Supporting Information

for submission to New J Chem

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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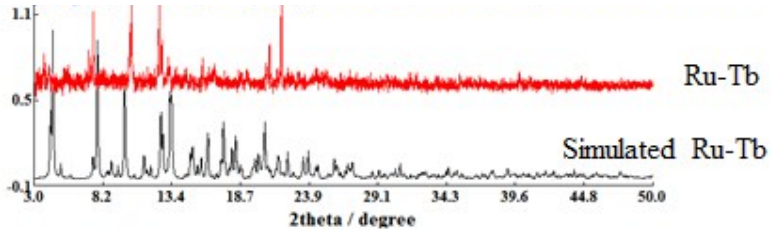


Fig. S1 PXRD patterns for the grounded crystalline sample of Tb-Ru complex compared with the simulated pattern based on the single-crystal data.

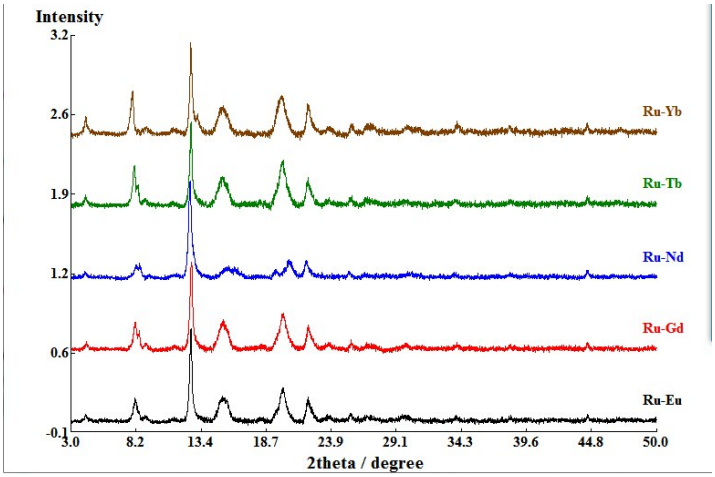


Fig. S2 PXRD patterns for the freshly precipitated samples of Ru-Ln isomorphous series.

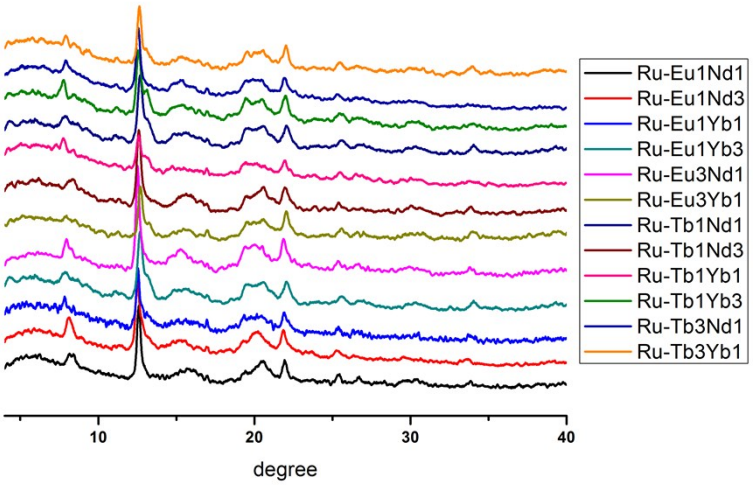


Fig. S3 PXRD patterns for Ln1-Ru-Ln2 isomorphous crystals.

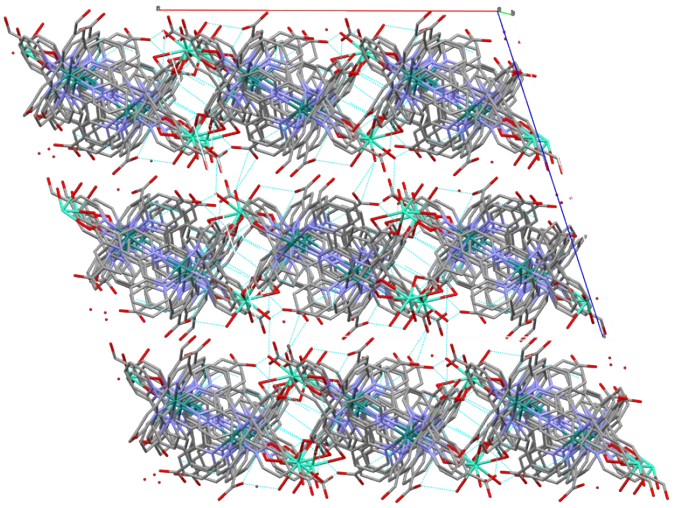


Fig. S4 Extended packing in the crystal lattice of complex Tb-Ru.

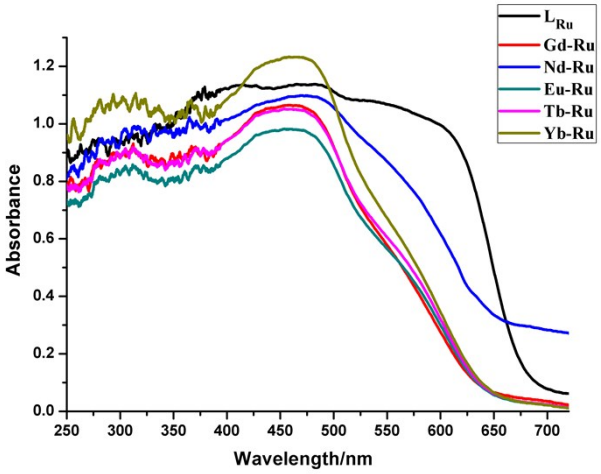


Fig. S5 Solid state UV-vis reflectance spectra for L_{Ru} and different Ln-Ru complexes.

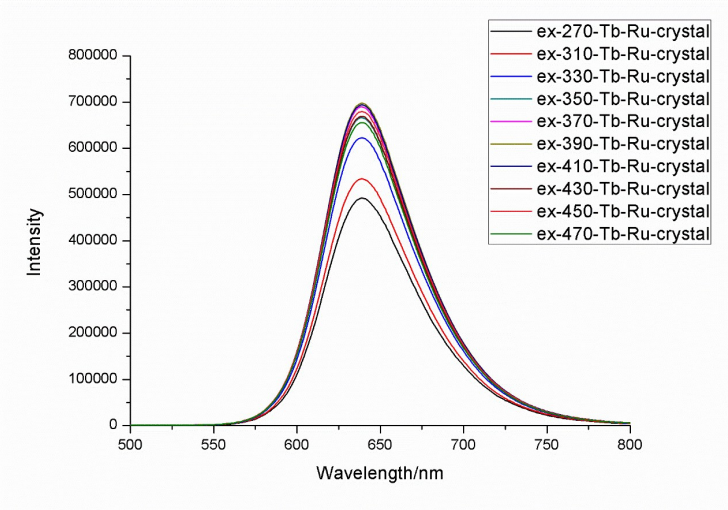


Fig. S6 Solid state excitation-wavelength-dependent emission spectra of Tb-Ru crystals.

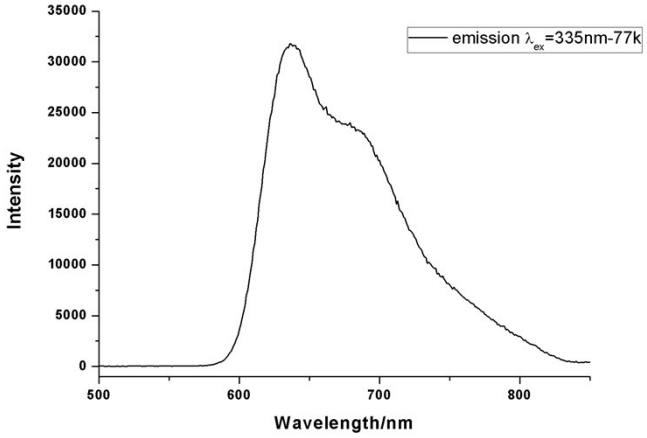
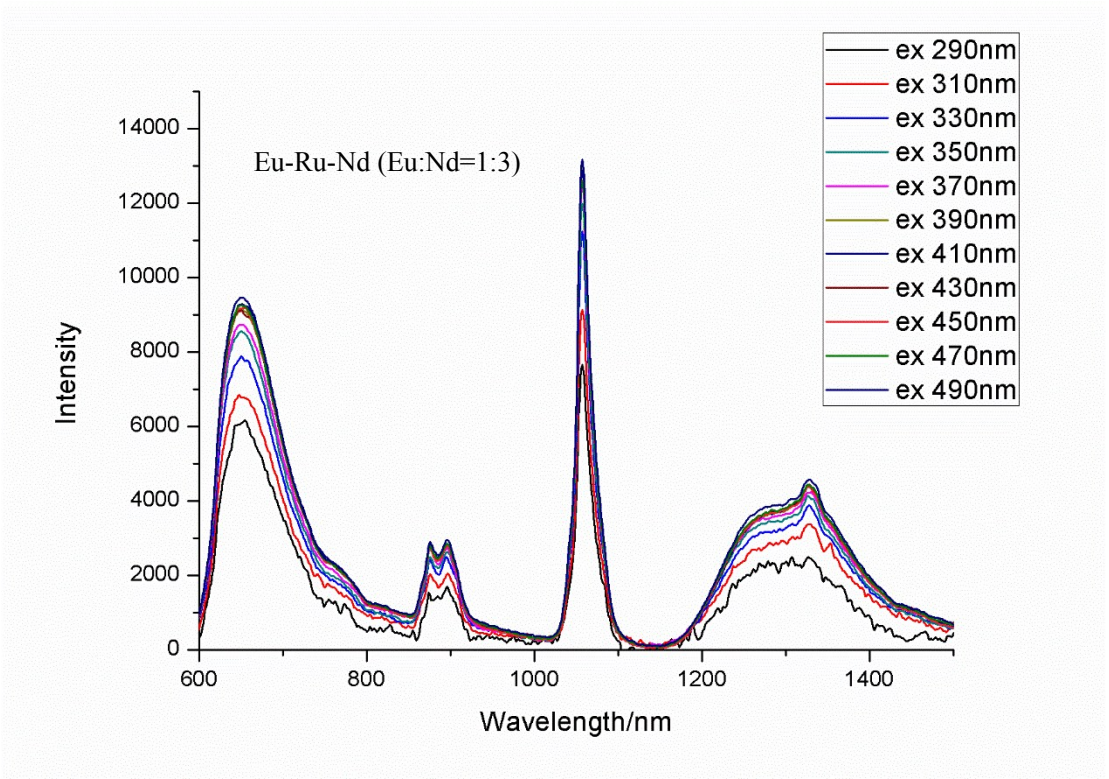
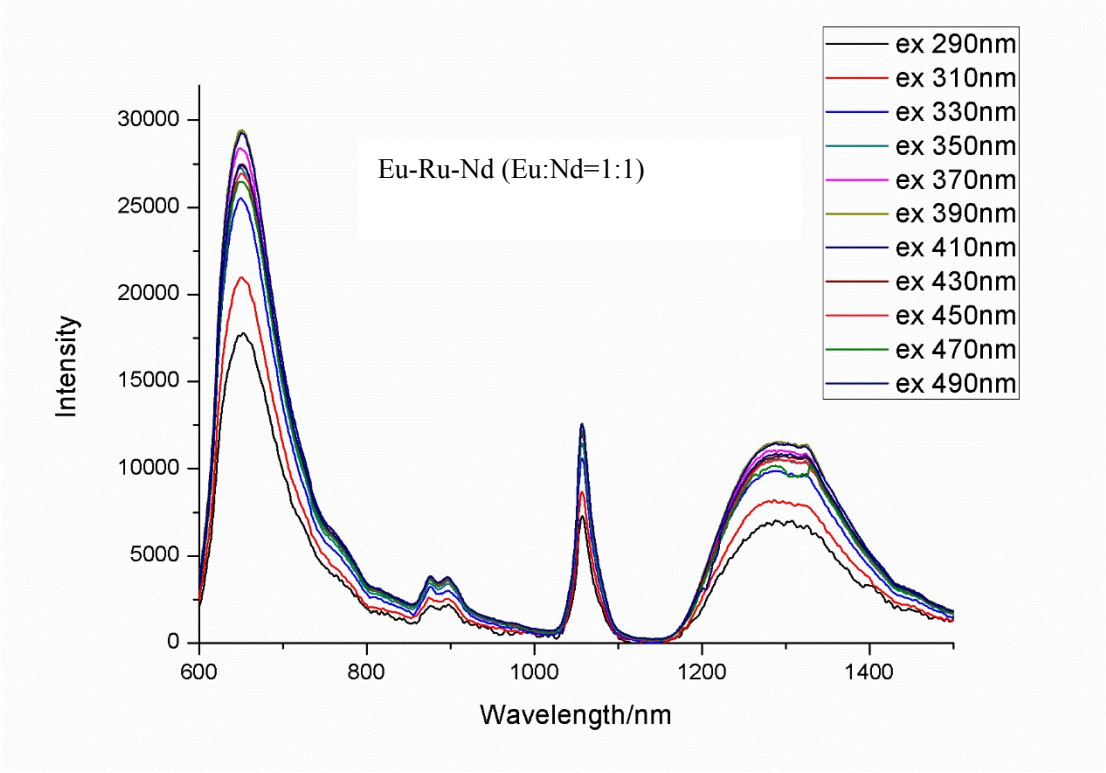


Fig. S7 Solid state phosphorescence of Gd-Ru complex at 77 K.

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ex 290nm
ex 310nm
ex 330nm
ex 350nm
ex 370nm
ex 390nm
ex 410nm
ex 430nm
ex 450nm
ex 470nm
ex 490nm
Intensity
Wavelength/nm
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15000
20000
25000
30000
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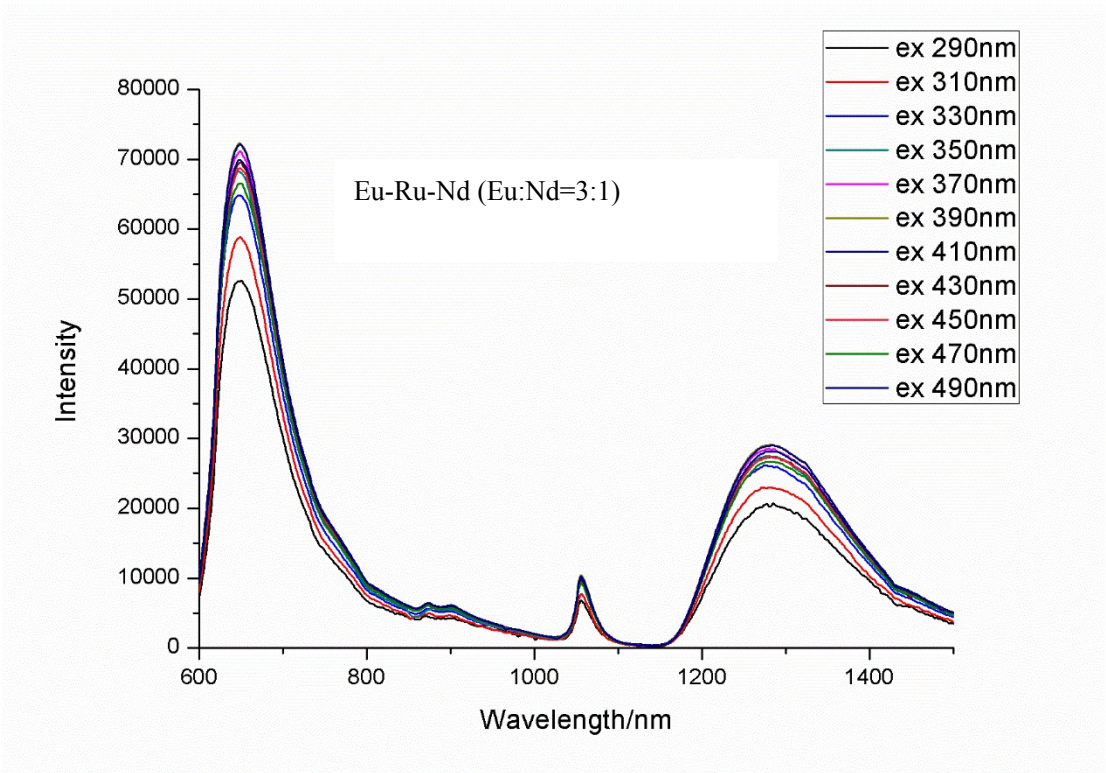
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ex 330nm
ex 350nm
ex 370nm
ex 390nm
ex 410nm
ex 430nm
ex 450nm
ex 470nm
ex 490nm
Intensity
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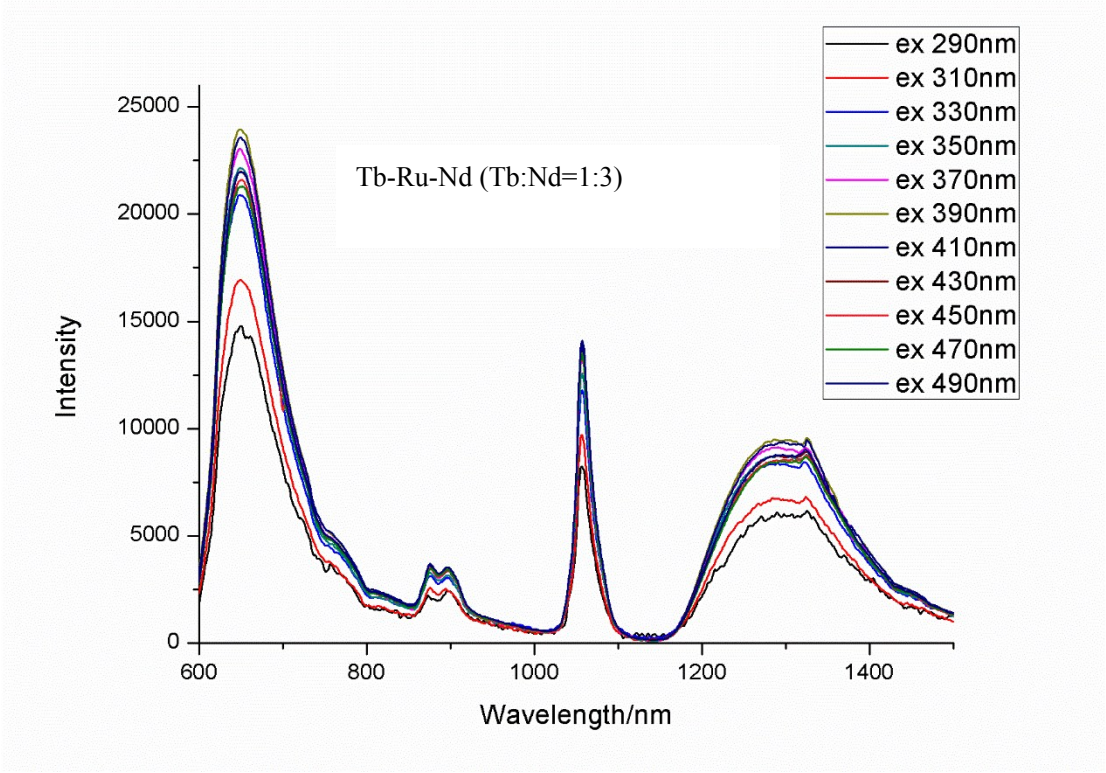
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ex 390nm
ex 410nm
ex 430nm
ex 450nm
ex 470nm
ex 490nm
Intensity
Wavelength/nm
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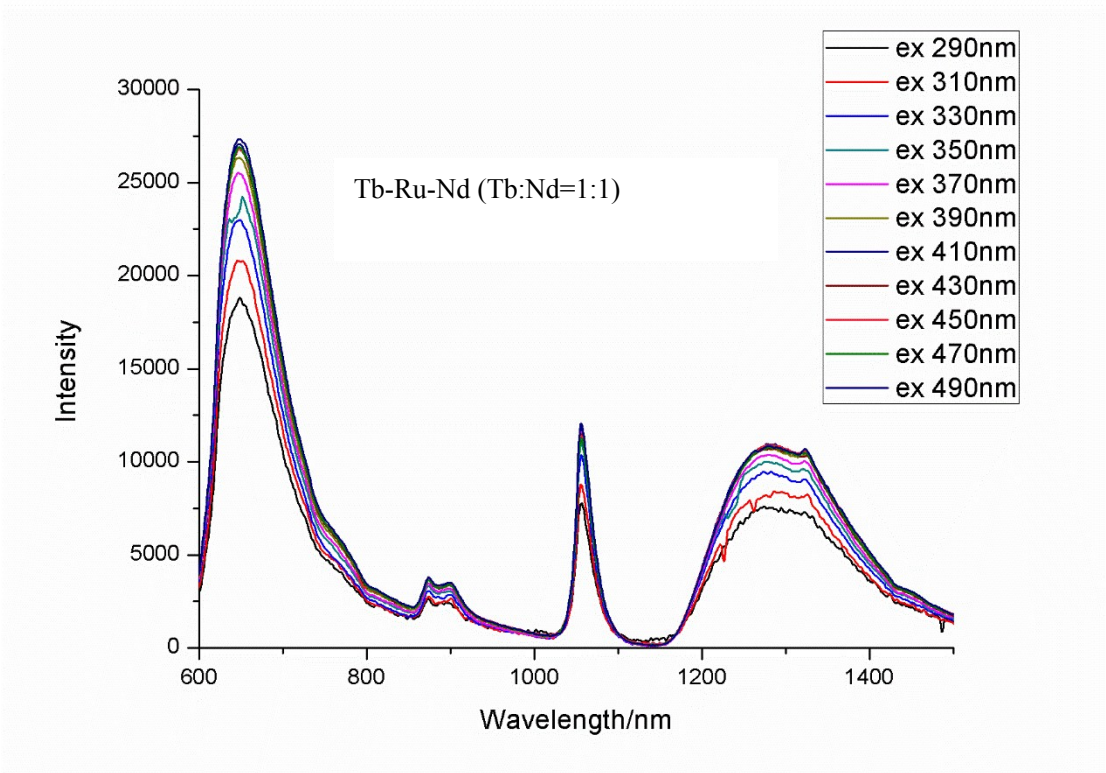
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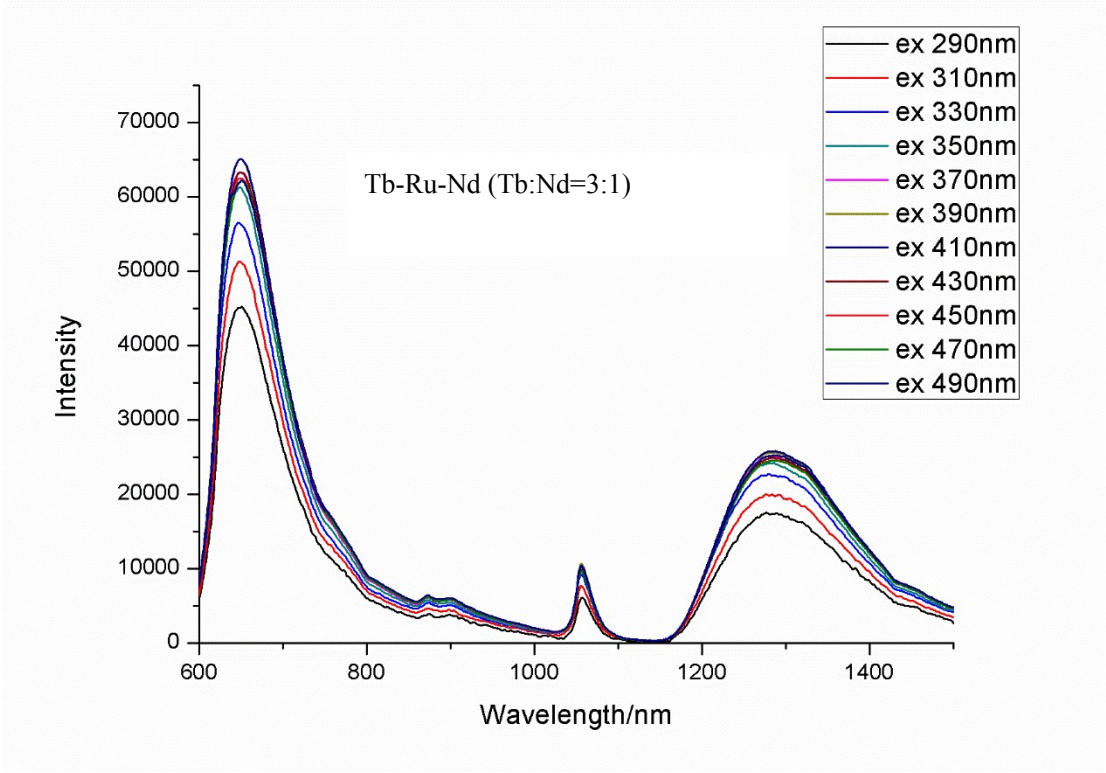
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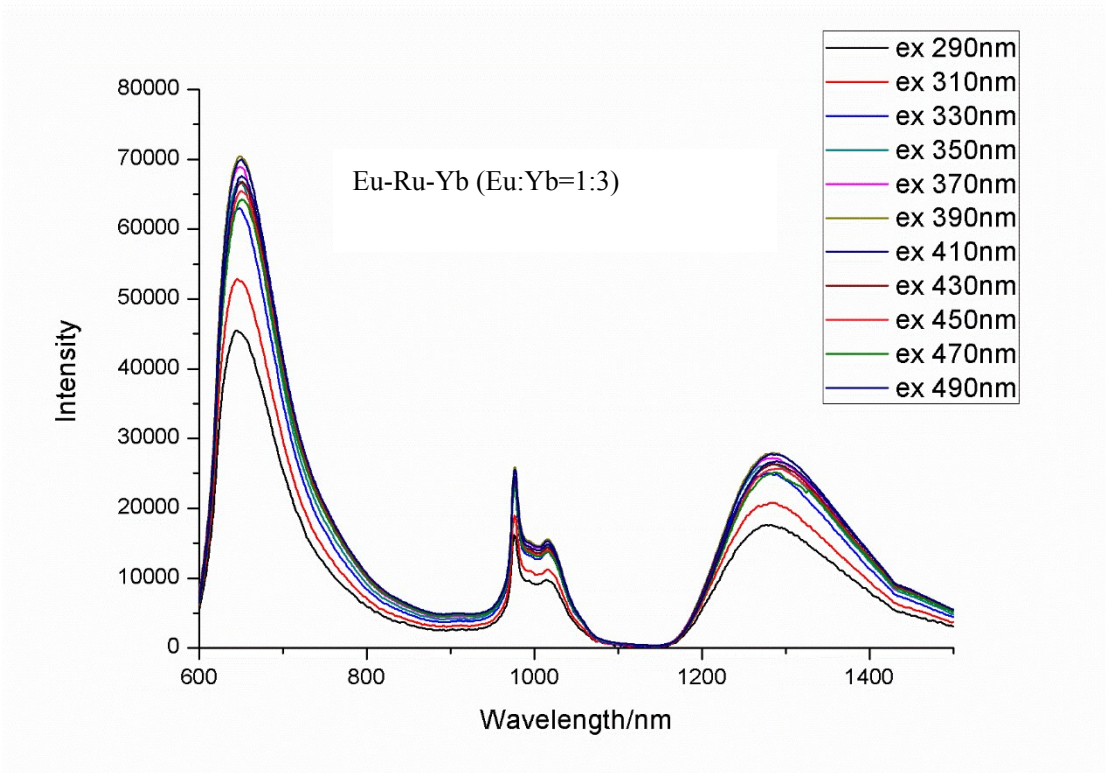
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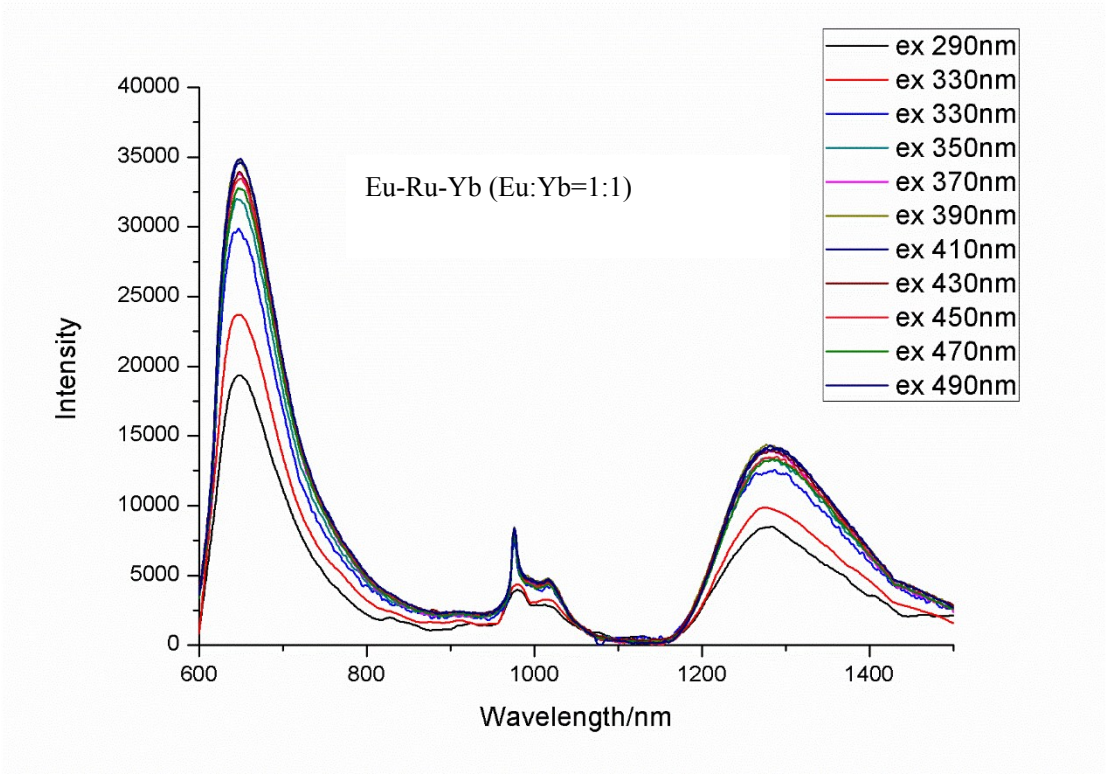
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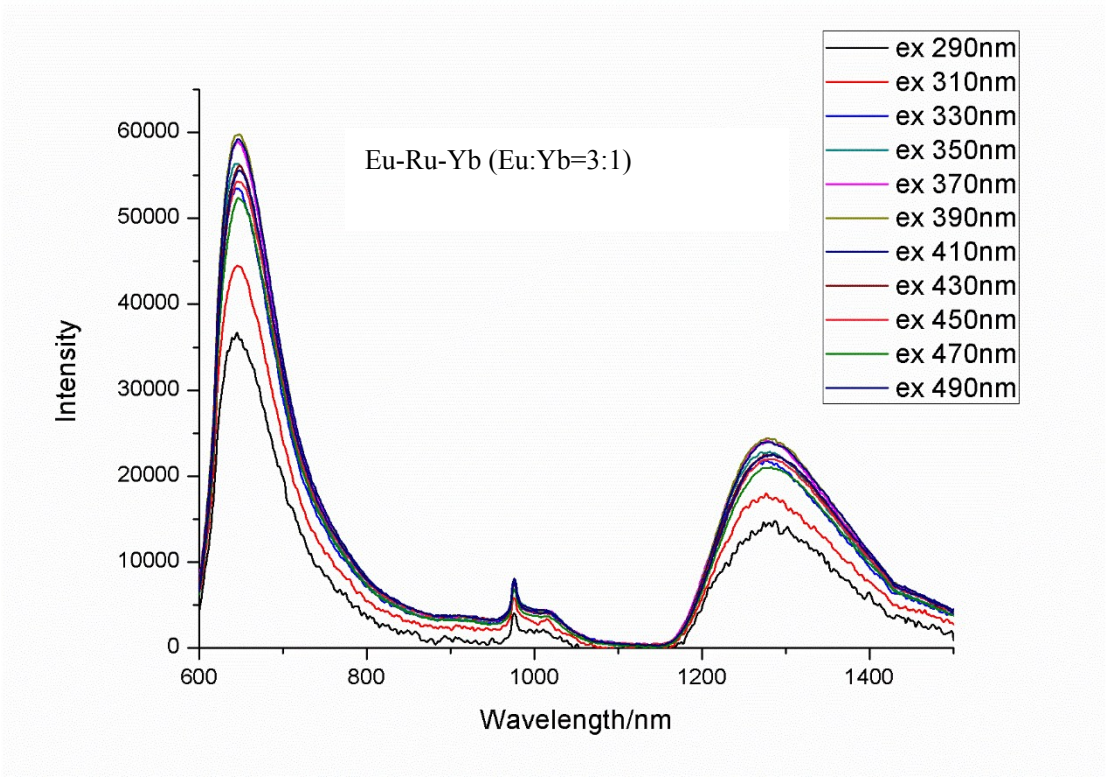
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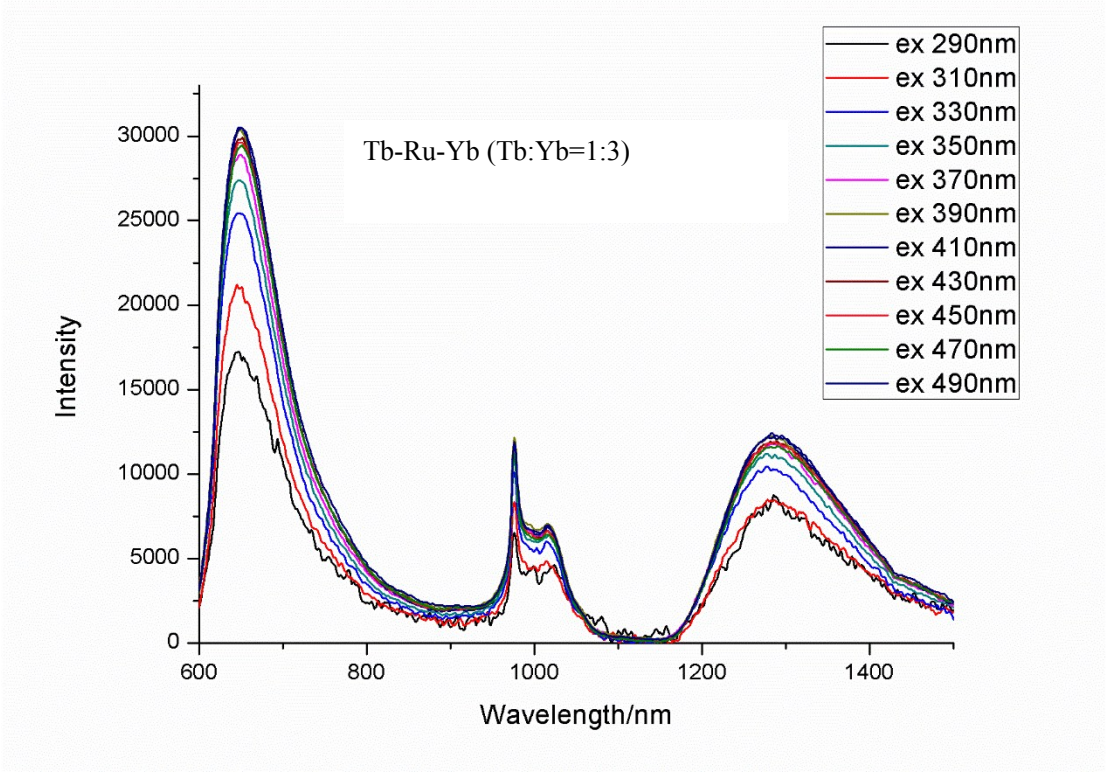
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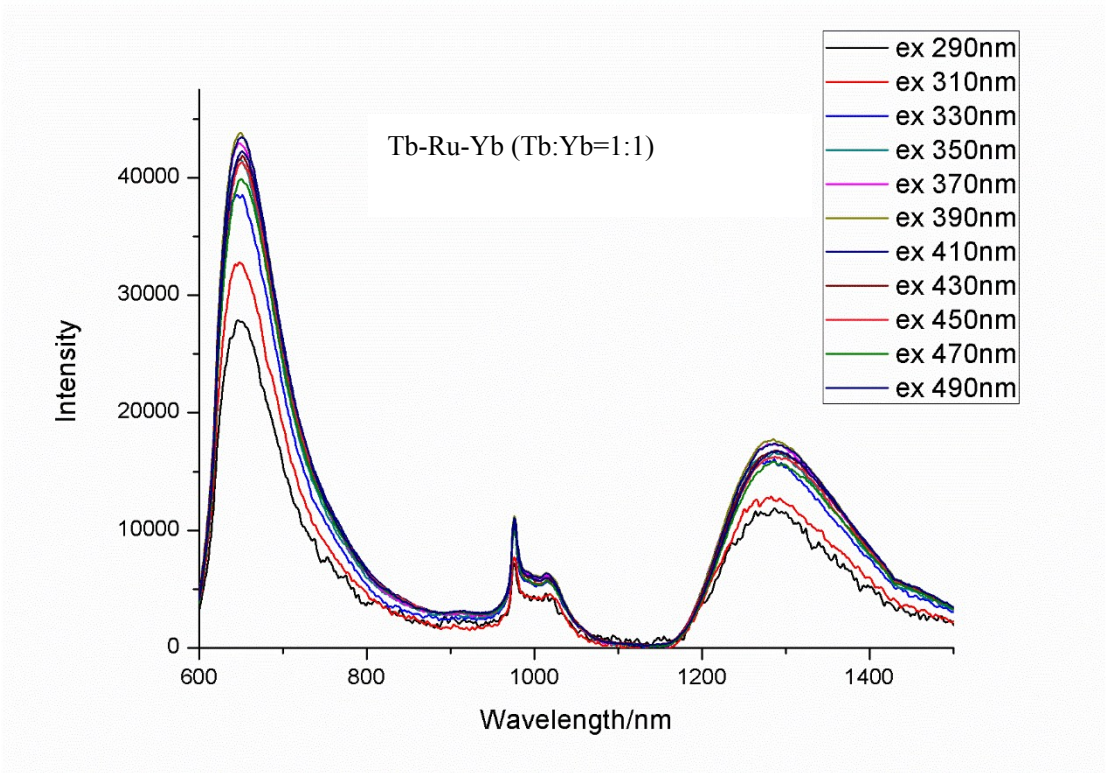
Wavelength/nm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Wavelength/nm

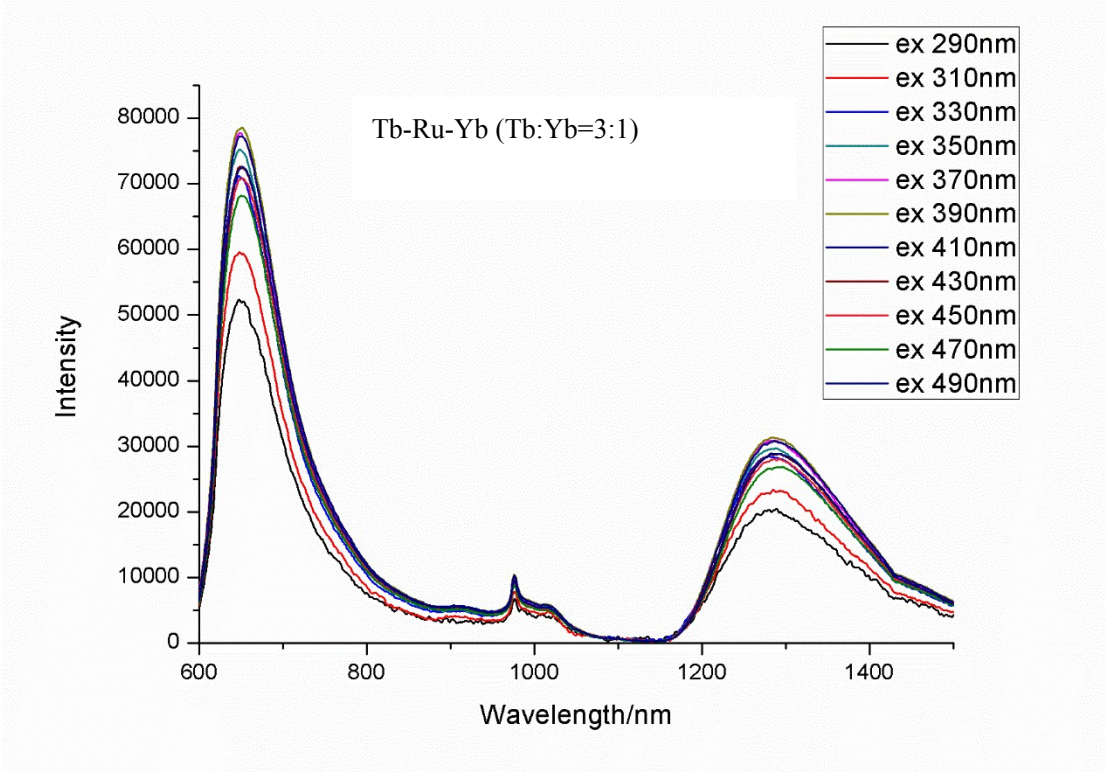

Fig. S8 Solid state excitation-wavelength-dependent emission spectra for trimetallic complexes.

Table S1. Selected bond distances (Å) and angles (°) for complex Tb-Ru.

Ru1-N1	2.041(12)	Ru1-N5	2.043(9)	Ru1-N2	2.044(11)
Ru1-N3	2.061(11)	Ru1-N6	2.066(9)	Ru1-N4	2.068(12)
Ru2-N7	2.045(13)	Ru2-N10	2.049(12)	Ru2-N11	2.053(10)
Ru2-N9	2.053(12)	Ru2-N8	2.067(10)	Ru2-N12	2.067(10)
Ru3-N15	2.044(12)	Ru3-N14	2.049(11)	Ru3-N18	2.050(10)
Ru3-N17	2.050(9)	Ru3-N16	2.068(10)	Ru3-N13	2.070(10)
Tb1-O6	2.365(7)	Tb1-O3	2.367(7)	Tb1-O3W	2.370(6)
Tb1-O1W	2.375(6)	Tb1-O10	2.384(6)	Tb1-O2W	2.395(7)
Tb1-O4	2.589(7)	Tb1-O5	2.606(8)	Tb1-O9	2.610(7)
N1-Ru1-N5	97.2(4)	N1-Ru1-N2	79.3(5)	N5-Ru1-N2	175.4(5)
N1-Ru1-N3	96.5(5)	N5-Ru1-N3	92.6(4)	N2-Ru1-N3	90.8(4)
N1-Ru1-N6	93.4(4)	N5-Ru1-N6	80.1(3)	N2-Ru1-N6	97.0(4)
N3-Ru1-N6	168.4(5)	N1-Ru1-N4	173.3(4)	N5-Ru1-N4	86.7(4)
N2-Ru1-N4	97.1(5)	N3-Ru1-N4	77.9(5)	N6-Ru1-N4	92.6(4)

Symmetry code: 'x, y, z'; '-x, y, -z+1/2'; 'x+1/2, y+1/2, z'; '-x+1/2, y+1/2, -z+1/2'; '-x, -y, -z'; 'x, -y, z-1/2'; '-x+1/2, -y+1/2, -z'; 'x+1/2, -y+1/2, z-1/2'

Table S2. Solid state excitation-wavelength-dependent quantum yields (QY) of different samples.

λex /nm	QY/%				
	LRu	Eu-Ru	Tb-Ru	Gd-Ru	Tb-Ru-crystal
335	5.1	12.7	11.7	11.0	21.8
370	5.8	14.7	13.2	13.0	22.1
410	5.4	13.6	12.4	12.6	21.6
450	4.8	12.8	11.9	11.2	21.1
490	5.4	13.0	12.1	11.9	21.6

Table S3. EA results for trimetallic complexes.

Sample	Formula	Calculated			Measured		
		C/%	H/%	N/%	C/%	H/%	N/%
Eu-Ru-Nd (Eu:Nd=1:3)	$[Eu_{0.25}Nd_{0.75}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_{11}$	41.80	3.43	9.39	41.82	3.00	9.17
Eu-Ru-Nd (Eu:Nd=1:1)	$[Eu_{0.5}Nd_{0.5}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_{11}$	41.77	3.43	9.39	41.83	3.03	9.20
Eu-Ru-Nd (Eu:Nd=3:1)	$[Eu_{0.75}Nd_{0.25}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_8$	42.57	3.27	9.57	42.41	3.02	9.41
Tb-Ru-Nd (Tb:Nd=1:3)	$[Tb_{0.25}Nd_{0.75}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_{11}$	41.77	3.43	9.39	41.61	3.03	9.14
Tb-Ru-Nd (Tb:Nd=1:1)	$[Tb_{0.5}Nd_{0.5}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_8$	42.55	3.27	9.56	42.42	2.99	9.42
Tb-Ru-Nd (Tb:Nd=3:1)	$[Tb_{0.75}Nd_{0.25}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_8$	42.49	3.27	9.55	42.31	3.00	9.31
Eu-Ru-Yb (Eu:Yb=1:3)	$[Eu_{0.25}Yb_{0.75}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_8$	42.29	3.25	9.50	41.93	3.01	9.29
Eu-Ru-Yb (Eu:Yb=1:1)	$[Eu_{0.5}Yb_{0.5}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_8$	42.38	3.26	9.52	42.18	2.94	9.33
Eu-Ru-Yb (Eu:Yb=3:1)	$[Eu_{0.75}Yb_{0.25}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_8$	42.46	3.27	9.54	42.25	2.97	9.37
Tb-Ru-Yb (Tb:Yb=1:3)	$[Tb_{0.25}Yb_{0.75}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_8$	42.27	3.25	9.50	41.92	2.98	9.27
Tb-Ru-Yb (Tb:Yb=1:1)	$[Tb_{0.5}Yb_{0.5}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_{10}$	41.77	3.36	9.39	41.40	2.99	9.22
Tb-Ru-Yb (Tb:Yb=3:1)	$[Tb_{0.75}Yb_{0.25}(L_{Ru})_3(H_2O)_3]\cdot(PF_6)_{2.5}(NO_3)_{0.5}(H_2O)_9$	42.10	3.31	9.46	42.01	3.04	9.25