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# Observation of cascade $f \rightarrow d \rightarrow f$ energy transfer in sensitizing near-infrared (NIR) lanthanide complexes containing Ru(II) polypyridine metalloligand

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Distinguishable  $d \rightarrow f$  or  $f \rightarrow d$  energy transfers depending on lanthanide ions are observed in isomorphous d-f heterometallic complexes containing Ru(II) metalloligand (L<sub>Ru</sub>), which lead to sensitized NIR emission (for Nd<sup>3+</sup> and Yb<sup>3+</sup>) or enhanced red emission of L<sub>Ru</sub> (for Eu<sup>3+</sup> and Tb<sup>3+</sup>), and represent the first eye-detectable evidence of  $f \rightarrow d$  energy transfer progress in Ln-Ru bimetallic complexes. Based on systematic luminescence and decay lifetime study, cascade  $f \rightarrow d \rightarrow f$  energy transfer has been proposed in Ln1-Ru-Ln2 trimetallic systems for improved NIR sensitization.

#### Introduction

During the past decades, sensitization of Ln(III) luminescence by using organic ligands as light antenna has received wide attention due to the potential applications in bioassays, sensors, lighting or displaying devices, and so on.<sup>1-3</sup> As an alternative approach, the use of d-block complexes (e.g.  $Ir^{3+}$ ,  $Ru^{2+}$ ,  $Os^{2+}$ ,  $Pt^{2+}$ ,  $Re^+$ ,  $Au^+$ ) as chromophores to sensitize the luminescence of Ln(III) centers has also been proved successful. Many types of transition metal chromophores have been employed to fabricate d-f heterometallic complexes, in which the d-block chromophores were found to display some advantages as energy donors to Ln-centers in comparison with organic ligands, including: (a) strong and wide absorbance of light in UV to visible regions, (b) intense emitting states helpful for  $d \rightarrow f$  energy-transfer or white-light modulation, and especially, (c) a long-lived and relatively low <sup>3</sup>MLCT (metal-toligand charge transfer) excited state suitable for sensitizing NIR-Ln(III) luminescence (e.g. Pr<sup>3+</sup>, Nd<sup>3+</sup>, Er<sup>3+</sup> and Yb<sup>3+</sup>).<sup>4-7</sup>

Metalloligand method provides an efficient and reproducible way to assemble *d-f* heterometallic complexes,<sup>8-10</sup> in which the preconstructed metal complexes (especially polypyridyl complexes of  $d^6$  and  $d^8$  metal ions) possess "free" donor groups to coordinate with  $Ln^{3+}$  ions instead of simple organic ligands. Such metalloligands incorporate the luminescent merits of *d*-block metal centers as well as coordination capabilities of organic ligands, thus providing versatile strategies to design novel *d-f* heterometallic complexes for sensitization of different  $Ln^{3+}$  ions with desirable luminescence properties. Up to now, a variety of *d-f* heteronuclear complexes have been assembled by metalloligand method, and either visible<sup>11-14</sup> or NIR<sup>15-18</sup> emissions of the incorporated Ln<sup>3+</sup>-centers have been achieved via  $d \rightarrow f$  energy transfer from the metalloligand MLCT states to Ln<sup>3+</sup>-centers. On the other hand, since the <sup>3</sup>MLCT energy state of the metalloligand is usually much lower than the  $\pi\pi^*$  state of organic chromophore, in principle, it is possible to observe  $f \rightarrow d$  back energy transfer from Ln<sup>3+</sup>-center to <sup>3</sup>MLCT state of the metalloligand. In this way, the luminescence of the metalloligand itself can be intensified, benefitting from the additional  $\pi\pi^* \rightarrow f \rightarrow d$  energy immigration besides the normal <sup>1</sup>MLCT  $\rightarrow$  <sup>3</sup>MLCT energy transfer. However, although B ünzli and others have suggested such kinds of energy transfer, seldom evidence has been observed yet.<sup>19,20</sup>

Herein, we use a Ru(II) polypyridine metalloligand to construct a series of isostructural heterometallic complexes with different Ln<sup>3+</sup> ions. Interestingly, we found that the redemission of Ru(II)-metalloligand is significantly affected by the incorporated Ln<sup>3+</sup>-centers, showing remarkable enhancement with Eu<sup>3+</sup> and Tb<sup>3+</sup> while quenched by Nd<sup>3+</sup> and Yb<sup>3+</sup>, which can be directly detected by naked eye. Further photoluminescence studies clearly indicate diversified energy transfer pathways between Ru(II)-metalloligand and different  $Ln^{3+}$  ions upon UV-vis excitations, including normal  $d \rightarrow f$ transitions for Nd<sup>3+</sup> and Yb<sup>3+</sup> and unprecedented  $f \rightarrow d$ transitions for Eu<sup>3+</sup> and Tb<sup>3+</sup>. This is in consistent with the fact that the <sup>3</sup>MLCT energy level of Ru(II)-metalloligand (~15 700 cm<sup>-1</sup>) lies between the accepting levels of visible-emitting Tb<sup>3+</sup>  $({}^{5}D_{4}, \sim 20,400 \text{ cm}^{-1}), \text{ Eu}^{3+} ({}^{5}D_{0}, \sim 17,500 \text{ cm}^{-1}), \text{ and NIR-}$ emitting Nd<sup>3+</sup> ( ${}^{4}F_{3/2}$ , ~11,000 cm<sup>-1</sup>), and Yb<sup>3+</sup> ( ${}^{2}F_{5/2}$ , ~10,000

cm<sup>-1</sup>). Based on these observations, a cascade  $f \rightarrow d \rightarrow f$  energy transfer process has been proposed and utilized to achieve better NIR sensitization in trimetallic systems combining both Eu/Tb and Nd/Yb centers with Ru(II)-metalloligand.

#### **Experimental**

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#### Materials and methods

Solvents were purchased from Sigma Aldrich and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. <sup>1</sup>H NMR spectra were recorded on a Varian/Mercury-Plus 300 NMR spectrometer. The elemental analyses were performed with Perkin-Elmer 240 elemental analyzer. The powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å). UV-Vis absorption spectra were recorded using a Shimadzu/ UV-250PC spectrophotometer. The photoluminescence spectra were measured on EDINBURGH FLS980 fluorescence spectrophotometer, which is equipped with an R5509-72 PMT detector. The measurements were performed in the solid state, and the emission/excitation spectra were corrected according to the instrumental sets. Luminescence lifetimes were measured by Time-Correlated Single Photon Counting (TCMPC) method using 405 nm picosecond pulsed diode laser as the excitation. Energy dispersive X-ray analysis (EDX) was measured on a Quanta 400 thermal FE environment scanning electron microscope with an INCA energy dispersive X-ray spectrometer.



**Scheme 1.** Synthesis route for the Ru(II) metalloligand and lanthanide complexes.

Synthesis of the Metalloligand L<sub>Ru</sub> (PF<sub>6</sub>)<sub>2</sub>. 1.16 g (2.39 mmol)  $Ru(Bpy)_2Cl_2$  (Bpy = 2,2'-bipyridine) and 1.04 g (3.46 mmol) diethyl 2,2'-bipyridine-4,4'-dicarboxylate were added into 250 ml round bottom flask, and then the mixture of 160 ml ethanol/water (v : v = 1:1) was added. The solution was refluxed under the protection of N<sub>2</sub> atmosphere for 8 hours. After that, the solution was cooled and distilled at low pressure to remove ethanol. 5 ml saturated water solution of KPF<sub>6</sub> was added to result in large quantity of red precipitates, which were filtered and washed with diethyl ether. The crude product was then added into 100 ml HCl solution (4 mol  $L^{-1}$ ) and refluxed under the protection of N<sub>2</sub> atmosphere for 12 hours. 5 ml saturated water solution of KPF<sub>6</sub> was further added into the resulting solution to result in red solids, which were filtered and washed with water and diethyl ether to get pure product of  $L_{Ru}$  (**PF**<sub>6</sub>)<sub>2</sub>. Yield: 1.79 g (80%). <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ): 9.24 (s, 2H), 8.86 (dd,  $J_1 = 2.4$  Hz,  $J_2 = 8.4$  Hz, 4H), 8.17 (m, 4H), 7.95 (d, J = 5.7 Hz, 2H), 7.87 (dd, J<sub>1</sub> = 1.5 Hz, J<sub>2</sub> = 6 Hz, 2H), 7.73

(d, J = 5.4 Hz, 2H), 7.69 (d, J = 5.1 Hz, 2H), 7.55 (t, J = 6.6 Hz, 2H), 7.50 (t, J = 6.6 Hz, 2H). EA anal. Calcd for C, 40.56; H, 2.55; N, 8.87 %; Found: C, 40.52; H, 2.27; N, 8.98 %.

Syntheses of Ln-Ru and Ln1-Ru-Ln2 Complexes. Bis- $(2,2)^{-1}$  bipyridine)-2,2'-bipyridine-4,4'-dicarboxylic acid-ruthenium (II) ( $\mathbf{L}_{Ru}$  (**PF**<sub>6</sub>)<sub>2</sub>, 19 mg, 0.03 mmol) was dissolved in water (3 ml) by the addition of LiOH (1.4 mg, 0.06 mmol) and followed by the addition of Tb(NO<sub>3</sub>)<sub>3</sub> 6H<sub>2</sub>O (4.5 mg, 0.01 mmol). A large quantity of precipitates appeared, which were separated by centrifugation. The mother liquid was left for natural evaporation and after two weeks, pink lamellar crystals ([Tb( $\mathbf{L}_{Ru}$ )<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>](PF<sub>6</sub>)<sub>2.5</sub>(NO<sub>3</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>n</sub>, Tb-Ru) suitable for single crystal diffraction were afforded. On the other hand, the precipitates separated by centrifugation in the above process were washed with water (1 ml × 2) to get the precipitate samples for luminescence study. All the other heterometallic Ln-Ru complexes were prepared in a similar way, and the trimetallic Ln1-Ru-Ln2 complexes were prepared by mixing two kinds of lanthanide nitrates with appropriate ratios in the reaction system.

 $[Eu(L_{Ru})_3(H_2O)_3]\ (PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_{12}\ (Eu-Ru):$  Yield: 65%. EA anal. Calcd for C, 41.44; H, 3.48; N, 9.31 %; Found: C, 41.63; H, 3.27; N, 9.10%.

 $[Gd(L_{Ru})_3(H_2O)_3]$   $(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_7(Gd-Ru)$ : Yield: 60%. EA anal. Calcd for C, 42.74; H, 3.21; N, 9.61 %; Found: C, 42.99; H, 3.58; N, 9.17%.

 $[Nd(L_{Ru})_{3}(H_{2}O)_{3}]$   $(PF_{6})_{2.5}(NO_{3})_{0.5}(H_{2}O)_{10}(Nd-Ru)$ : Yield: 50%. EA anal. Calcd for C, 42.10; H, 3.39; N, 9.46 %; Found: C, 42.38; H, 3.75; N, 9.25%.

 $[Yb(L_{Ru})_3(H_2O)_3]$   $(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_9$  (Yb-Ru): Yield: 55%. EA anal. Calcd for C, 41.94; H, 3.31; N, 9.42 %; Found: C, 42.34; H, 3.42; N, 9.15 %.

 $[Eu_xNd_y(L_{Ru})_3(H_2O)_3]$  (PF<sub>6</sub>)<sub>2.5</sub>(NO<sub>3</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>15</sub> (Eu-Ru-Nd, x + y = 1, x : y = 1 : 3, 1 : 1 and 3 : 1, respectively). Yield: 45 ~ 50%. EDX results: feeding ratio, Ru : Eu : Nd = 1 : 0.08 : 0.25 (x : y = 1 : 3); Found, Ru : Eu : Nd = 1 : 0.09 : 0.25; feeding ratio, Ru : Eu : Nd = 1 : 0.17 : 0.17 (x : y = 1 : 1); Found, Ru : Eu : Nd = 1 : 0.16 : 0.17; feeding ratio, Ru : Eu : Nd = 1 : 0.25 : 0.08 (x : y = 3 : 1); Found, Ru : Eu : Nd = 1 : 0.22 : 0.08.

 $[Eu_xYb_y(L_{Ru})_3(H_2O)_3]$  (PF<sub>6</sub>)<sub>2.5</sub>(NO<sub>3</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>15</sub> (Eu-Ru-Yb, x + y = 1, x : y = 1 : 3, 1 : 1 and 3 : 1, respectively). Yield: 50 ~ 55%. EDX results: feeding ratio, Ru : Eu : Yb = 1 : 0.08 : 0.25 (x : y = 1 : 3); Found, Ru : Eu : Yb = 1 : 0.08 : 0.25; feeding ratio, Ru : Eu : Yb = 1 : 0.17 : 0.17 (x : y = 1 : 1); Found, Ru : Eu : Yb = 1 : 0.15 : 0.17; feeding ratio, Ru : Eu : Yb = 1 : 0.25 : 0.08 (x : y = 3 : 1); Found, Ru : Eu : Yb = 1 : 0.22 : 0.10.

 $[Tb_xNd_y(L_{Ru})_3(H_2O)_3]$  (PF<sub>6</sub>)<sub>2.5</sub>(NO<sub>3</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>15</sub> (Tb-Ru-Nd, x + y = 1, x : y = 1 : 3, 1 : 1 and 3 : 1, respectively). Yield: 45 ~ 50%. EDX results: feeding ratio, Ru : Tb : Nd = 1 : 0.08 : 0.25 (x : y = 1 : 3); Found, Ru : Tb : Nd = 1 : 0.07 : 0.25; feeding ratio, Ru : Tb : Nd = 1 : 0.17 : 0.17 (x : y = 1 : 1); Found, Ru : Tb : Nd = 1 : 0.16 : 0.17; feeding ratio, Ru : Tb : Nd = 1 : 0.25 : 0.08 (x : y = 3 : 1); Found, Ru : Tb : Nd = 1 : 0.23 : 0.09. Published on 11 April 2016. Downloaded by University of California - San Diego on 16/04/2016 04:48:22.

 $[Tb_xYb_y(L_{Ru})_3(H_2O)_3] (PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_{15} (Tb-Ru-Yb, <math>x + y = 1$ , x : y = 1 : 3, 1 : 1 and 3 : 1, respectively). Yield:  $45 \sim 50\%$ . EDX results: feeding ratio, Ru : Tb : Yb = 1 : 0.08 : 0.25 (x : y = 1 : 3); Found, Ru : Tb : Yb = 1 : 0.07 : 0.24; feeding ratio, Ru : Tb : Yb = 1 : 0.17 : 0.17 (x : y = 1 : 1); Found, Ru : Tb : Yb = 1 : 0.17 : 0.17; feeding ratio, Ru : Tb : Yb = 1 : 0.25 : 0.08 (x : y = 3 : 1); Found, Ru : Tb : Yb = 1 : 0.24 : 0.08.

Crystallography. Single-crystal reflection data were collected on an Oxford Gemini S Ultra diffractometer with the Enhance X-ray Source of Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å) using the  $\omega$ - $\phi$  scan technique.<sup>21</sup> Empirical absorption correction was applied using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm.<sup>22</sup> Structural solution and refinement against F<sup>2</sup> were carried out using the SHELXL programs.<sup>23</sup> All the non-hydrogen atoms were refined with anisotropic parameters, while H atoms were placed in calculated positions and refined using a riding model, except for the H atoms of water molecules, which were found by electron cloud density (Q peaks). Crystal data for complex Tb-Ru:  $C_{96}H_{104}F_{15}N_{18}O_{32}F_{25}Ru_{3}Tb$ ,  $M_r = 2861.53$ , monoclinic, space group C2/c, a = 23.9537(5), b = 41.5149(9), c = 23.8634(4) Å,  $\beta =$ 108.316(2) °, V = 22528.4(8) Å<sup>3</sup>, Z = 8,  $D_c = 1.687$  g cm<sup>-3</sup>, T = 150K. Refinement of 17406 parameters converged at final  $R_1$  [for data with  $I > 2\sigma$  (I)] = 0.0826,  $wR_2$  (all data) = 0.2516. CCDC number: 1047975. The selected bond lengths and bond angles for compounds are listed in Table S1.

#### **Results and discussion**



**Fig. 1** (a) Molecular structure of complex Tb-Ru (green for Tb, pink for Ru, blue for N, gray for C, red for O, percentage of probability 30%. Solvated water, anions and H atoms are omitted for clarity). (b)

Interdigitation of two Tb( $L_{Ru}$ )<sub>3</sub> structural units through hydrogen bonding and  $\pi$ - $\pi$  stacking.

Construction of *d-f* Heteronuclear Complexes from Ru(II) Metalloligand. The series of *d*-*f* heteronuclear complexes were prepared by using the pre-constructed mononuclear Ru(II) complex bis-(2,2'-bipyridine)-2,2'-bipyridine-4,4'-dicarboxylic acidruthenium(II) ( $L_{Ru}$ ) as the metalloligand. In  $L_{Ru}$ , each Ru(II) ion is coordinated by three bipyridine organic ligands with one of them possessing two dicarboxylic groups for further coordination to Ln<sup>3+</sup> ions (Fig. 1). The bimetallic Ln-Ru (Ln = Eu, Tb, Gd, Nd and Yb) complexes were obtained by dissolving the deprotonated Ru(II) metalloligand in water with the aid of LiOH and followed by the addition of hydrated Ln(NO<sub>3</sub>)<sub>3</sub> salts, offering both polycrystalline and single-crystal samples. The crystalline products are apt to effloresce in the air, therefore, the powder X-ray diffraction (PXRD) analysis only afforded a poor scattering pattern (Fig. S1) with informative small peaks compared with the simulation. However, the elemental analyses and the PXRD patterns of the freshly precipitated samples of Ln-Ru series proved that all as-prepared bimetallic complexes are isostructural (Fig. S2). So we only analyzed the single-crystal structure of Tb-Ru complex as the representative. The trimetallic Eu(Tb)-Ru-Nd(Yb) systems were generated in a similar way by mixing two Ln(NO<sub>3</sub>)<sub>3</sub> in varied ratios together with the metalloligand L<sub>Ru</sub> (Table 1). Formation of isomorphous polycrystalline phases was confirmed by PXRD analyses, which present major diffraction peaks as the single-lanthanide samples, although displaying obvious broadening in the peak profiles (Fig. S3).

As shown in Fig. 1a, in complex Tb-Ru, the Ru(II)-center in  $L_{Ru}$  is coordinated with six N atoms from three bipyridine ligands in an octahedral geometry, and the Tb(III)-center is 9-coordinated with six O atoms from three metalloligands (each using only one bidentate carboxylic group, and the other remaining uncoordinated) together with three water molecules, having an approximately three-capped trigonal prismatic geometry. Every two Tb(L<sub>Ru</sub>)<sub>3</sub> structural units are interdigitated and further extended in the crystal lattice with the aid of hydrogen bonding and  $\pi$ - $\pi$  stacking (Figs. 1b and S4). Bond distances and angles around individual metal centers are in accordance with usual Ru(II) and Tb(III) complexes as listed in Table S1 (Ru-N: 2.02(1)~2.08(1) Å; Tb-O: 2.37(1)~2.61(1) Å), and the closest Ru…Tb, Ru…Ru and Tb…Tb separations are about 8.4, 8.1 and 6.1 Å. It is well known that either  $\Lambda$ - or  $\Delta$ - stereoconfiguration can be formed around the 6-coordinated Ru(II) center, and herein, in each  $Tb(L_{Ru})_3$  structural unit, the same handedness is found for the three  $L_{Ru}$  metalloligands. However, different handedness is found for the L<sub>Ru</sub> metalloligands in neighboring Tb(L<sub>Ru</sub>)<sub>3</sub> structural units. Therefore, as a whole, the crystal structure is racemic.

**Photoluminescence and**  $d \rightarrow f / f \rightarrow d$  **Energy Transfer in Ln-Ru Complexes.** The UV-vis absorption spectra (Fig. 2a) of L<sub>Ru</sub> metalloligand and Ln-Ru complexes in water solution cover a wide range from 220-500 nm. In the UV region (<400 nm), the absorptions are mainly associated with the  $\pi$ - $\pi$ \* electronic transitions from the bpy moieties and d-d\* transitions of Ru(II) in the Published on 11 April 2016. Downloaded by University of California - San Diego on 16/04/2016 04:48:22.

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metalloligand.<sup>24</sup> From the major peak centered at 287 nm, we estimate the lowest excited  $\pi\pi^*$  state of the organic chromophore at about 34 843 cm<sup>-1</sup>. Whereas the salient peak centered at 460 nm in the visible region indicates the <sup>1</sup>MLCT (metal-ligand charge transfer) of L<sub>Ru</sub> metalloligand at about 21 739 cm<sup>-1</sup>.<sup>25</sup> In the solid state, the reflectance spectra (Fig. S5) of metalloligand and complexes extend to ~700 nm due to packing effect, but still bearing the characteristic peaks around 460 and 300 nm. Excitation of  $L_{\text{Ru}}$  in the solid state produces a red emission centered at 693 nm (Fig. 2b, Table 1), originated from the <sup>3</sup>MLCT state of the metalloligand with the lifetime and absolute quantum yield tested to be 469 ns and 4.0% at room temperature (r.t.), respectively, which are comparable with other [Ru(bipy)<sub>3</sub>]<sup>2+</sup>-based chromophores.<sup>26-28</sup>

Table 1. Photophysical data for the Ru-based MLCT emission and Ln-based NIR emission in L<sub>Ru</sub>, Ln-Ru and Ln1-Ru-Ln2.

emission is significantly blue-shifted to ~630 nm, owing to the changes in metalloligand structure brought by the Eu/Tb<sup>3+</sup> coordination. Noticeably, the decay lifetimes of this Ru-based MLCT emission are increased to 820 and 760 ns at r.t. in Eu-Ru and Tb-Ru complexes, together with the distinct increase of absolute quantum yields (12.7% and 11.7%) in comparison with the pure metalloligand (5.1%). As seen in Fig. 2d, complexes Eu-Ru and Tb-Ru look much brighter than L<sub>Ru</sub> under UV radiation, indicative of obviously enhanced Ru-based emission upon coordination with Eu<sup>3+</sup> and Tb<sup>3+</sup>. Furthermore, the Tb-Ru crystals show similar emitting profile (Fig. S6), but brighter emission and higher quantum yield (21.8%) than the corresponding precipitated powders, probably due to better crystalline packing and less quenching effect of the solvated water molecules.

Em-MLCT					Em-Ln(III)			
Complex	λ <sub>max</sub>	τ	τ	QY*	$\lambda_{max}$	τ	τ	
	(nm)	(ns, r.t.)	(ns, 77K)	(%)	(nm)	(ns, r.t.)	(ns, 77 K)	
L <sub>Ru</sub>	693	469	1567	5.1	-	-	-	-
Eu-Ru	630	820	2276	12.7	-	-	-	
Tb-Ru		760	1658	11.7	-	-	-	
Gd-Ru		908	2588	11.0				
Nd-Ru	650	14	247	0.4	1059	106	424	-
Eu-Ru-Nd (Eu:Nd=1:3)		27	602	0.5		144	1090	
Eu-Ru-Nd (Eu:Nd=1:1)		112	776	0.8		191	1342	
Eu-Ru-Nd (Eu:Nd=3:1)		164	1593	1.9		262	1519	
Tb-Ru-Nd (Tb:Nd=1:3)		56	321	0.8		153	695	
Tb-Ru-Nd (Tb:Nd=1:1)		102	1263	0.9		181	743	
Tb-Ru-Nd (Tb:Nd=3:1)		186	1670	1.8		292	1070	
Yb-Ru	630	71	1135	1.2	998	595	1662	-
Eu-Ru-Yb (Eu:Yb=1:3)		125	621	1.6		758	1265	
Eu-Ru-Yb (Eu:Yb=1:1)		200	1301	2.7		816	1614	
Eu-Ru-Yb (Eu:Yb=3:1)		312	1705	4.3		935	2040	
Tb-Ru-Yb (Tb:Yb=1:3)		132	1207	1.5		778	1740	
Tb-Ru-Yb (Tb:Yb=1:1)		170	1547	2.7		814	2276	
Tb-Ru-Yb (Tb:Yb=3:1)		334	2005	4.4		991	2508	



After coordination with  $Eu/Tb^{3+}$  ions, the resulting d-fheterometallic Eu-Ru and Tb-Ru complexes do not emit the characteristic  $f \rightarrow f$  luminescence of Ln<sup>3+</sup> ions, but still give out a broad red emission similar to that of pure L<sub>Ru</sub>. However, the



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**Fig. 2** (a) UV-vis absorption spectra of the metalloligand and Ln-Ru complexes at room temperature  $(5 \times 10^{-5} \text{ mol L}^{-1}, \text{ water})$ ; (b) Solid state excitation and emission spectra of  $L_{Ru}$  and Eu-Ru, Tb-Ru complexes; (c) Solid state excitation and NIR emission spectra of Nd-Ru, Yb-Ru complexes (the broad emission in visible region is from  $L_{Ru}$  metalloligand); (d) Photographs for  $L_{Ru}$  and different Ln-Ru complexes under visible light (upper) and 365 nm UV radiation (lower).

The absence of  $f \rightarrow f$  emissions of Eu/Tb<sup>3+</sup> in two Ln-Ru complexes indicates inefficient <sup>3</sup>MLCT  $\rightarrow f(d \rightarrow f)$  energy transfer from L<sub>Ru</sub> metalloligand to the excited *f*-levels, which is expectable since the triplet state (~15 698 cm<sup>-1</sup>) of the metalloligand estimated from phosphorescent data of Gd-Ru complex at 77 K (Fig. S7) is lower than  ${}^{5}D_{0}$  of Eu<sup>3+</sup> (17 500 cm<sup>-1</sup>) and  ${}^{5}D_{4}$  of Tb<sup>3+</sup> (20 400 cm<sup>-1</sup>). On the contrary, the reverse energy transfer  $f \rightarrow {}^{3}MLCT$   $(f \rightarrow d)$  is adequate to take place if Eu/Tb<sup>3+</sup> ions are directly sensitized by the excited  $\pi\pi^*$  state of the organic chromophore. The above speculation is supported by the observation that the Ru-based red emission in two Ln-Ru complexes is more effectively excited in the UV region (< 400 nm) while the pure metalloligand  $L_{Ru}$  shows the highest excitation in visible region (> 400 nm). As seen from Figure 3, the excitation-emission dependence studies evidently reveal that the most intensive Ru-based red emission of the free metalloligand  $L_{Ru}$ is achieved at excitation wavelength ~470 nm, indicating a dominant  $^{1}MLCT \rightarrow ^{3}MLCT$  energy transfer process. In contrast, for the two Ln-Ru complexes, the Ru-based red emission is more preferably excited at shorter wavelengths below 400 nm, suggesting that the higher excited  $\pi\pi^*$  state of the organic chromophore is involved in energy transfer. This result evidently justifies a  $\pi\pi^* \rightarrow f \rightarrow {}^{3}MLCT$ energy immigration process, accounting for the enhanced <sup>3</sup>MLCT emission in bimetallic Eu/Tb-Ru complexes. Therefore, the two Ln-Ru complexes can emit brighter Ru-based red emission with longer decay lifetimes and higher quantum yields than the free metalloligand  $L_{Ru}$ . In former reports, Bünzli and co-workers have suggested that there might be  $f \rightarrow d$  energy transfer from Ln(III) to Ru(II) in a Ln<sup>III</sup>-DOTA-Bipy-Ru<sup>II</sup> system,<sup>19</sup> yet they did not observe any intensified luminescence of Ru-metalloligand after Ln<sup>3+</sup> coordination. While our cases represent direct and eye-detectable evidence for sensitizing Ru-based MLCT emission by Ln<sup>3+</sup> ions coordination, which provides a secondary sensitizing pathway via a  $\pi\pi^* \to f \to d$  process besides normal <sup>1</sup>MLCT  $\to$  <sup>3</sup>MLCT energy transfer approach (Scheme 2).



Fig. 3 (a-c) Solid state excitation-wavelength-dependent emission spectra of  $L_{Ru}$  ligand (a), and Eu-Ru (b) and Tb-Ru (c) complexes. (d)

Emission intensity-excitation wavelength relationship of  $L_{Ru}$  ligand and Eu-Ru and Tb-Ru complexes.

On the other hand, the <sup>3</sup>MLCT energy state of  $L_{Ru}$  (~15 698 cm<sup>-1</sup>) is suitable for sensitizing the NIR luminescence of Yb<sup>3+</sup> and Nd<sup>3+</sup> via  $d \rightarrow f$  energy transfer. As demonstrated in Scheme 2, the  ${}^{4}F_{3/2}$  of  $Nd^{3+}$  and  ${}^{2}F_{5/2}$  of  $Yb^{3+}$  energy levels are around 10 000 cm<sup>-1</sup>, which are appropriate to happen  $d \rightarrow f$  transition from L<sub>Ru</sub>-metalloligand. Especially, Nd<sup>3+</sup> has dense and multiple energy levels between 10 000~15 000 cm<sup>-1</sup>, which allows significant overlap with the <sup>3</sup>MLCT state of L<sub>Ru</sub>. Therefore, in Nd-Ru complex, efficient energy transfer occurs from Ru(II) to Nd(III) and intense NIR emissions at 900 and 1059 nm ( ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}, {}^{4}I_{11/2}$ ) were observed (Fig. 2c). The room temperature decay lifetime detected at 1059 nm is about 106 ns, amounting to a quantum yield  $\Phi_{Nd}$  of 0.04% as calculated from the natural lifetime of Nd<sup>3+</sup> ions (0.25 ms). Simultaneously, the emission intensity of L<sub>Ru</sub> itself was greatly hampered and the decay lifetime of its red emission decreased to 14 ns (Table 1). In Yb-Ru complex, the NIR luminescence of Yb<sup>3+</sup> was detected at 998 nm ( ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ ) with the decay lifetime and calculated  $\Phi_{\rm Yb}$  of 595 ns and 0.03%, respectively. And the lifetime of L<sub>Ru</sub> emission was decreased to 71 ns. According to the energy transfer efficiency ( $\eta$ ) equation,

 $\eta = 1 - \tau_q^{-1} / \tau_u^{-1}$ ,

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in which  $\tau_q$  refers to the "quenched" lifetime of Ru-metalloligand with Yb/Nd coordination and  $\tau_u$  refers to its "unquenched" lifetime in Gd-Ru complex, the Ru  $\rightarrow$  Nd and Ru  $\rightarrow$  Yb energy-transfer efficiency  $\eta$  were calculated to be 0.98 and 0.92 at room temperature, respectively.<sup>29</sup>



Scheme 2. Diagram indicating the main energy levels and potential energy transfer processes in different Ln-Ru complexes, showing a cascade  $f \rightarrow d \rightarrow f$  energy transfer pathway by designing trimetallic systems.

**Cascade**  $f \rightarrow d \rightarrow f$  energy transfer in Ln1-Ru-Ln2 **Trimetallic Complexes.** Observation of above distinguishable  $d \rightarrow f$  and  $f \rightarrow d$  energy transfer in isomorphous bimetallic Ln-Ru complexes prompts us to design trimetallic Ln1-Ru-Ln2 systems to achieve a cascade  $f \rightarrow d \rightarrow f$  energy transfer process by incorporating both Eu/Tb<sup>3+</sup> and Nd/Yb<sup>3+</sup> ions with the Rumetalloligand. Since the Ln-Ru structural units are densely packed in crystal lattice with suitable Ru…Ln separation (~8 Å), it is possible to accomplish an energy immigration from Eu/Tbcenter to L<sub>Ru</sub> and then to Nd/Yb-center with the Rumetalloligand acting as both a wide UV-vis absorption antenna and energy transfer bridge. We therefore prepared a series of trimetallic Ln1-Ru-Ln2 samples by mixing Eu/Tb<sup>3+</sup> and Nd/Yb<sup>3+</sup> ions in the isomorphous crystals as listed in Table 1. The ratios of the different Ln<sup>3+</sup> ions integrated in the trimetallic are confirmed by samples energy-dispersive X-ray spectroscopy (EDX), which are basically in consistent with the feeding ratios.



**Fig. 4** Solid state emission of Ln1-Ru-Ln2 (Ln1 = Eu or Tb, Ln2 = Nd or Yb) complexes compared with Nd-Ru and Yb-Ru (the broad emission in visible region is from  $L_{Ru}$  metalloligand,  $\lambda_{ex} = 335$  nm).

As shown in Fig. 4, the trimetallic Ln1-Ru-Ln2 complexes show similar emission profiles as those for Nd-Ru and Yb-Ru complexes. Both the metalloligand based broad emissions and characteristic NIR emissions of Nd<sup>3+</sup> and Yb<sup>3+</sup> ions are observed, while the absence of characteristic emissions from Eu<sup>3+</sup> and Tb<sup>3+</sup> ions manifests the similar  $f \rightarrow d$  energy transfer as described in Eu/Tb-Ru systems. The decay lifetime studies provide more evidance about the energy transfer processes in these complexes. For Eu-Ru-Nd system with Eu:Nd metal ratios ranging from 1:3 to 1:1 and 3:1, the lifetime of the RuJournal Name

based emission changes steadily from 27 to 112 and 164 ns, respectively, falling between the pure Eu-Ru (820 ns) and Nd-Ru (14 ns) complexes. This means that the increase of Eu:Nd ratio leads to an increase in the decay lifetime of <sup>3</sup>MLCT emission, showing an intensified energy transfer from Eu<sup>3+</sup> to L<sub>Ru</sub> metalloligand. Moreover, this increase of Eu:Nd ratio also results in a constant increase in the decay lifetime of Nd<sup>3+</sup>-NIR emission (144, 191 and 262 ns). The calculated quantum yield based on Nd<sup>3+</sup>-emission also increases from 0.04% of Nd-Ru to 0.10% of Eu-Ru-Nd with Eu:Nd ratio of 3:1 at room temperature, and reaches to 0.61% under 77 K. These results indicate that the energy transfer from  $Eu^{3+}$  to  $L_{Ru}$  can further immigrate to Nd<sup>3+</sup>, leading to a steady increase of decay lifetime and luminescence quantum efficiency. Similar results have also been testified in Tb-Ru-Nd, Eu-Ru-Yb and Tb-Ru-Yb trimetallic systems (Table 1).

Based on above observations, we may propose a cascade  $f \rightarrow d \rightarrow f$  energy transfer process useful for alternative and improved NIR sensitization in Ln1-Ru-Ln2 trimetallic systems shown in Scheme 2. Firstly, the  $\pi \rightarrow \pi^*$  transition-related excited state of Ru-metalloligand absorbs UV light and passes energy to the accepting *f*-levels of Eu<sup>3+</sup> or Tb<sup>3+</sup>, and then transfers to the <sup>3</sup>MLCT energy state of Ru-metalloligand via a  $\pi\pi^* \rightarrow f \rightarrow d$  pathway. Consecutively, the <sup>3</sup>MLCT state of L<sub>Ru</sub>-metalloligand transfers energy to the accepting *f*-levels of Nd<sup>3+</sup> or Yb<sup>3+</sup> via a  $d \rightarrow f$  pathway, leading to finally intensified NIR emission compared to the single  $d \rightarrow f$  energy transfer process in bimetallic Ln-Ru systems.

#### Conclusions

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In summary, the coordination of  $\text{Ln}^{3+}$  ions with a polypyridyl Ru-metalloligand results in either intensified red emission of the metalloligand itself via  $f \rightarrow d$  energy transfer or sensitized NIR emission of Ln ions via  $d \rightarrow f$  energy transfer in bimetallic Ln-Ru systems. The dual energy transfer probabilities generated in the trimetallic Ln1-Ru-Ln2 systems further provide a novel  $f \rightarrow d \rightarrow f$  energy transfer pathway, leading to an overall enhanced  $\text{Ln}^{3+}$ -NIR luminescence. This may open a new arena for the design and modulation of  $\text{Ln}^{3+}$ -based luminescent materials.

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#### Notes and references

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- (a) E. G. Moore, A. P. S. Samuel, K. N. Raymond, Acc. Chem. Res., 2009, 42, 542-552; (b) J. Feng, H. J. Zhang, Chem. Soc. Rev., 2013, 42, 387-410; (c) A. de Bettencourt-Dias, P. S. Barber, S. Bauer, J. Am. Chem. Soc., 2012, 134, 6987-6994; (d) B. Li, H. M. Wen, Y. Cui, G. Qian, B. Chen, Prog. Polym. Sci., 2015, 48, 40-84; (e) J.-C. G. B ünzli, Chem. Rev. 2010, 110, 2729-2755; (f) J.-C. G. B ünzli, C. Piguet, Chem. Soc. Rev. 2005, 34, 1048-1077.
- (a) A. D'Aléo, F. Pointillart, L. Ouahab, C. Andraud, O. Maury, *Coord. Chem. Rev.*, 2012, **256**, 1604-1620; (b) F. Artizzu, M. L. Mercuri, A. Serpe, P. Deplano, *Coord. Chem. Rev.*, 2011, **255**, 2514-2529; (c) J. M. Stanley, B. J. Holliday, *Coord. Chem. Rev.*, 2012, **256**, 1520-1530; (d) L. V. Meyer, F. Schönfeld, K. Müller-Buschbaum, *Chem Commun.*, 2014, **50**, 8093-8108.
- (a) L.-J. Xu, G.-T. Xu, Z.-N. Chen, *Coord. Chem. Rev.*, 2014, 273-274, 47-62; (b) S. V. Eliseeva, J.-C. G. Bünzli, *Chem. Soc. Rev.*, 2010, 39, 189-227; (c) M. C. Heffern, L. M. Matosziuk, T. J. Meade, *Chem. Rev.*, 2014, 114, 4496-4539; (d) S. Roy, A. Chakraborty, T. K. Maji, *Coord. Chem. Rev.*, 2014, 273-274, 139-164.
- (a) S. J. Bradberry, A. J. Savyasachi, M. Martinez-Calvo, T. Gunnlaugsson, *Coord. Chem. Rev.*, 2014, **273-274**, 226-241; (b) C. M. G. dos Santos, A. J. Harte, S. J. Quinn, T. Gunnlaugsson, *Coord. Chem. Rev.*, 2008, **252**, 2512-2527; (c) S. Swavey, R. Swavey, *Coord. Chem. Rev.*, 2009, **253**, 2627-2638.
- (a) S. I. Klink, H. Keizer, F. C. J. M. van Veggel, *Angew. Chem. Int. Ed.*, 2009, **39**, 4319-4321; (b) A. M. Nonat, C. Allain, S. Faulkner, T. Gunnlaugsson, *Inorg. Chem.*, 2010, **49**, 8449-8456.
- W. S. Perry, S. J. A. Pope, C. Allain, B. J. Coe, A. M. Kenwright, S. Faulkner, *Dalton Trans.* 2010, *39*, 10974-10983.
- S. D. Bergman, D. Gut, M. Kol, C. Sabatini, A. Barbieri, F. Barigelletti, Inorg. Chem., 2005, 44, 7943-7950.
- D. W. Feng, Z. Y. Gu, J. R. Li, H. L. Jiang, Z. W. Wei; H. C. Zhou, Angew. Chem. Int. Ed., 2012, 51, 10307-10310.
- (a) C. Wang, K. E. Dekrafft, W. B. Lin, J. Am. Chem. Soc., 2012, 134, 7211-7214; (b) A. J. Hallett, B. M. Kariuki, S. J. A. Pope, *Dalton Trans.*, 2011, 40, 9474-9481.
- S. R. Halper, L. Do, J. R. Stork, S. M. Cohen, J. Am. Chem. Soc., 2006, 128, 15255-15268.
- (a) J.-C. G. Bünzli, *Coord. Chem. Rev.*, 2015, **293-294**, 19-47; (b) P. A. Smith, C. Crawford, N. Beedoe, Z. Assefa, R. E. Sykora, *Inorg. Chem.*, 2012, **51**, 12230-12241.
- (a) A. P. S. Samuel, J. Xu, K. N. Raymond, *Inorg. Chem.*, 2009, 48, 687-698; (b) D. Sykes, A. J. Cankut, N. M. Ali, A. Stephenson, S. J. P. Spall, S. C. Parker, J. A.Weinstein, M. D. Ward, *Dalton Trans.*, 2014, 43, 6414-6428.

- (a) M. Tropiano, N. L. Kilah, M. Morten, H. Rahman, J. J. Davis, P. D. Beer, S. Faulkner, *J. Am. Chem. Soc.*, 2011, **133**, 11847-11849; (b) G. Dehaen, S. V. Eliseeva, P. Verwilst, S. Laurent, L. Vander Elst, R. N. Muller, W. De Borggraeve, K. Binnemans, T. N. Parac-Vogt, *Inorg. Chem.*, 2012, **51**, 8775-8783; (c) A. M. Nonat, S. J. Quinn, T. Gunnlaugsson, *Inorg. Chem.*, 2009, **48**, 4646-4648.
- (a) P. Coppo, M. Duati, V. N. Kozhevnikov, J. W. Hofstraat, L. De Cola, Angew. Chem. Int. Ed., 2005, 44, 1806-1810; (b) D. Sykes, M. D. Ward, Chem. Commun., 2011, 47, 2279-2281.
- (a) L. J. Charbonnière, S. Faulkner, C. Platas-Iglesias, M. Regueiro-Figueroa, A. Nonat, T. Rodr guez-Blas, A. de Blas, W. S. Perryd, M. Tropiano, *Dalton Trans.*, 2013, 42, 3667-3681; (b) T. Lazarides, N. M. Tart, D. Sykes, S. Faulkner, A. Barbieri, M. D. Ward, *Dalton Trans.*, 2009, 3971-3979.
- (a) M. Tropiano, C. J. Record, E. Morris, H. S. Rai, C. Allain, S. Faulkner, *Organometallics*, 2012, **31**, 5673-5676; (b) S. Singaravadivel, E. Babu, M. Velayudham, K.-L. Lu, S. J. Rajagopal, *Organomet. Chem.*, 2013, **738**, 49-54.
- (a) Q.-H. Wei, Y.-F. Lei, W.-R. Xu, J.-M. Xie, G.-N. Chen, *Dalton Trans.*, 2012, **41**, 11219-11225; (b) L. Li, S. Zhang, L. Xu, Z.-N. Chen, J. Luo, *J. Mater. Chem. C*, 2014, **2**, 1698-1703; (c) L.-Y. Zhang, Y.-J. Hou, M. Pan, L. Chen, Y.-X. Zhu, S.-Y. Yin, G. Shao, C.-Y. Su, *Dalton Trans.*, **2015**, *44*, 15212-15219; (d) S. Torelli, D. Imbert. M. Cantuel, G. Bernardinelli, S. Delahaye, A. Hauser, J.-C. G. Bünzli, C. Piguet, *Chem. Eur. J.*, **2005**, *11*, 3228-3242.
- (a) E. D. Piazza, L. Norel, K. Costuas, A. Bourdolle, O. Maury, S. Rigaut, J. Am. Chem. Soc., 2011, 133, 6174-6176; (b) E. G. Moore, M. Benaglia, G. Bergamini, P. Ceroni, Eur. J. Inorg. Chem., 2015, 414-420; (c) K. Sénéchal-David, S. J. A. Pope, S. Quinn, S. Faulkner, T. Gunnlaugsson, Inorg. Chem., 2006, 45, 10040-10042; (d) Z.-N. Chen, C.-H. Huang, Organometallics, 2014, 33, 3275-3282; (e) M. Gagliardo, F. Rizzo, M. Lutz, A. L. Spek, G. P. M. van Klink, A. E. Merbach, L. De Cola, G. van Koten, Eur. J. Inorg. Chem., 2007, 18, 2853.
- (a) M. V. López, S. V. Eliseeva, J. M. Blanco, G. Rama, M. R. Bermejo, M. E. Vázquez, J.-C. G. Bünzli, *Eur. J. Inorg. Chem.*, 2010, 4532-4545;
  (b) G. Dehaen, P. Verwilst, S. V. Eliseeva, S. Laurent, L. V. Elst, R. Muller, W. M. D. Borggraeve, K. Binnemans, T. N. Parac-Vogt, *Inorg. Chem.*, 2011, **50**, 10005-10014.
- A. J. M. Xavier, N. A. Samy, M. W. B. Paul, B. Brainard, M. Letticia, V. Alexander, *New J. Chem.*, 2015, **39**, 4284-4294.
- CrysAlis CCD and RED, Oxford Diffraction Ltd., Version 1.171.31.7, 2006.
- 22. CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.31.7, 2006.
- Sheldrick, G. M. SHELX 97, Program for Crystal Structure Solution and Refinement, G\u00fcttingen University, 1997.
- (a) Y. Halpin, D. Dini, H. M. Y. Ahmed, L. Cassidy, W. R. Browne, J. G. Vos, *Inorg. Chem.*, 2010, **49**, 2799-2807; (b) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85-277.
- F. Schramm, V. Meded, H. Fliegl, K. Fink, O. Fuhr, Z. Qu, W. Klopper, S. Finn, T. E. Keyes, M. Ruben, *Inorg. Chem.*, 2009, 48, 5677-5684.
- G. J. Wilson, A. Launikonis, W. H. F. Sasse, A. W.-H. Mau, J. Phys. Chem. A, 1997, 101, 4860-4866.
- 27. R. T. F. Jukes, J. Kühni, N. Salluce, P. Belser, L. De Cola, F. Hartl, *Dalton Trans.*, 2009, 3993-4002.

- N. M. Shavaleev, L. P. Moorcraft, S. J. A. Pope, Z. R. Bell, S. Faulkner, M. D. Ward, *Chem. Eur. J.*, 2003, 9, 5283-5291.
- (a) T. Lazarides, D. Sykes, S. Faulkner, A. Barbieri, Ward, M. D. Chem. Eur. J., 2008, 14, 9389-9399; (b) M. D. Ward, Coord. Chem. Rev., 2010, 254, 2634-2642.

#### Table of Contents (TOC) entry

A possible approach to achieve multiple  $f \rightarrow d$ ,  $d \rightarrow f$  and cascade  $f \rightarrow d \rightarrow f$  energy transfer processes in heteronuclear Ru-Ln and Ln1-Ru-Ln2 complexes.

