

# Tunable Emission based on Lanthanide (III) Metal-Organic Frameworks: An Alternative Approach to White Lights

Song Dang,<sup>a</sup> Jian-Han Zhang,<sup>b</sup> and Zhong-Ming Sun,<sup>\*a,b</sup>

<sup>a</sup>State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, P.R. China.

<sup>b</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P.R. China.

## Table of Contents

|                                   |    |
|-----------------------------------|----|
| 1. Crystal data for Y(Er)L.....   | S2 |
| 2. PXRD Analysis.....             | S4 |
| 3. Luminescence Measurements..... | S4 |

1. Crystal data for Y(Er)L

Table S1. Bond lengths [Å] and angles [deg] for YL.

|                    |            |                    |            |
|--------------------|------------|--------------------|------------|
| Y(1)-O(4)#1        | 2.314(5)   | Y(1)-O(6)#5        | 2.436(3)   |
| Y(1)-O(5)#2        | 2.340(3)   | Y(1)-O(5)#4        | 2.449(3)   |
| Y(1)-O(5)#3        | 2.340(3)   | Y(1)-O(5)#5        | 2.449(3)   |
| Y(1)-O(3)          | 2.373(5)   | Y(1)-O(4)          | 2.414(5)   |
| Y(1)-O(6)#4        | 2.436(3)   | O(4)#1-Y(1)-O(5)#2 | 84.82(14)  |
| O(4)#1-Y(1)-O(5)#3 | 84.82(14)  | O(5)#2-Y(1)-O(5)#3 | 65.75(16)  |
| O(4)#1-Y(1)-O(3)   | 152.24(17) | O(5)#2-Y(1)-O(3)   | 117.96(12) |
| O(5)#3-Y(1)-O(3)   | 117.96(12) | O(4)#1-Y(1)-O(4)   | 152.67(16) |
| O(5)#2-Y(1)-O(4)   | 72.36(13)  |                    |            |

Symmetry transformations used to generate equivalent atoms:

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

Table S2. Bond lengths [Å] and angles [deg] for ErL.

|                     |            |                     |            |
|---------------------|------------|---------------------|------------|
| Er(1)-O(1)          | 2.310(5)   | Er(1)-O(3)          | 2.432(3)   |
| Er(1)-O(2)#1        | 2.345(3)   | Er(1)-O(2)#3        | 2.457(4)   |
| Er(1)-O(2)#2        | 2.345(3)   | Er(1)-O(2)          | 2.457(4)   |
| Er(1)-O(6)#2        | 2.356(5)   | Er(1)-C(11)#2       | 2.767(7)   |
| Er(1)-O(1)#2        | 2.411(5)   | Er(1)-C(12)#3       | 2.831(5)   |
| Er(1)-O(3)#3        | 2.432(3)   | Er(1)-C(12)         | 2.831(5)   |
| O(1)-Er(1)-O(2)#1   | 84.41(14)  | O(1)-Er(1)-O(2)#2   | 84.41(14)  |
| O(2)#1-Er(1)-O(2)#2 | 66.04(16)  | O(1)-Er(1)-O(6)#2   | 152.34(16) |
| O(2)#1-Er(1)-O(6)#2 | 118.22(12) | O(2)#2-Er(1)-O(6)#2 | 118.22(12) |
| O(1)-Er(1)-O(1)#2   | 152.24(16) | O(2)#1-Er(1)-O(1)#2 | 72.45(13)  |
| O(2)#2-Er(1)-O(1)#2 | 72.45(13)  | O(6)#2-Er(1)-O(1)#2 | 55.42(15)  |
| O(1)-Er(1)-O(3)#3   | 101.65(14) | O(2)#1-Er(1)-O(3)#3 | 136.65(19) |
| O(2)#2-Er(1)-O(3)#3 | 71.85(17)  | O(6)#2-Er(1)-O(3)#3 | 73.51(10)  |

Symmetry transformations used to generate equivalent atoms:

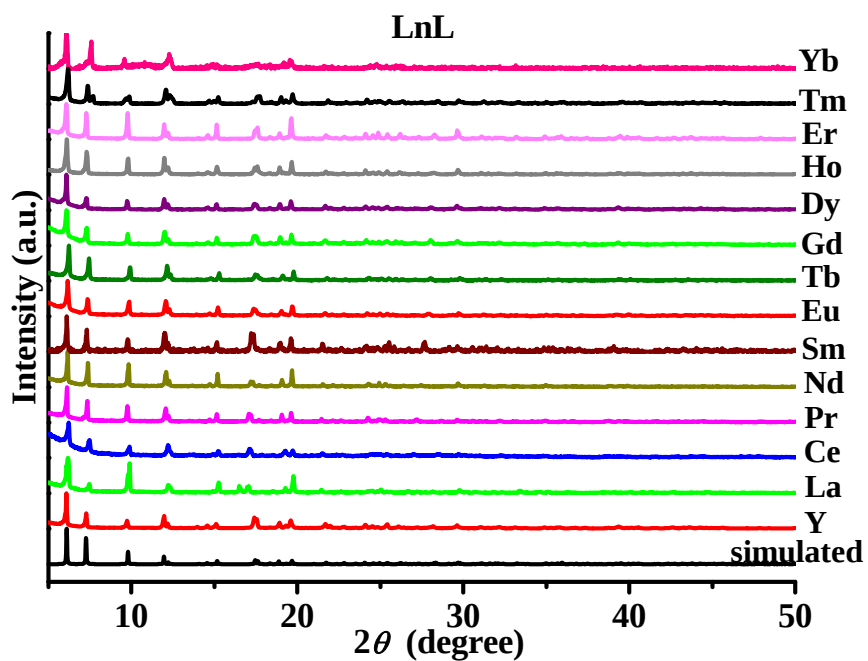
#1 x,-y,z+1/2   #2 -x+2,-y,z+1/2   #3 -x+2,y,z

**Table S3.** Cell parameters of all **LnL**.

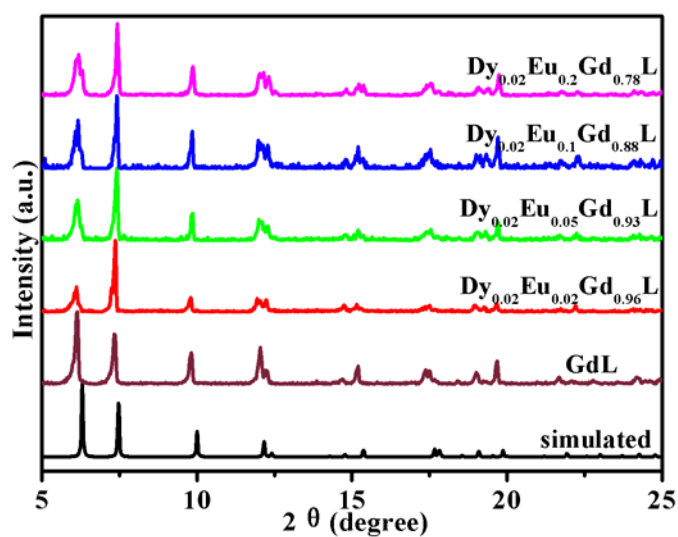
$C_{108}H_{28}Ln_4O_{44}$  (Ln = Y, La, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb), Space group,  $Cmc2_1$ ,  $\alpha = \beta = \gamma = 90^\circ$

| Ln | <i>a</i> / Å | <i>b</i> / Å | <i>c</i> / Å | <i>V</i> / Å <sup>3</sup> |
|----|--------------|--------------|--------------|---------------------------|
| Y  | 18.036(6)    | 24.175(5)    | 6.986(6)     | 3046.464                  |
| La | 17.97        | 23.82        | 7.521        | 3219.329                  |
| Pr | 17.92        | 23.85        | 7.26         | 3102.866                  |
| Nd | 18.07        | 24.16        | 7.273        | 3175.182                  |
| Eu | 18.29        | 24.49        | 7.24         | 3242.956                  |
| Gd | 17.90        | 23.85        | 7.06         | 3014.020                  |
| Tb | 18.16        | 24.41        | 7.10         | 3147.328                  |
| Dy | 18.03        | 24.23        | 7.02         | 3066.806                  |
| Ho | 18.66        | 24.74        | 7.24         | 3342.334                  |
| Er | 18.037(2)    | 24.308(3)    | 6.9817(9)    | 3061.154                  |
| Tm | 18.03        | 22.90        | 7.02         | 2898.467                  |
| Yb | 18.30        | 23.41        | 7.24         | 3083.184                  |

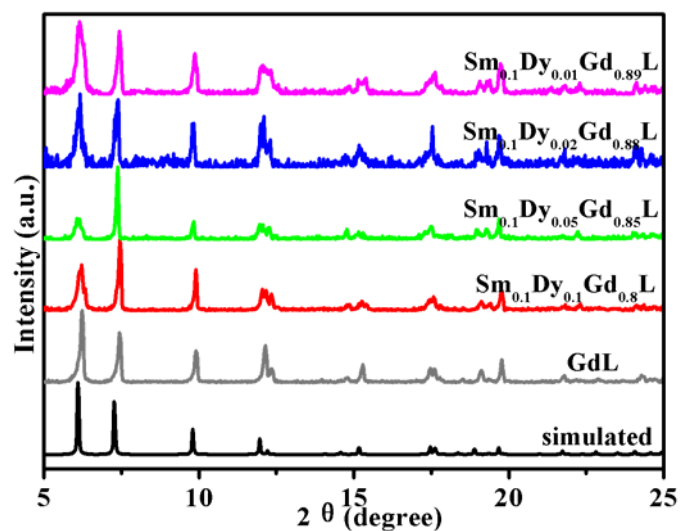
## 2. PXRD Analysis



**Fig. S1** Powder XRD patterns of compounds in the range from 5 to 50 degrees.

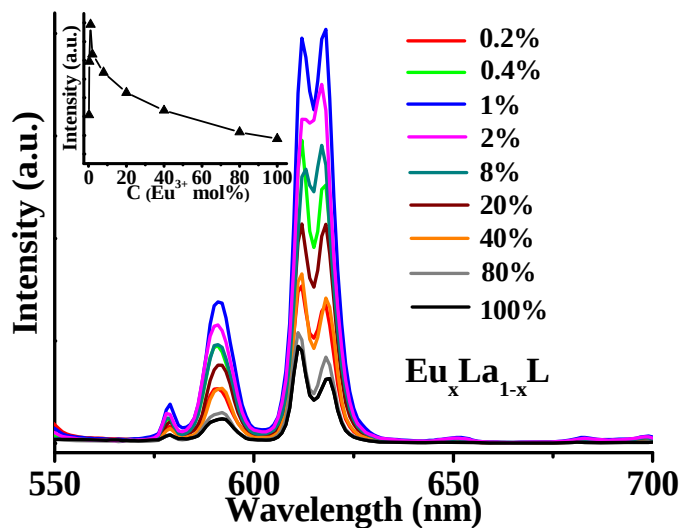


**Fig. S2** Powder XRD patterns of Dy and Eu codoped compounds.

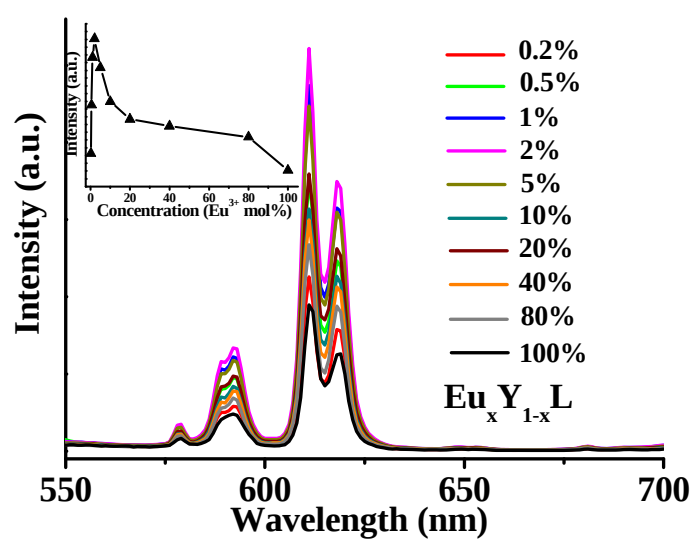


**Fig. S3** Powder XRD patterns of Dy and Sm codoped compounds.

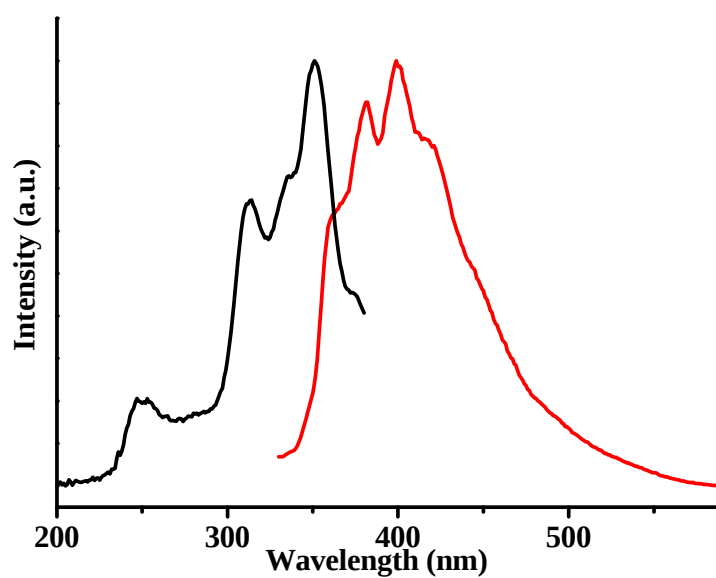
### 3. Luminescent Measurements



**Fig. S4** PL emission spectra of  $\text{Eu}_x\text{La}_{1-x}\text{L}$ , solid samples. The inset figures indicate corresponding transition intensities of doped  $\text{Eu}_x\text{La}_{1-x}\text{L}$  as a factor of doping concentration  $x$ .



**Fig. S5** PL emission spectra of  $\text{Eu}_x\text{Y}_{1-x}\text{L}$ , solid samples. The inset figures indicate corresponding transition intensities of doped  $\text{Eu}_x\text{Y}_{1-x}\text{L}$  as a factor of doping concentration  $x$ .



**Fig. S6** Excitation (black,  $\lambda_{\text{em}} = 400 \text{ nm}$ ) and (red,  $\lambda_{\text{ex}} = 310 \text{ nm}$ ) emission spectra of  $\text{H}_3\text{L}$ .

**Table S4.** CIE coordinates of  $\text{Dy}_x\text{Eu}_y\text{Gd}_{1-x-y}\text{L}$  ( $\lambda_{\text{ex}} = 290 \text{ nm}$ ).

| $\text{Dy}_x\text{Eu}_y\text{Gd}_{1-x-y}\text{L}$          | CIE (X, Y)     |
|------------------------------------------------------------|----------------|
| $\text{Dy}_{0.02}\text{Eu}_{0.02}\text{Gd}_{0.96}\text{L}$ | (0.310, 0.319) |
| $\text{Dy}_{0.02}\text{Eu}_{0.05}\text{Gd}_{0.93}\text{L}$ | (0.355, 0.313) |
| $\text{Dy}_{0.02}\text{Eu}_{0.1}\text{Gd}_{0.88}\text{L}$  | (0.373, 0.304) |
| $\text{Dy}_{0.02}\text{Eu}_{0.2}\text{Gd}_{0.78}\text{L}$  | (0.379, 0.281) |

**Table S5.** CIE coordinates of  $\text{Sm}_x\text{Dy}_y\text{Gd}_{1-x-y}\text{L}$  ( $\lambda_{\text{ex}} = 290 \text{ nm}$ ).

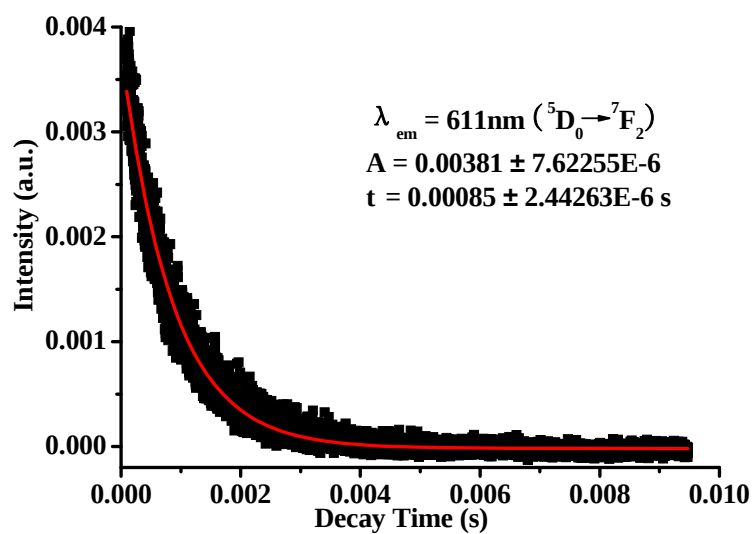
| $\text{Sm}_x\text{Dy}_y\text{Gd}_{1-x-y}\text{L}$         | CIE (X, Y)     |
|-----------------------------------------------------------|----------------|
| $\text{Sm}_{0.1}\text{Dy}_{0.01}\text{Gd}_{0.89}\text{L}$ | (0.350, 0.323) |
| $\text{Sm}_{0.1}\text{Dy}_{0.02}\text{Gd}_{0.88}\text{L}$ | (0.319, 0.321) |
| $\text{Sm}_{0.1}\text{Dy}_{0.05}\text{Gd}_{0.85}\text{L}$ | (0.306, 0.321) |
| $\text{Sm}_{0.1}\text{Dy}_{0.1}\text{Gd}_{0.8}\text{L}$   | (0.292, 0.325) |

**Luminescence Decay measurements on the  $\text{LnL}$  and  $\text{Ln}^{3+}$  doped materials**

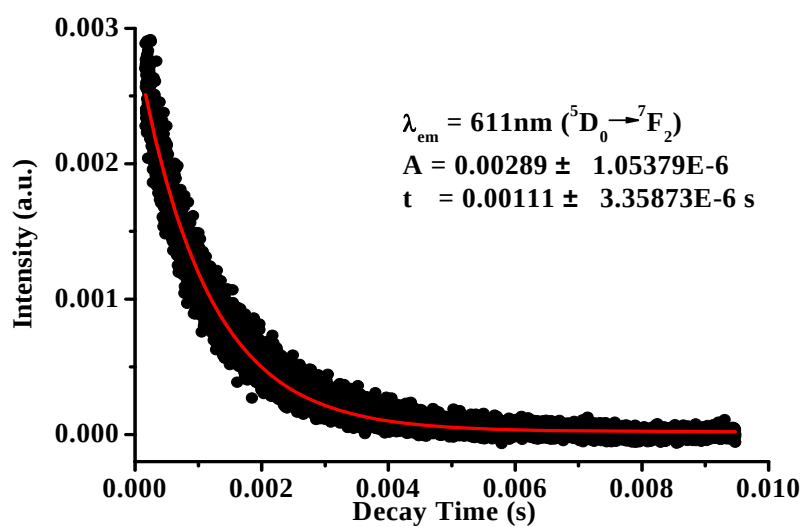
The luminescence lifetimes have been recorded in order to explore the coordination environment around the lanthanide ions. The luminescence decay curves were fit well with monoexponential decays, using the following equation:

$$y = Ae^{(-x/t)} + y_0$$

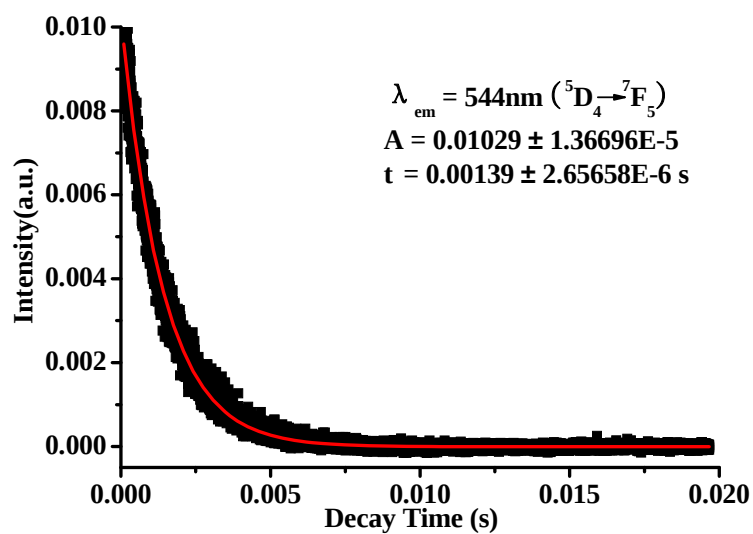
which confirms that all lanthanide ions occupy the same average local environment with each samples.



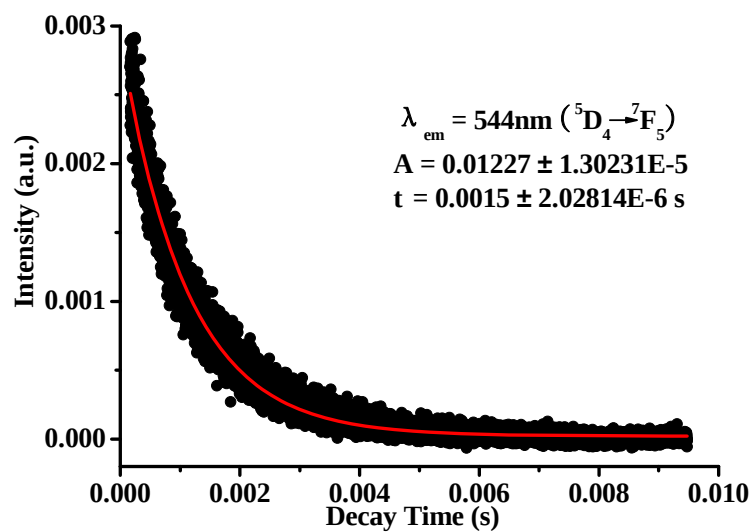
**Fig. S7** Luminescence decay curve for the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  (611 nm) emission of EuL.



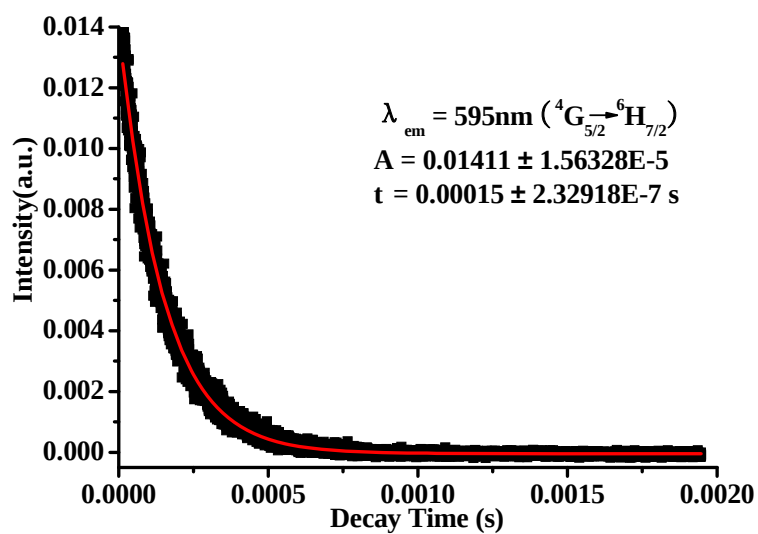
**Fig. S8** Luminescence decay curve for the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  (611 nm) emission of  $\text{Eu}_{0.02}\text{Gd}_{0.98}\text{L}$ .



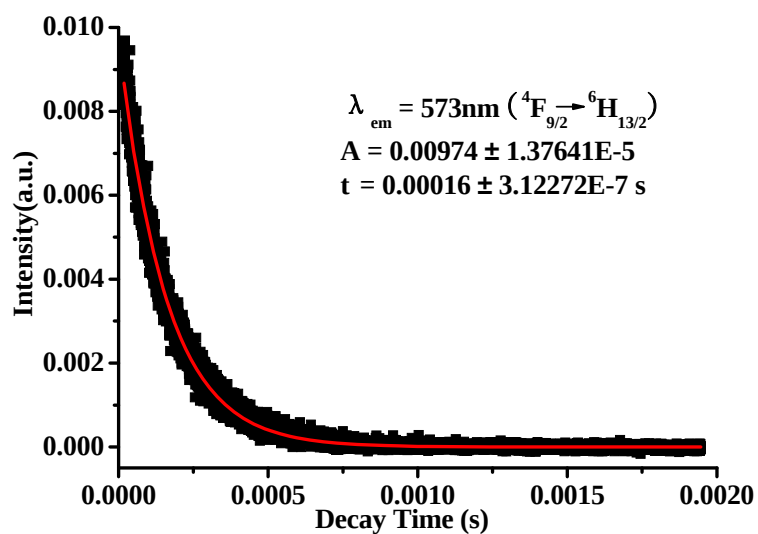
**Fig. S9** Luminescence decay curve for the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  (544 nm) emission of TbL.



**Fig. S10** Luminescence decay curve for the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  (544 nm) emission of  $\text{Tb}_{0.08}\text{La}_{0.92}\text{L}$ .



**Fig. S11** Luminescence decay curve for the  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$  (595 nm) emission of  $\text{Sm}_{0.1}\text{Gd}_{0.9}\text{L}$ .



**Fig. S12** Luminescence decay curve for the  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$  (573 nm) emission of  $\text{Dy}_{0.02}\text{Gd}_{0.98}\text{L}$ .