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Synthesis, structure, and tunable white-light emission of

heteronuclear Zn_2Ln_2 arrays using a zinc complex as ligand

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New heteronuclear Zn_2Ln_2 clusters $[Zn_2L_2Ln_2(hfac)_6)]$ (Ln = Eu (**1**), Tb (**2**) and Dy (**3**)) have been synthesized based on a flexible Schiff base (H_2L = *N,N′*-bis(salicylidene)-3,6-dioxa-1,8-diaminooctane) and β-diketonate ligand (hfac = hexafluoroacetylacetonate). The structures of the isomorphous complexes **1**–**3** were determined by single-crystal X-ray crystallography. Photophysical studies indicate that the short intramolecular distance of Zn···Ln allows energy transfer from Zn_2L_2-based sensitizers to the Eu(III) and Tb(III) centres, the lanthanide luminescence is indeed "lighted up" by excitation of the zinc complex. More interestingly, white-light emission was realized by codoping Eu(III) ion into the Dy(III) complex for the first time.

Introduction

Luminescent lanthanide complexes have attracted a great deal of attention for many years due to their potential applications as functional materials in tunable lasers, amplifiers for optical communications, luminescent probes for analyses, and efficient light conversion molecular devices. [1] However, for lanthanide ions, because the f–f transitions are parity forbidden, the absorption coefficients are normally very low and the emissive rates are slow. In order to overcome this, well-designed organic chromophores have been used to excite lanthanide ions as sensitizers (antenna effect). [2] On the other hand, the use of strongly absorbing d-block chromophores as sensitisers for the visible emission from lanthanides has attracted more and more attention from 2000. [3] In Zn(II)-Ln(III) complexes, the energy used to sensitize the Ln(III) ion originated from the ^{3}LC or ^{1}LC excited state of the ligands. [4]

For the past few years, research on white light emitting materials is currently an expanding field in luminescent lanthanide complexes. [5] This is because lanthanide complexes display interesting optical properties such as emission in the primary color range (red, blue and green) that fully spans the entire visible spectrum. [6] Generally, Eu(III), Tb(III) and Gd(III)/La(III) complexes emit red, green and blue light, respectively (RGB; the three primary colors). [7] White light emission are generally achieved by co-doping Eu(III) and/or Tb(III) ions into the corresponding isostructural complexes (Ln = La and Gd) through adjusting the ratio of the lanthanide ions. [8] For example, Zheng et al. used a combination of blue-emitting ligand/La(III), green-emitting Tb(III) and red-emitting Eu(III) units to generate white light from a La(III)/Tb(III)/Eu(III)-MOFs. [9] Another strategy for generating white light emission is named as two-component approach [10] by mixing two complementary colors, such as blue-green and red lights. [11] For example, Li et al dope Eu(III) ions into Gd(III) or La (III) frameworks. [12] However, the two-component approach is new and very rare for white-light emission based on LnOFs.

Based on the consideration above, we have engaged in the heteronuclear 3d-4f clusters with photoluminescent properties. We present three heteronuclear Zn_2Ln_2 clusters $[Zn_2L_2Ln_2(hfac)_6)]$ (Ln = Eu (**1**), Tb (**2**) and Dy (**3**)). White-light emitting materials by doping isostructural Eu(III) into Dy(III) compounds was achieved. This is the first example of obtaining white-light via a two-component Eu(III)-doped Dy(III) framework.

Experimental section

Materials and general measurements

All operations were performed in an open atmosphere. The H_2L ligand and the purcursor $Zn_2L_2·H_2O$ was prepared according to the reported procedure. [13] The lanthanide precursors $Ln(hfac)_3·2H_2O$ (Ln = Eu, Tb and Dy) were synthesized according to the literature. [14] All the other chemicals were obtained from commercial sources and used without further purification. Fourier transform infrared (FT-IR) data were recorded on a Perkin-Elmer 60000 spectrophotometer in the region 4000−400 cm^{-1} using KBr disks. UV−vis spectra (in CH_3OH) were recorded on a Shimadzu UV2240 spectrophotometer. Elemental C, H and N analyses were performed using a Perkin-Elmer 2400 analyzer. Fluorescence spectra for complexes were recorded on a FLSP920 spectrophotometer equipped with a xenon lamp and quartz carrier at room temperature. Luminescence lifetimes were recorded on a single photon counting

spectrometer with a microsecond pulse lamp as the excitation. The overall quantum yields of The photoluminescent quantum yields of both europium and terbium complexes were measured in anintegrating sphere.

Synthesis of complexes 1–3

Synthesis of [Zn$_2$L$_2$Eu$_2$(hfac)$_6$)] (1). All complexes were synthesized by the same method. The synthesis of complex **1** is detailed herein. Eu(hfac)$_3$·2H$_2$O (0.209 g, 0.25 mmol) was dissolved in 10 mL of CHCl$_3$ and then added to a solution of 8 mL of CHCl$_3$ containing Zn$_2$L$_2$·H$_2$O (0.109 g, 0.25 mmol). After one hour of refluxing, n-hexane was diffused into the solution at room temperature to give yellow single crystals which are suitable for X-ray study. Yield: 0.139 g (46.6%). Anal. (wt%) Calcd for C$_{70}$H$_{50}$Eu$_2$F$_{36}$N$_4$O$_{20}$Zn$_2$ (2385.80): C, 35.35; H, 2.12; N, 2.36 ; Found: C, 36.23; H, 2.33; N, 2.92 ; IR (KBr, cm^{-1}): 2937 w, 1653 s, 1542 m, 1491 s, 1257 vs, 1206 s, 1137 vs, 882 w, 801 s, 750 m, 660 s, 579 s, 459 w. UV-Vis spectrum in CH$_3$OH [λ_{max} (nm)]: 237, 271, 303.

Synthesis of [Zn$_2$L$_2$Tb$_2$(hfac)$_6$)] (2). Yield: 0.128 g (42.7%). Anal. (wt%) Calcd for C$_{70}$H$_{50}$F$_{36}$N$_4$O$_{20}$Tb$_2$Zn$_2$ (2395.95): C, 35.04; H, 2.10; N, 2.33; Found: C, 35.19; H, 2.17; N, 2.52; IR (KBr, cm^{-1}): 2928 w, 1653 s, 1560 m, 1512 m, 1257 vs, 1206 s, 1146 vs, 882 w, 801 s, 762 m, 660 s, 579 s, 447 w. UV-Vis spectrum in CH$_3$OH [λ_{max} (nm)]: 238, 271, 303.

Synthesis of [Zn$_2$L$_2$Dy$_2$(hfac)$_6$)] (3). Yield: 0.131 g (43.3%). Anal. (wt%) Calcd for C$_{70}$H$_{50}$Dy$_2$F$_{36}$N$_4$O$_{20}$Zn$_2$ (2406.88): C, 34.93; H, 2.09; N, 2.33; Found: C, 34.7981; H, 2.12; N, 2.40 ; IR (KBr, cm^{-1}): 2928 w, 1662 s, 1560 m, 1479 m, 1197 vs, 1200 s, 1146 vs, 894 w, 792 s, 750 m, 660 s, 588 s, 459 w. UV-Vis spectrum in CH$_3$OH [λ_{max} (nm)]: 236, 271, 303.

Synthesis of Dy$_x$Eu$_y$ material 4 and 5

For the isostructural complexes **4** and **5**, the synthetic methods of Dy$_{0.958}$Eu$_{0.042}$ (**4**) and Dy$_{0.960}$Eu$_{0.040}$ (**5**) are the same as above mentioned by using the corresponding Ln(hfac)$_3$·2H$_2$O as the starting materials in stoichiometric ratios. The molar ratios of lanthanide ions in the resulting mixed-lanthanide complexes were confirmed by inductively coupled plasma spectroscopy (ICP) (Table S1†).

[Zn$_2$L$_2$(Dy$_{0.958}$Eu$_{0.042}$)$_2$(hfac)$_6$)] (4). IR (KBr, cm^{-1}): 2930 w, 1662 s, 1562 m, 1481 m, 1197 vs, 1200 s, 1150 vs, 892 w, 792 s, 752 m, 661 s, 588 s, 459 w. UV-Vis spectrum in CH$_3$OH [λ_{max} (nm)]: 238, 271, 303.

[$Zn_2L_2(Dy_{0.960}Eu_{0.040})_2(hfac)_6$)] (5). IR (KBr, cm^{-1}): 2927 w, 1664 s, 1561 m, 1480 m, 1196 vs, 1201 s, 1144 vs, 895 w, 792 s, 751 m, 660 s, 588 s. UV-Vis spectrum in CH$_3$OH [λ_{max} (nm)]: 236, 270, 305.

X-ray crystallograph. Crystallography: Diffraction intensity data for single crystals of complexes were collected on a Rigaku R-AXIS RAPID imaging-plate X-ray diffractometer at 293 K. The structures were solved by the direct method and refined by the Full-matrix least squares on F^2 using the SHELXTL-97 software package. [15] All non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC 969096, 970647 and 1433397 for complexes **1**–**3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Results and discussion

Syntheses

Heteronuclear complexes **1-3** were synthesized according to a two-step process. Firstly, the precursor $Zn_2L_2 \cdot H_2O$ was synthesized by reactions of the Schiff base ligand with the $Zn(OAc)_2 \cdot 2H_2O$ in a molar ratio of 1:1 carried out in CH$_3$OH/H$_2$O by heated to 60°C under stirring. Secondly, tetrametallic Zn_2Ln_2 complexes were synthesized by reactions of the precursor $Zn_2L_2 \cdot H_2O$ with the $Ln(hfac)_3 \cdot 2H_2O$ in a molar ratio of 1:1 carried out in CHCl$_3$ by refluxing. The immediate color change of the solution upon addition of $Ln(hfac)_3 \cdot 2H_2O$ indicates instant occurrence of the coordination reaction. Yellow crystals suitable for X-ray analysis were obtained by slow diffusion of n-hexane into the solution for one week.

Crystal structures

X-ray crystallographic analysis has revealed that complexes **1-3** are isomorphic, as revealed by comparison of their powder X-ray diffraction (PXRD) patterns (Fig. 1). Powder X-ray diffraction (PXRD) patterns of complexes **1-3** are in agreement with the simulated ones from the respective single-crystal X-ray data. The differences in intensity are due to the preferred orientation of the powder samples. Taking **1** as example, the complex crystallizes in a monoclinic space group P21/c and contains species without any solvents (Fig. 2a). Complex **1** consists of two Eu(III) ions, two

Zn(II) ions, six hexafluoroacetylacetonate and two Schiff base ligands. In the asymmetric unit of **1**, the tetranuclear Zn_2Eu_2 complex comprises two ZnEu units linked together by two bridging flexible Schiff base ligands in which the Eu···Zn distances are similar with 3.3496(8). The Zn(II) and Eu(III) ions are bridged by the phenolic oxygen atoms O1 and O2a from two different ligands. Each Eu(III) ion exhibits eight-coordinated environments from two hydroxyl oxygen atoms that were from two ligands, six oxygen atoms from three bidentate hexafluoroacetylacetonate molecules, forming a dicapped trigonal prismatic geometry. The distorted trigonal prism shown is composed of O(3), O(2a), O(1), O(5), O(7) & O(6) atoms. The O(4) & O(8) atoms are at the vertices of each square pyramid (Fig. 2b). Schiff base (SB) 3d-4f complexes were usually developed by use of 3d-metal complexes with N_2O_2 donor atoms Schiff base ligands, M(SB), as neutral ligands to coordinatively saturate a 4f-element cation in some β-diketonates, $Ln(hfac)_3$, thus yielding dinuclear complexes of general formula $[M(SB)Ln(hfac)_3]$.[16] This flexible Schiff-base ligands show a "stretched" configuration to bridge lanthanide ions, forming tetranuclear structure. The average bond length of the Eu−O (hexafluoroacetylacetonate oxygen atoms) is 2.398 Å, which is slightly longer than that of Eu−O (Schiff base ligands oxygen atom, 2.355 Å). The Zn(II) ion is five-coordinated by two imine nitrogen atoms, two phenol oxygen atoms and one oxygen atom from the two different imine-phenolate ligands, forming a distorted trigonal bipyramidal geometry (Fig. 2c). The average Zn–O and Zn–N bond distances involving the ligand are 2.002 and 2.008 Å, respectively. The two Eu(III) and Zn(II) ions are precisely coplanar, as shown in Fig. 2d. The two Schiff base ligands are located on opposite sides of the Zn_2Eu_2 plane. The central part of the dinuclear entity is occupied by the ZnO_2Eu core. The four atoms of this bridging entity are not exactly coplanar, leading to a roof-shaped ZnO_2Eu motif. The dihedral angle between the planes O(1)–Zn(1)–O(2a) and O(1)–Eu(1)–O(2a) is 38.4°. The angle Eu(1)–O(1)–Zn(1) is 100.3(2)° and the angle Eu(1)–O(2a)–Zn(1) is 100.06(19)°. The dihedral angle between the Eu(1)–O(1)–Zn(1) and Eu(1)–O(2a)–Zn(1) planes is 48.86(10)°.
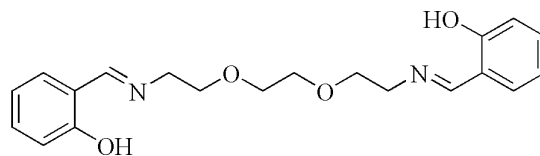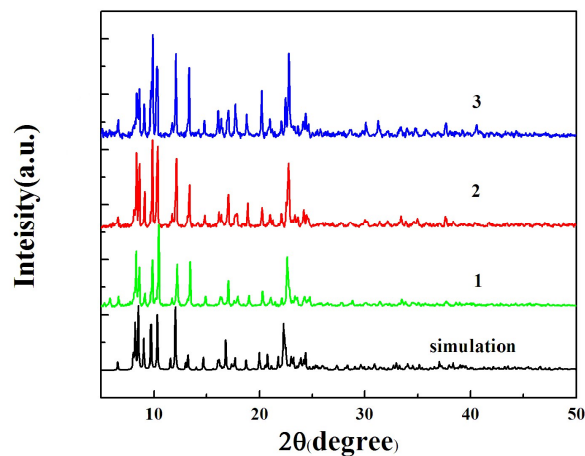
Scheme 1. Structure of flexible ligand H_2L
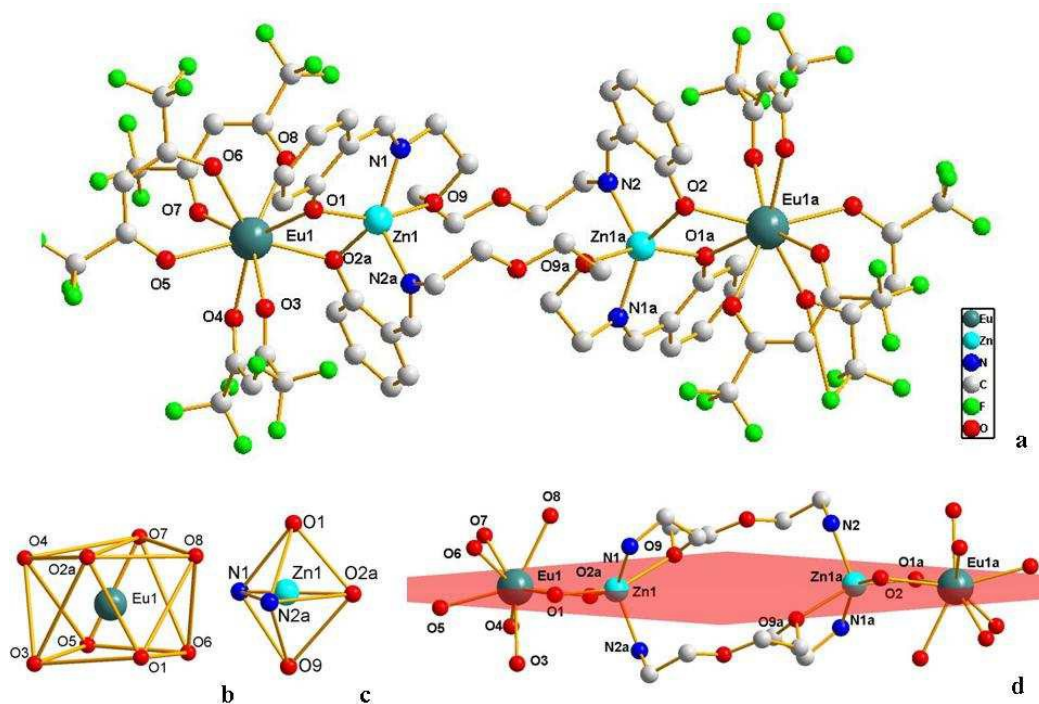
Fig. 1 PXRD patterns for **1**–**3**.

Fig. 2 (a) The crystal structure of **1**, all hydrogen atoms and dissociative molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Eu1–O1 2.335(5), Eu1–O6 2.351(5), Eu1–O2 2.375(4), Eu1–O7 2.378(5), Eu1–O3 2.383(5), Eu1–O5 2.392(5), Eu1–O4 2.411(5), Eu1–O8 2.472(5), Eu1–Zn1 3.3496(8), Zn1–O2 1.983(5), Zn1–N2 2.006(6), Zn1–N1 2.010(6), Zn1–O1 2.020(5), Zn1–O9 2.265(5); Eu(1)–O(1)–Zn(1) 100.3(2), Eu(1)–O(2a)–Zn(1) 100.06(19); (b) Perspective view of coordination polyhedron for the Eu(III) ions in **1**; (c) Perspective view of coordination polyhedron for the Zn(II) ions in **1**; (d) Side view of the planar Zn_2Eu_2 core.

Table 1 Crystallographic data for complexes **1–3**

Crystal data	1	2	3
CCDC Number	969096	970647	1433397
Empirical formula	$C_{70}H_{50}Eu_2F_{36}N_4O_{20}Zn_2$	$C_{70}H_{50}Tb_2F_{36}N_4O_{20}Zn_2$	$C_{70}H_{50}Dy_2F_{36}N_4O_{20}Zn_2$
Formula weight	2385.80	2385.80	2406.88
Temperature (K)	293	293	293
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
space group	*P21/c*	*P21/c*	*P21/c*
a (Å)	12.0462(4)	12.083(2)	12.043(2)
b (Å)	21.1841(7)	21.174(4)	21.089(4)
c (Å)	18.9992(11)	19.121(7)	19.045(7)
α (°)	90	90	90
β (°)	115.060(4)	114.84(4)°	114.57(2)
γ (°)	90	90	90
V (Å^3)	4392.0(3)	4434(2)	4399(2)
Z	2	2	2
Calculated density (Mg/m^3)	1.804	1.797	1.817
Absorption coefficient (mm^{-1})	2.092	2.253	2.361
F(000)	2336	2344	2348
θ range	3.01 to 25.00	3.22 to 25.00	3.01 to 25.00
Limiting indices	-14<=h<=14	-12<=h<=14	-14<=h<=14
	-25<=k<=24	-25<=k<=23	-17<=k<=25
	-16<=l<=22	-22<=l<=16	-16<=l<=22
Reflections collected	17977	17999	17508
Completeness to theta = 27.48°	99.8 %	99.8 %	99.8 %
Data / restraints / parameters	7719 / 7 / 604	7793 / 5 / 604	7742 / 38 / 613
Goodness-of-fit on F^2	1.051	1.047	1.064
Final R indices [I>2σ(I)]	$R_1 = 0.0582$	$R_1 = 0.0608$	$R_1 = 0.0540$
	$wR_2 = 0.1551$	$wR_2 = 0.1690$	$wR_2 = 0.1428$
R indices (all data)	$R_1 = 0.0877$	$R_1 = 0.0874$	$R_1 = 0.0813$
	$wR_2 = 0.1735$	$wR_2 = 0.1875$	$wR_2 = 0.1573$

Luminescence properties

The UV-vis absorption data of **1–3**, H_2L, $Zn_2L_2 \cdot H_2O$ and $Eu(hfac)_3 \cdot H_2O$ are presented in Fig. 3. In MeOH, H_2L consists of three main absorption at *ca.* 216, 254, 313 nm, which are assigned to the π-π^* transition of Ar–OH chromophores and the imine group. For the precursor $Zn_2L_2 \cdot H_2O$ displayed a red shift as a result of changes in the energy levels of the ligand orbitals upon coordination. For $Eu(hfac)_2 \cdot 2H_2O$, there is only a single intense absorption band at *ca.* 303 nm assigned as intra-ligand π–π^* hexafluoro-acetylacetone (Hhfac) transitions. As for **1–3**, there are three sets of absorption bands at *ca.* 238, 273 and 303 due to the intraligand transitions of the intra-ligand transition of H_2L and Hhfac ligands, respectively.
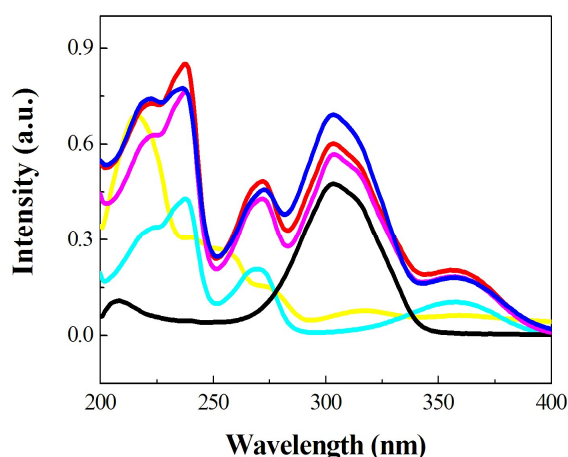

Fig. 3 The UV-vis absorption spectra of H_2L (yellow), $Zn_2L_2 \cdot H_2O$ (cyan), $Eu(Hfac)_3 \cdot 6H_2O$ (black), **1** (magenta), **2** (red) and **3** (blue).

When complex **1** was excited at 310 nm, five typical emission bands of Eu(III) ion are observed, 580 nm ($^5D_0 \rightarrow {}^7F_0$), 592 nm ($^5D_0 \rightarrow {}^7F_1$), 615 nm ($^5D_0 \rightarrow {}^7F_2$), 650 nm ($^5D_0 \rightarrow {}^7F_3$) and 694 nm ($^5D_0 \rightarrow {}^7F_4$). The emission spectrum of complex **1** exhibits a single narrow band at 615 nm. No emission band at 434 nm from $Zn_2L_2 \cdot H_2O$ is observed (Fig. S2), suggesting that the energy transfer from the precursor $Zn_2L_2 \cdot H_2O$ to the Eu(III) centre is very efficient. When excited at 310 nm，the emission spectrum of **2** exhibits a weak broad emission band at 440–550 nm, with an emission maximum at approximately 480 nm which should be assigned to the π–π^* electronic transition form the ligand. The other four typical emission bands of Tb(III) ion are observed at 491 nm ($^5D_4 \rightarrow {}^7F_6$), 545 nm ($^5D_4 \rightarrow {}^7F_5$), 585 nm ($^5D_4 \rightarrow {}^7F_4$), 621 nm ($^5D_4 \rightarrow {}^7F_3$). The

emission band at 545 nm is the most intensive of all four bands. Obviously, the emission spectrum suggests that both the precursor $Zn_2L_2 \cdot H_2O$ and the terbium ion are co-luminescent in complex **2**, implying that $Zn_2L_2 \cdot H_2O$ can only partly sensitize the luminescence of Tb(III) ion and the absorbed energy of $Zn_2L_2 \cdot H_2O$ in **2** is incompletely transferred to the lanthanide ions in solid state. The luminescence quantum yields of complexes **1** and **2** were also determined by means of an integrating sphere at room temperature under the excitation wavelength that maximizes the emissions of the lanthanide ions. The solid-state measurement gives a quantum yield of 37.4% for Eu(III) complex **1** and 3.0% for Tb(III) complex **2**. The lifetime of **1** and **2** is respectively 124.7 μs and 42.8 μs. (Fig. S4 and S5) To the best of our knowledge, such a high quantum yield is unprecedented for Schiff base Zn(II)–Eu(III) heterometallic complexes.[16a, 17] It seems that the synergistic interactions between Hhfac and $Zn_2L_2 \cdot H_2O$ ligands may play an essential role to maximize the luminescence efficiency of the Zn(II)–Eu(III) heterometallic complex. Here, the neutral ligand $Zn_2L_2 \cdot H_2O$ serves as a sensitizer for Eu(III). On the other hand, this fact can be attributed to the fully exclusion of solvent molecules coordination to Ln(III) ions, which are the most important lanthanide luminescent quenchers, [18] by the eight-coordination of diketonate and $Zn_2L_2 \cdot H_2O$ ligands.

The emission spectrum of complex **3** (Fig. 4) excited at 310 nm displays emission maxima at 482 nm covering the blue-green region, which arises from the π*–π transition of the ligands owing to its high energy emitting level. The enhancement and 48 nm red-shift in **3** compared to the band of precursor $Zn_2L_2 \cdot H_2O$ (434 nm Fig. S2) may be attributed to the coordination of the precursor to the lanthanide ions. The energy absorbed by precursor $Zn_2L_2 \cdot H_2O$ cannot transfer to Dy(III) ions. Therefore, **3** exhibits the $Zn_2L_2 \cdot H_2O$ fluorescence while the characteristic band of Dy(III) ion did not appear.
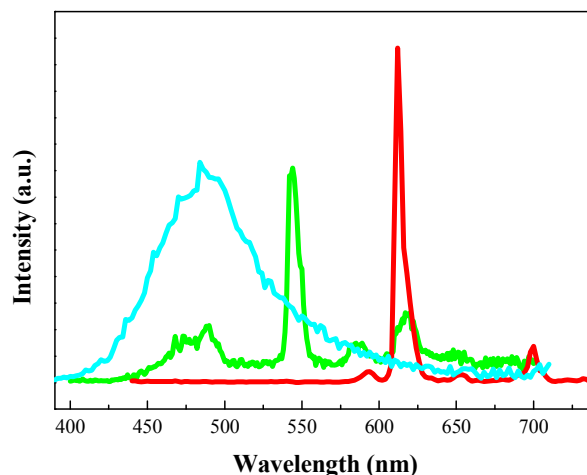
Fig. 4 The luminescent emission spectra for complexes **1** (red), **2** (green) and **3** (cyan) in the solid state at room temperature.

In general, the widely accepted energy transfer mechanism of the luminescence lanthanide complexes is proposed by Crosby.[19] In order to make the energy transfer effective, the energy-level match between the lowest triplet energy level (T_1) of the ligand and the lowest excited state level of Ln(III) ion becomes one of the most important factors dominating the luminescence properties of the complexes. On account of the difficulty in observing the phosphorescence spectrum of the ligand, the emission spectrum of the complex [$Zn_2L_2Gd_2(hfac)_6$)] at 77 K was used to estimate the triplet state energy level of the ligand. The single state energy ($^1\pi\pi^*$) level of H_2L is estimated by referencing its absorbance edge, which is 25000 cm^{-1} (400 nm). The triplet (T_1) energy levels were calculated by referring to the lower wavelength emission peaks of the corresponding phosphorescence spectrum of Gd(III) complex, which are 20619 cm^{-1} (485 nm) (Fig. S6) It is known that the gap $\Delta E(T_1–Ln(III)$ should be intermediate for maximum energy transfer. Therefore, the energy gaps between the triplet state of H_2L and the resonance energy level of Ln(III) (Ln = Eu, Tb, Dy) are calculated (Fig. 5). Their energy gaps, $\Delta E(T_1–^5D_0)$, $\Delta E(T_1 – ^5D_4)$, $\Delta E(T_1 –^4F_{9/2})$ are 3119, 219 and -881 cm^{-1} for **1-3**, respectively. Therefore, it is easily understandable that energy transfer from Zn_2L_2 to Eu(III) is very sufficient whereas to Tb(III) is incomplete, for Dy(III) the energy transfer does not occur.
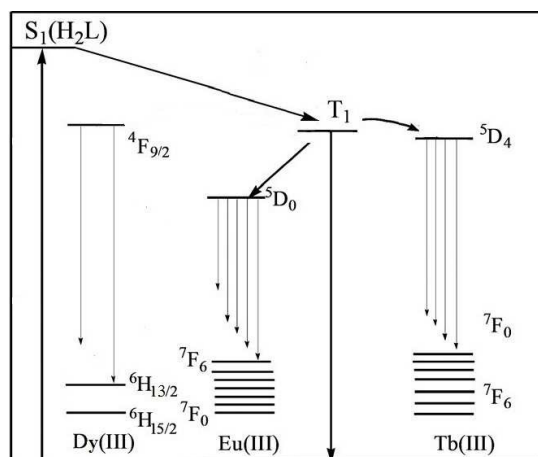
10

Fig. 5 Schematic energy level diagram and energy transfer processes for complexes **1-3**, S_1, first excited singlet state; T_1, first excited triplet state.

Considering that complex **3** provides blue-green light, by means of the Eu(III) ion (red emission) singly doped into the Dy(III) framework, it will therefore be possible to construct white emitting material. So the Dy_xEu_y material was produced by one-pot synthesis and its phase purity was verified by powder X-ray diffraction (PXRD) analysis (Fig. S3). The content of Eu(III) ion was confirmed by inductively coupled plasma (ICP) spectroscopy. The emission spectra of $Dy_{0.958}Eu_{0.042}$, $Dy_{0.960}Eu_{0.040}$ material reveal a broad emission band in the region of 400 to 580 nm from the precursor $Zn_2L_2 \cdot H_2O$ and characteristic emission peaks at 579, 591, 613, 650 and 694 nm from the Eu(III) ion (Fig. 6-8). As expected, white light emission is realized by the Eu(III) ion singly doped into the Dy(III) framework. It reveals that the emission color of the doped materials can be finely tuned by varying the doping ratio, and white-light emission of the doped material with the molar ratio of 95.8:4.2 (Dy(III)/Eu(III)) was obtained at CIE chromaticity coordinates A(0.335, 0.333), B(0.330, 0.327), C(0.322, 0.328) with an excitation wavelength of 300, 310 and 320 respectively (Fig S6). A (0.335, 0.333) is very closed to international pure white light CIE chromaticity coordinates (0.333, 0.333). (Fig 8) The CIE coordinates D(0.333, 0.324), E(0.330, 0.328), F(0.321, 0.326) for $Dy_{0.960}Eu_{0.040}$ sample with an excitation wavelength of 300, 310 and 320 respectively, are listed in Fig. S8 and table S2. The quantum yield of the white emission is 3.0% and 2.7% for $Dy_{0.958}Eu_{0.042}$, $Dy_{0.960}Eu_{0.040}$, respectively.
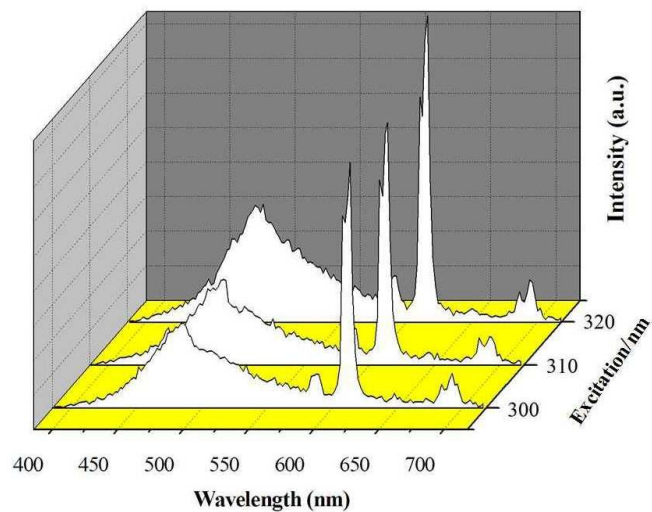
Fig. 6 The luminescent emission spectra of the doped complex $Dy_{0.958}Eu_{0.042}$ excited at 300, 310, 320 nm respectively.

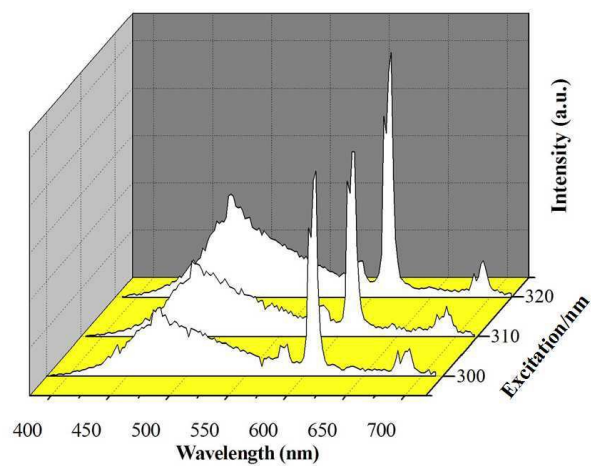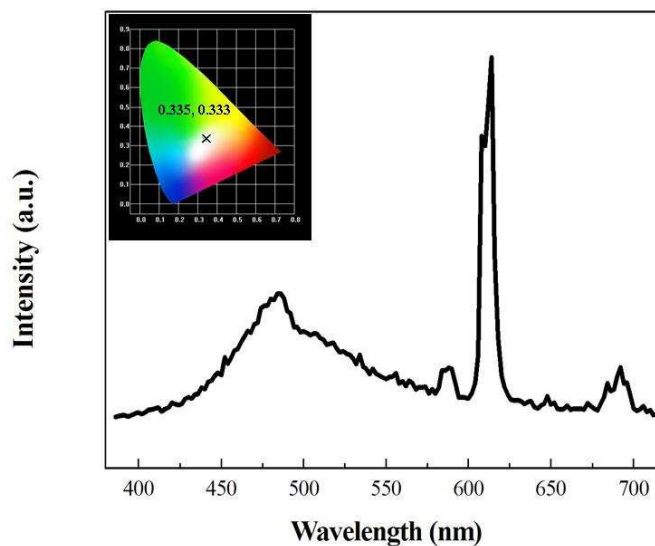**Fig. 7** The luminescent emission spectra of the doped complex $Dy_{0.960}Eu_{0.040}$ excited at 300, 310, 320 nm respectively.

Fig. 8 The luminescent emission spectrum of doped complex $Dy_{0.958}Eu_{0.042}$ excited at 300 nm. Inset: CIE-1931 chromaticity diagram and optical image of a powder sample of doped complex $Dy_{0.958}Eu_{0.042}$ excited at 300 nm.

Conclusions

In summary, three heterometallic Zn_2Ln_2 clusters (Ln = Eu (**1**), Tb (**2**) and Dy (**3**)) have easily been synthesized by reaction of precursors Schiff base zinc(II) complex ($Zn_2L_2 \cdot H_2O$) and $Ln(hfac)_3 \cdot 2H_2O$ in $CHCl_3$/n-hexane. The blue-green emission of the Dy(III) framework in combination with red emission of the Eu(III) ion in a system produce white light emission, which may provide a new route for the rational design of molecule white-light-emitting materials.

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White-light emission was realized by codoping Eu(III) ion in the Dy(III) complex for the first time.