cbphen) with a suitable triplet energy level to sensitize Eu^{III} ion. After molecular structure modulation, this complex exhibits a much stronger luminescence at room temperature than our previous Ir(dfppy)$_2$(phen5f) complex. The Ir^{III}-Eu^{III} bimetallic complexes show intense characteristic emission from Eu^{III} ion, and the green emission from iridium(III) center was almost quenched completely. The quantum yields are 0.11 for $Eu(TTA)_3 \cdot 2H_2O$, 0.10 for **Ir_3-Eu** and 0.44 for **Ir-Eu**, respectively, confirming $Ir(dfppy)_2(cbphen)$ is a good sensitizer for Eu^{III} ions. By the introduction of the iridium complex, the excitation wavelength of Eu^{III} ion was extended to visible range (470 nm).

Acknowledgments

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Appendix A. Supplementary material

CCDC 764289 contains the supplementary crystallographic data for $Ir(dfppy)_2(cbphen)$.

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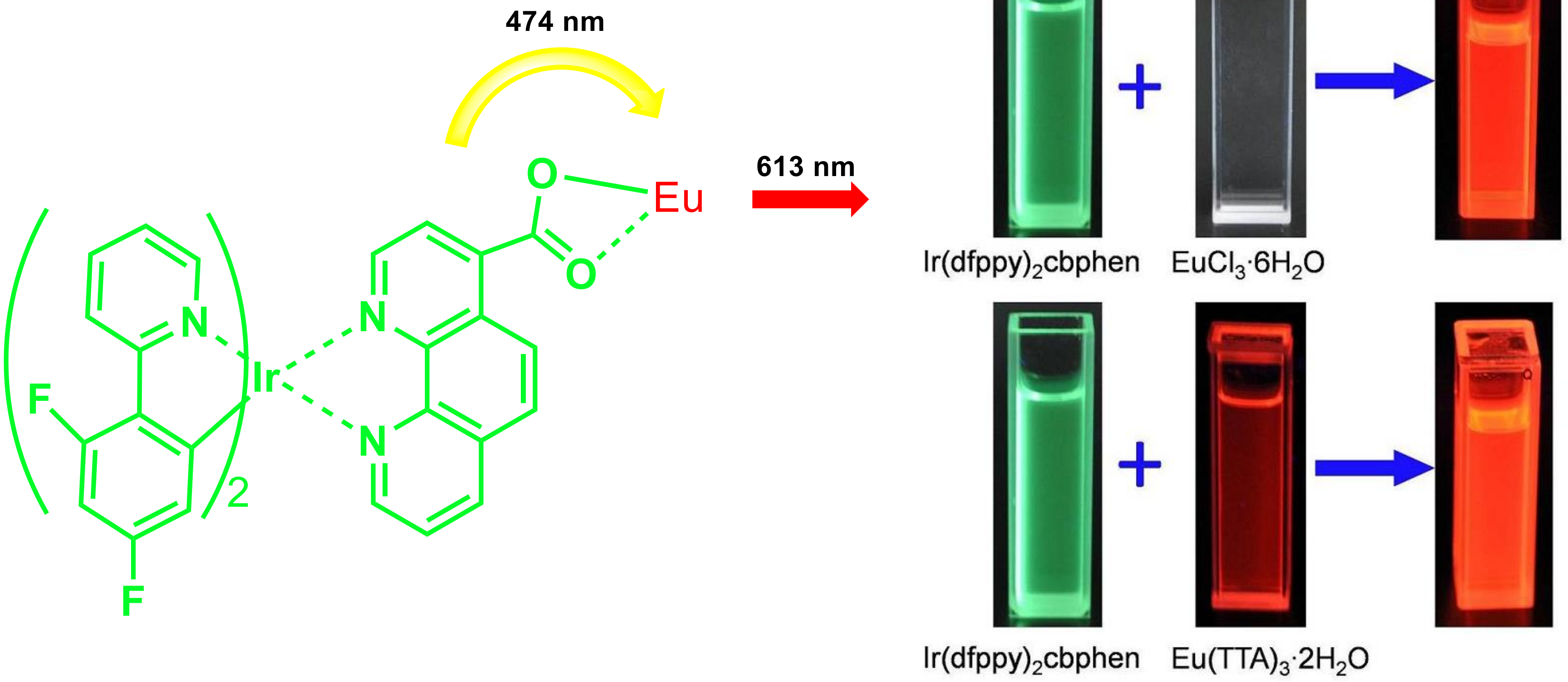
474 nm
613 nm
O
Eu
O
N
N
N
Ir
F
F
2
Ir(dfppy)2cbphen
EuCl3·6H2O
Ir(dfppy)2cbphen
Eu(TTA)3·2H2O

Highlights

> A green-emitting iridium(III) complex Ir(dfppy)$_2$(cbphen) was synthesized and fully characterized with X-ray single crystal structure.

> The iridium(III) complex was applied in sensitizing europium ion in both titration experiment and in Ir^{III}-Eu^{III} bimetallic complexes.

> Only intense characteristic emission from Eu^{3+} ion was obtained with high quantum yield.

> Excitation wavelength of Eu^{3+} ions in Ir^{III}-Eu^{III} bimetallic complexes was extended to visible range (470 nm).