Electronic Supplementary Information (ESI)

Novel bimetallic Lanthanide metal-organic frameworks (Ln-MOFs) for color-tuning through energy-transfer between visible-emitting and near-infrared-emitting Ln^{3+} ions

Min Zeng[ab], Chuanlang Zhan[ab*] and Jiannian Yao[ab]

(a) Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China.

(b) University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.

*E-mail: clzhan@iccas.ac.cn.

Table S1 Crystallographic Data for NdL_2

	NdL_2
Empirical formula	$C_{14}\ H_7\ N_2\ Nd\ O_8$
Formula weight	475.46
Temperature (K)	173.15
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbcn
a (Å)	a = 9.973(4)
b (Å)	b = 8.757(4)
c (Å)	c = 15.809(6)
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$)	1380.6(10)
Z	4
Density (calculated)	2.287 mg/m^3
Absorption coefficient	3.814 mm^{-1}
F(000)	916
Crystal size	0.386 x 0.183 x 0.136 mm^3
θ_{min}, θ_{max} (°)	3.289 to 27.497°
Index ranges	-12<=h<=12, -11<=k<=11, -20<=l<=20
Reflections collected	5346
Independent reflections	1549 [R(int) = 0.0486]
Completeness to theta = 25.242°	97.6 %
Max. and min. transmission	1.00000 and 0.56743
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1549 / 0 / 114
Goodness-of-fit on F^2	1.156
R1, wR2 [I>2σ (I)]	0.0314, 0.0916
R1, wR2 [all data]	0.0321, 0.0925
Largest diff. peak and hole	0.803 and -0.948 $e.Å^{-3}$

Table S2 Selected bond lengths (Å) and angles (°) for NdL_2

Nd1-N1#1	2.622(2)	O1-Nd1-O4#5	74.87(9)
Nd1-N1#2	2.622(2)	O1#3-Nd1-O4#4	74.87(9)
Nd1-O1#3	2.382(2)	O1-Nd1-O4#4	77.14(9)
Nd1-O1	2.382(2)	O1#3-Nd1-O4#5	77.14(9)
Nd1-O2#2	2.411(2)	O2#1-Nd1-N1#2	70.37(7)
Nd1-O2#1	2.411(2)	O2#2-Nd1-N1#2	64.53(7)
Nd1-O4#4	2.442(3)	O2#2-Nd1-N1#1	70.37(7)
Nd1-O4#5	2.442(3)	O2#1-Nd1-N1#1	64.53(7)
N1#1-Nd1-N1#2	120.50(9)	O2#2-Nd1-O2#1	78.97(10)
O1-Nd1-N1#2	123.50(7)	O2#1-Nd1-O4#4	110.61(9)
O1-Nd1-N1#1	78.70(7)	O2#1-Nd1-O4#5	133.52(9)
O1#3-Nd1-N1#2	78.70(7)	O2#2-Nd1-O4#4	133.52(9)
O1#3-Nd1-N1#1	123.50(7)	O2#2-Nd1-O4#5	110.61(9)
O1#3-Nd1-O1	137.96(11)	O4#4-Nd1-N1#2	75.97(9)
O1#3-Nd1-O2#1	145.57(7)	O4#4-Nd1-N1#1	155.71(9)
O1#3-Nd1-O2#2	74.27(8)	O4#5-Nd1-N1#2	155.71(9)
O1-Nd1-O2#2	145.57(7)	O4#5-Nd1-N1#1	75.97(9)
O1-Nd1-O2#1	74.27(8)	O4#4-Nd1-O4#5	95.22(15)

Symmetry codes:#1 -x+1/2,y+1/2,z,#2 x+1/2,y+1/2,-z+1/2, #3 -x+1,y,-z+1/2 , #4 -x+1/2,-y+1/2,z-1/2 #5 x+1/2,-y+1/2,-z+1

Table S3 Crystallographic Data for Nd_2L_3

	Nd_2L_3
Empirical formula	C21 H13 N3 Nd2 O14
Formula weight	819.82
Temperature (K)	173.15
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 1 21/c 1
a (Å)	a = 6.4925(13)
b (Å)	b = 17.852(4)
c (Å)	c = 9.350(2)
α (°)	90
β (°)	94.942(3)
γ (°)	90
Volume ($Å^3$)	1079.7(4)
Z	2
Density (calculated)	2.522 mg/m^3
Absorption coefficient	4.846 mm^{-1}
F(000)	784
Crystal size	0.291 x 0.212 x 0.109 mm^3
θ_{min}, θ_{max} (°)	3.149 to 27.483°
Index ranges	-8<=h<=8, -23<=k<=22, -12<=l<=11
Reflections collected	8672
Independent reflections	2474 [R(int) = 0.0490]
Completeness to theta = 25.242°	99.8 %
Max. and min. transmission	1.00000 and 0.46277
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2474 / 0 / 176
Goodness-of-fit on F^2	1.167
R1, wR2 [I>2σ (I)]	0.0322, 0.0751
R1, wR2 [all data]	0.0330, 0.0757
Largest diff. peak and hole	1.368 and -1.491 $e.Å^{-3}$

Table S4 Selected bond lengths (Å) and angles (°) for Nd_2L_3

C7-Nd1#1	2.955(4)	O2#4-Nd1-O7	66.63(11)
N2-Nd1#3	2.691(4)	O3#5-Nd1-C7#5	24.66(11)
Nd1-O1	2.417(3)	O3#5-Nd1-N2#3	133.83(10)
Nd1-O2#4	2.424(3)	O3#5-Nd1-O4#5	49.78(9)
Nd1-O3#5	2.577(3)	O4#5-Nd1-C7#5	25.75(10)
Nd1-O4#5	2.679(3)	O4#3-Nd1-C7#5	114.78(11)
Nd1-O4#3	2.496(3)	O4#5-Nd1-N2#3	135.24(10)
Nd1-O5	2.426(3)	O4#3-Nd1-N2#3	62.02(10)
Nd1-O6#6	2.460(3)	O4#3-Nd1-O3#5	90.14(10)
Nd1-O7	2.556(3)	O4#3-Nd1-O4#5	138.48(10)
		O4#3-Nd1-O7	133.16(10)
N2#3-Nd1-C7#5	144.71(11)	O5-Nd1-C7#5	75.34(11)
O1-Nd1-C7#5	102.43(11)	O5-Nd1-N2#3	69.39(11)
O1-Nd1-N2#3	74.69(10)	O5-Nd1-O3#5	71.09(11)
O1-Nd1-O2#4	140.59(11)	O5-Nd1-O4#5	75.06(11)
O1-Nd1-O3#5	125.20(10)	O5-Nd1-O4#3	82.45(12)
O1-Nd1-O4#3	136.53(10)	O5-Nd1-O6#6	140.77(11)
O1-Nd1-O4#5	76.72(10)	O5-Nd1-O7	141.43(11)
O1-Nd1-O5	86.20(11)	O6#6-Nd1-C7#5	143.53(11)
O1-Nd1-O6#6	80.38(11)	O6#6-Nd1-N2#3	71.53(11)
O1-Nd1-O7	76.06(10)	O6#6-Nd1-O3#5	144.74(11)
O2#4-Nd1-C7#5	80.62(12)	O6#6-Nd1-O4#5	135.42(10)
O2#4-Nd1-N2#3	124.30(11)	O6#6-Nd1-O4#3	82.47(11)
O2#4-Nd1-O3#5	69.60(11)	O6#6-Nd1-O7	69.91(11)
O2#4-Nd1-O4#3	70.29(10)	O7-Nd1-C7#5	75.50(11)
O2#4-Nd1-O4#5	99.50(10)	O7-Nd1-N2#3	134.58(11)
O2#4-Nd1-O5	131.40(11)	O7-Nd1-O3#5	91.52(11)
O2#4-Nd1-O6#6	75.47(11)	O7-Nd1-O4#5	67.71(10)

Symmetry codes: #1 -x+1, y+1/2,-z+1/2, #3 -x+1,-y+1,-z+1, #4 x,-y+1/2,z+1/2, #5 -x+1,y-1/2,-z+1/2 #6 x-1,y,z

Table S5. The x value in $M_{1-x}Nd_xL_2$ during synthesis (theor) and as determined by ICP-MS analysis of the final product

Theor	ICP-MS		
M	Eu	Tb	Dy
0.60	0.58	0.58	0.58
0.40	0.42	0.40	0.41
0.33	0.34	0.34	0.32
0.25	0.25	0.24	0.25
0.15	0.15	0.14	0.15

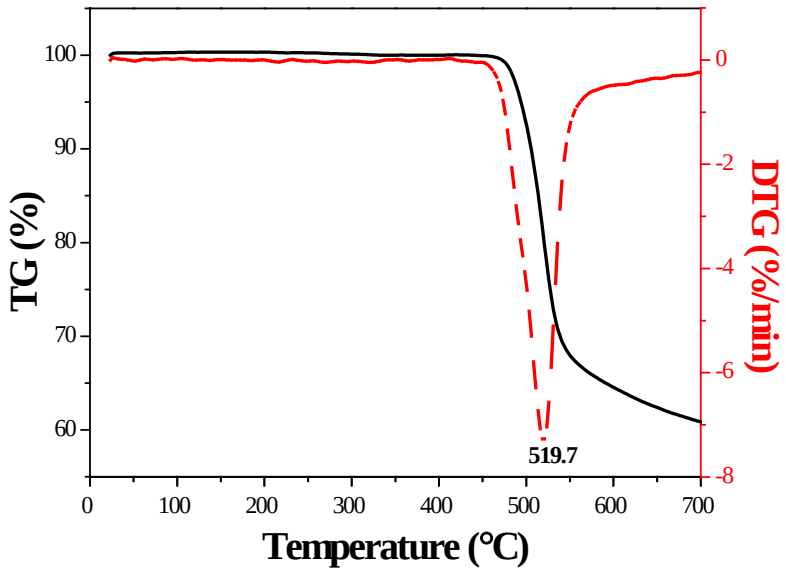

Fig. S1. TG/DTG curves for NdL_2.

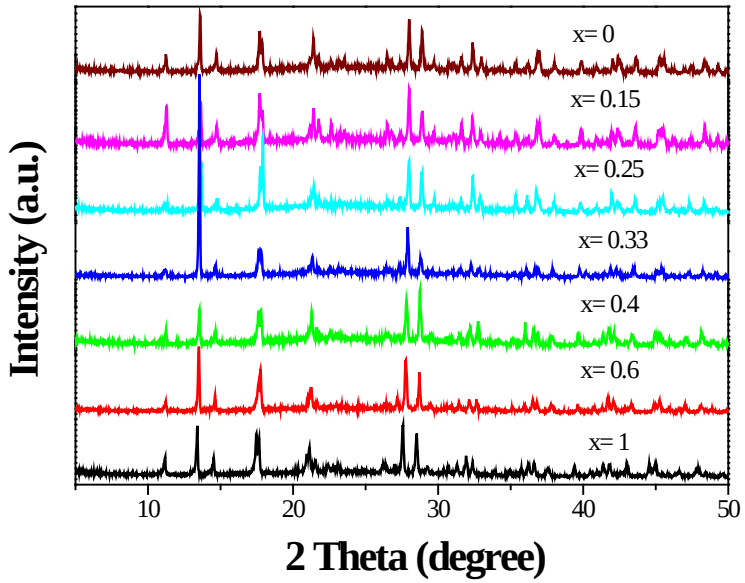

Fig. S2. Measured PXRD patterns of bimetallic $Tb_{1-x}Nd_xL_2$.

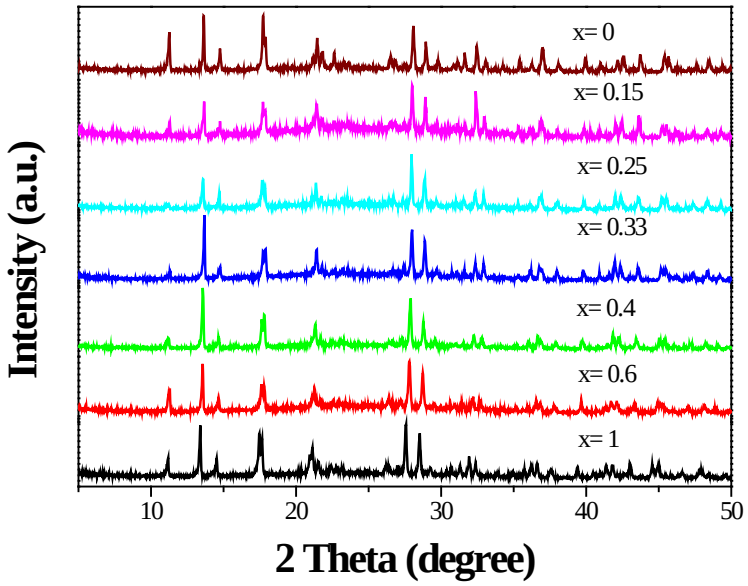

Fig. S3. Measured PXRD patterns of bimetallic $Dy_{1-x}Nd_xL_2$.

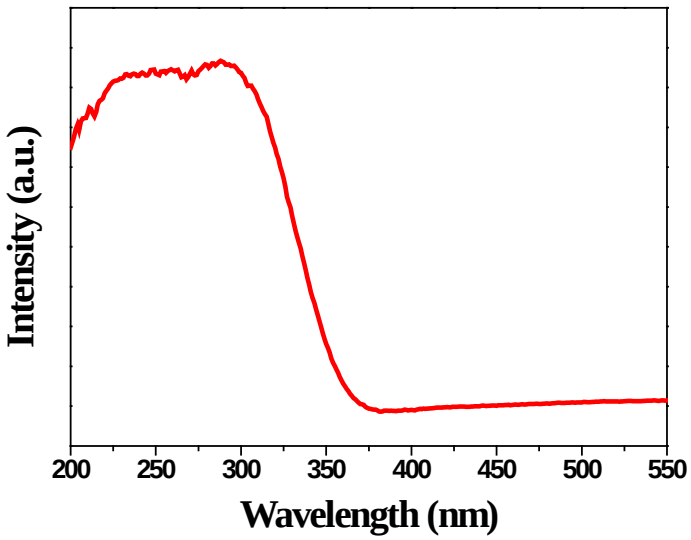

Fig. S4. Solid-state UV-vis absorption spectrum of L

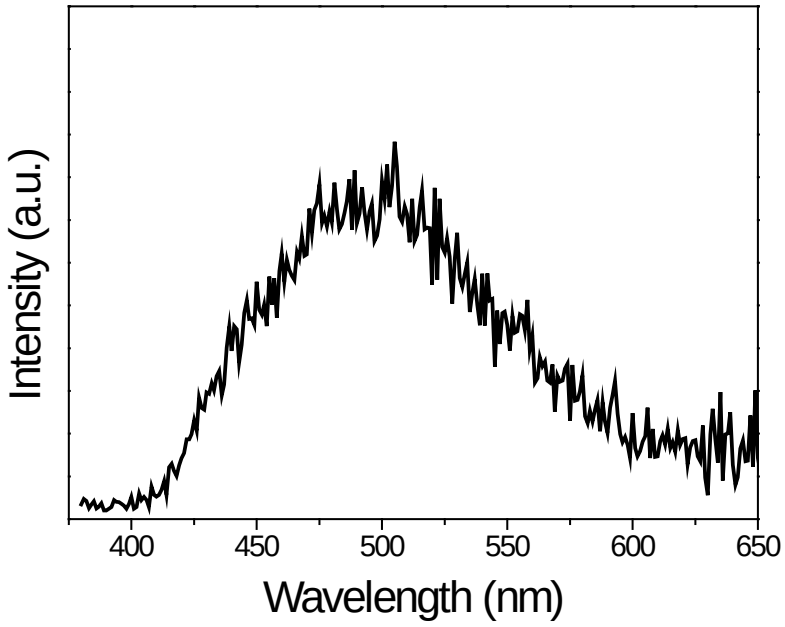

Fig. S5. Phosphorescence spectrum of GdL_2 at 77 K.

(Note: The triplet state of L was determined from the phosphorescence spectrum of GdL_2. The phosphorescence from the Gd-MOF is justified by the absence of any ionic resonance levels below the triplet state of the chelate. The triplet state energy levels were determined from the shortest wavelength phosphorescence band of the GdL_2.[1])

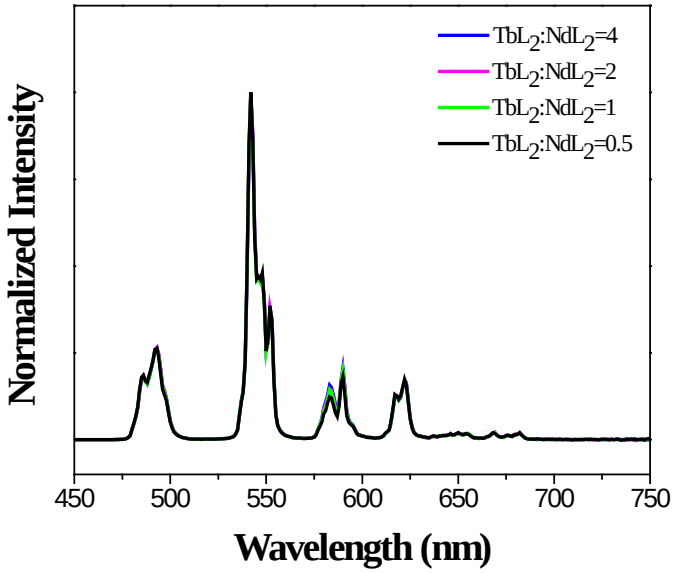

Fig. S6 Solid-state emission spectra of the physical mixture of TbL_2 and NdL_2 with different ratios

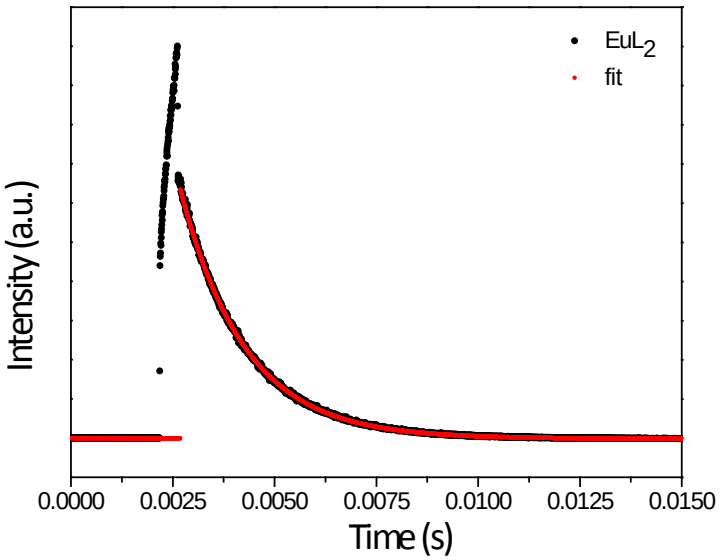

Fig. S7 Time-resolved emission decay curves of EuL_2 (612 nm)

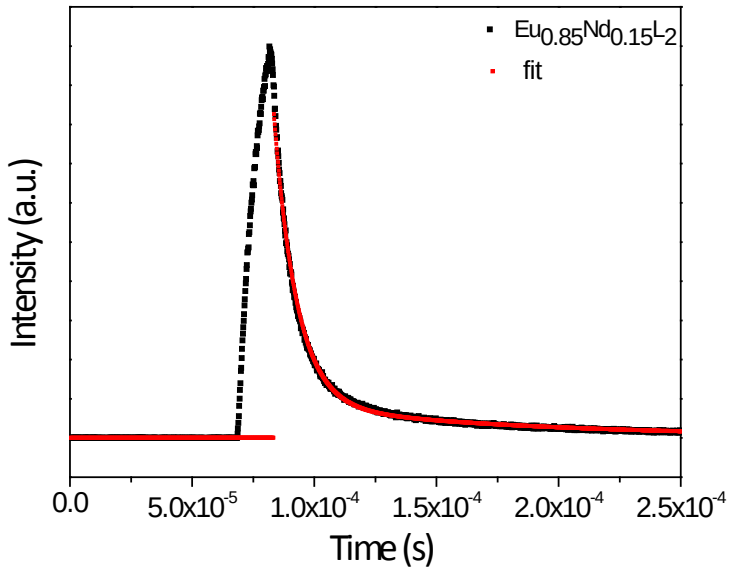

Fig. S8 Time-resolved emission decay curves of $Eu_{0.85}Nd_{0.15}L_2$ (612 nm)

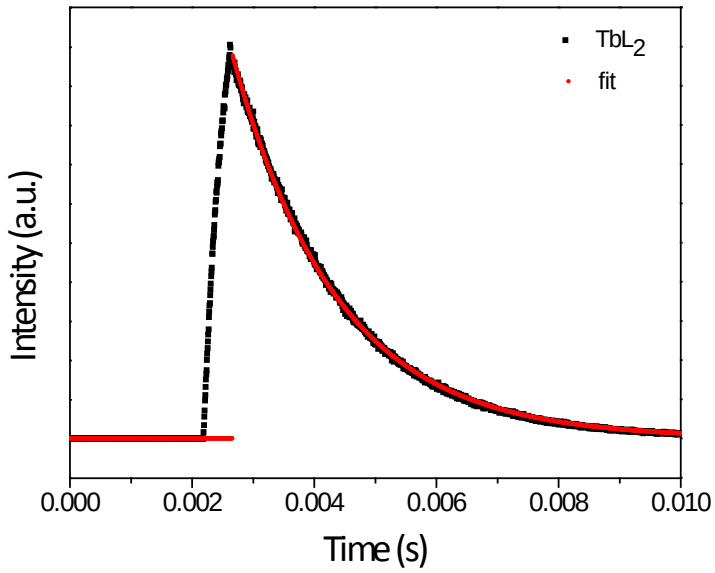

Fig. S9 Time-resolved emission decay curves of TbL_2 (542 nm)

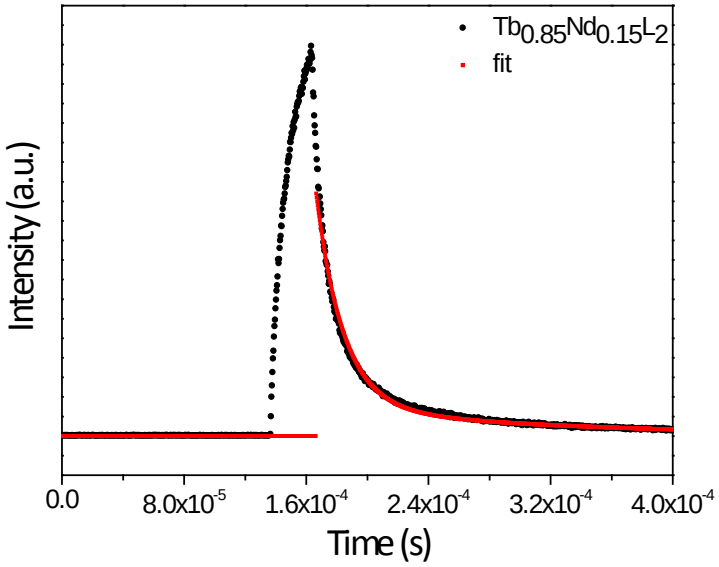

Fig. S10 Time-resolved emission decay curves of $Tb_{0.85}Nd_{0.15}L_2$ (542 nm)

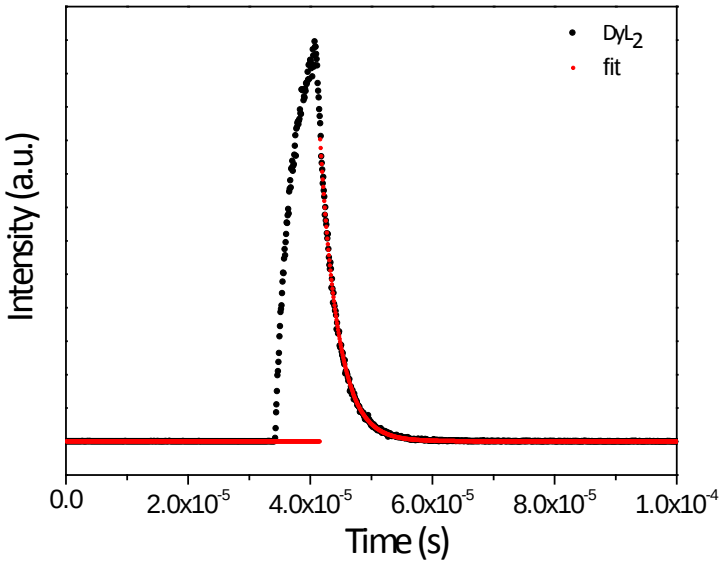

Fig. S11 Time-resolved emission decay curves of DyL_2 (571 nm)

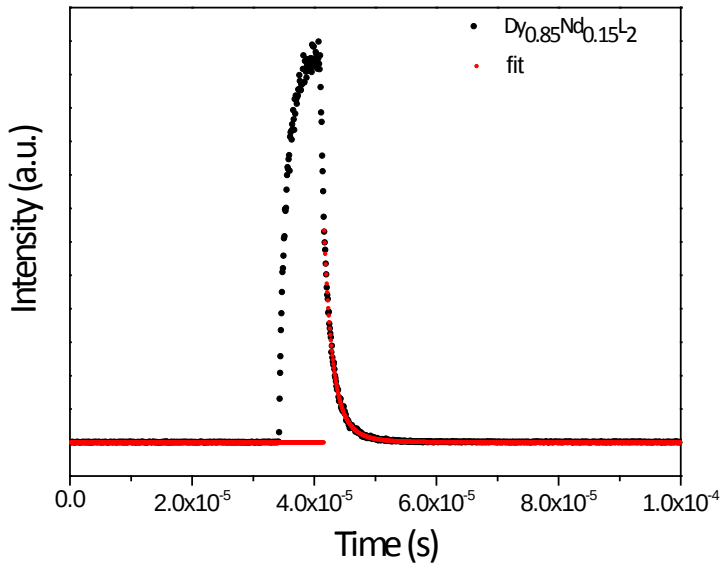

Fig. S12 Time-resolved emission decay curves of $Dy_{0.85}Nd_{0.15}L_2$(571 nm)

Table S6 Fluorescent lifetimes of LnL_2 and $M_{1-X}Nd_xL_2$ (M= Eu, Tb or Dy)

Sample	τ1 (s)	τ2 (s)	Average Life Time(s)
EuL_2	1.58E-03		1.58E-03
$Eu_{0.85}Nd_{0.15}L_2$	9.57E-05	9.28E-06	1.83E-05
TbL_2	1.71E-03		1.71E-03
$Tb_{0.85}Nd_{0.15}L_2$	1.49E-04	1.78E-05	3.36E-05
DyL_2	2.93E-06		2.93E-06
$Dy_{0.85}Nd_{0.15}L_2$	1.22E-06	3.03E-06	1.66E-06

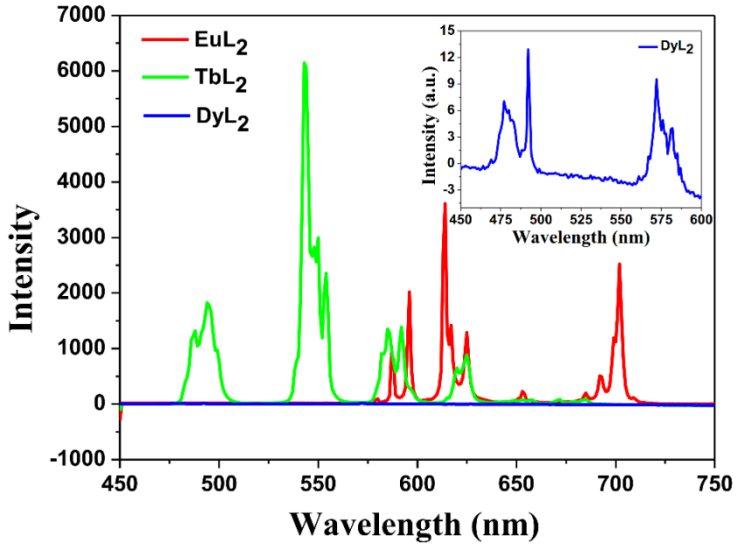

Fig. S13 Emission spectra of EuL_2 (red), TbL_2 (green) and DyL_2 (blue), respectively.

1. B. D. Chandler, D. T. Cramb and G. K. H. Shimizu, *Journal of the American Chemical Society*, 2006, **128**, 10403-10412.