Supporting Information

A Eu/Tb-codoped Coordination Polymer Luminescent Thermometer

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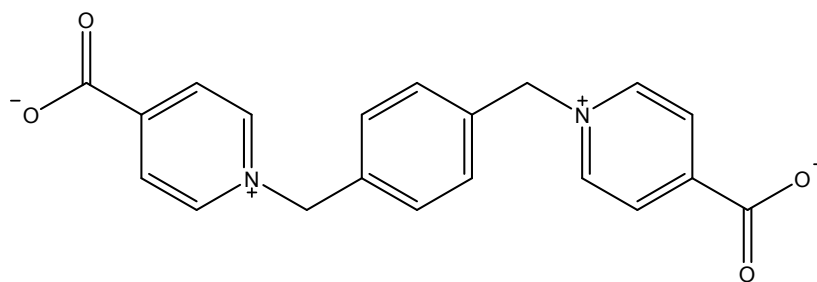[b]University of Chinese Academy of Sciences, Beijing, 100049, China

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Scheme 1. The structure of the ligand **L** (1,4-bis(pyridinil-4-carboxylato)-l,4-dimethylbenzene).
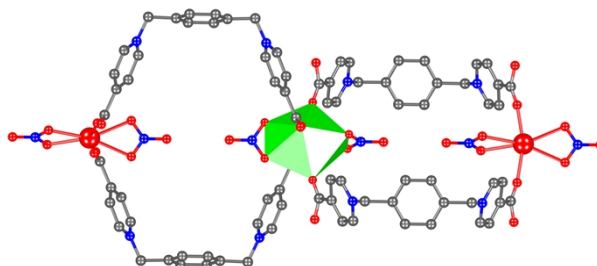

Fig. S1 A distorted dodecahedron geometry of europium ion.
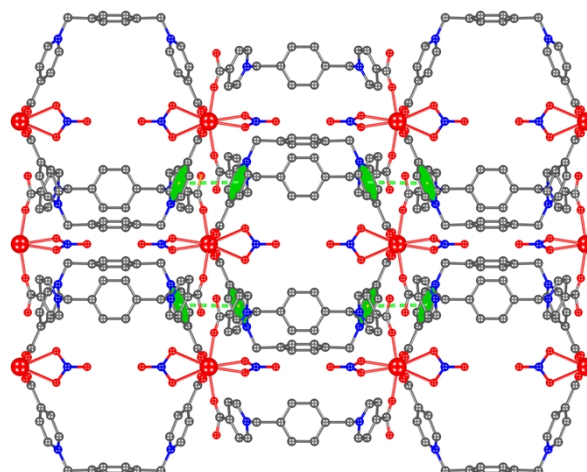

Fig. S2 The packing diagram of **EuL** along *b*-axis. All the hydrogen atoms, chlorine atoms, and water moleculers have been omitted for clarity (green dot line: π···π contact).
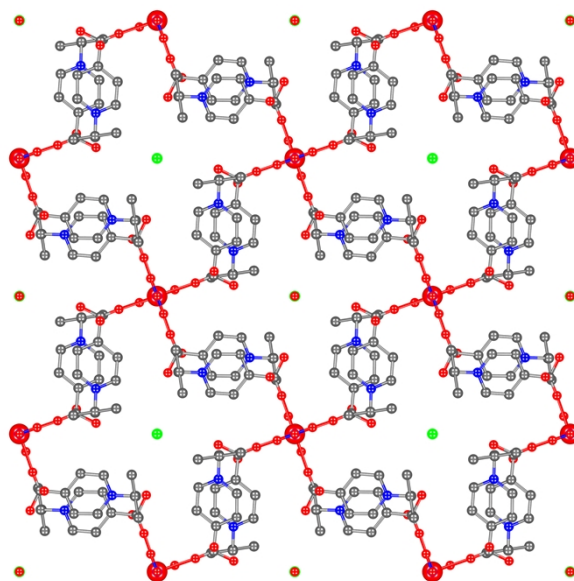
Fig. S3 The packing diagram of **EuL** along *c*-axis. All the hydrogen atoms have been omitted for clarity.
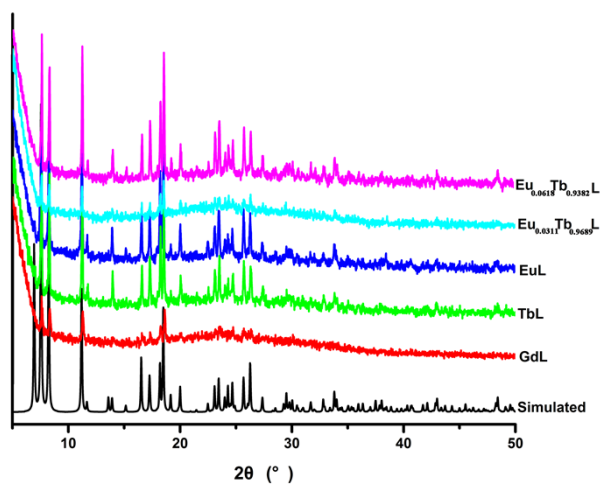

Fig. S4 Powder X-ray diffraction patterns of simulated from the X-ray single structure of **EuL**, as-synthesized **GdL**, **TbL**, **EuL**, **Eu$_{0.0311}$Tb$_{0.9689}$L,** and **Eu$_{0.0618}$Tb$_{0.9382}$L**.
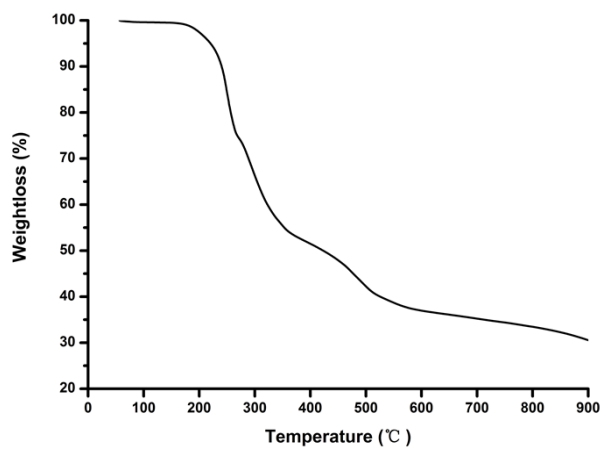

Fig. S5 The TGA curve of compound **EuL**.

Experimental Section

Materials and Measurements

All starting materials and solvents were reagent grade, commercially available and used without further purification. ([H_2L]Cl_2) was synthesized according to the reported procedures.[1] Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. TG analyses were performed on a Perkin−Elmer Thermal Analysis Pyris Diamond heated from room temperature to 900 ºC under a N_2 atmosphere at a rate of 10 ºC min^{-1} (Fig. S5). The experimental powder X-ray diffraction data (PXRD) were collected on a Bruker D8-FOCUS diffractometer equipped with Cu Kα1 (λ = 1.5406 Å; 1600 W, 40 kV, 40 mA) at a scan speed of 8° min$^{−1}$. The simulated PXRD patterns were calculated by using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center. ICP was measured by ICAP 6000 Series (Thermo Fisher Scientific). The ligand [H_2L]Cl_2 luminescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer equipped with a 150W xenon lamp as the excitation source. The temperature-dependent luminescence spectra and the luminescence decay curve were recorded on an Edinburgh Instrument FLSP-920 spectrometer.

Synthesis of **LnL**: $Ln(NO_3)_2 \cdot 6H_2O$ (Ln= Eu, Tb, and Gd) (0.25 mmol), [H_2L]Cl_2 (0.1 mmol) and DMF (6 mL) was sealed in a 15 mL Teflon-lined stainless-steel autoclave under autogenous pressure and heated at constant 85 °C for 3 days and then was cooled to room temperature slowly. The resulting tetragonal-shaped crystals were collected. Elemental analysis for $C_{40}H_{36}N_6ClO_{17}Eu$ (**EuL**) (1060.16) (%): calcd. C 45.32, H 3.42, N 7.93; found C 45.35, H 3.39, N 7.96.

$C_{40}H_{36}N_6ClO_{17}Tb$ (**TbL**) (1067.12) (%): calcd. C 45.02, H 3.40, N 7.87; found C 45.09, H 3.45, N 7.85.

$C_{40}H_{36}N_6ClO_{17}Gd$ (**GdL**) (1065.45) (%): calcd. C 45.09, H 3.41, N 7.89; found C 45.05, H 3.45, N 7.92.

Synthesis of Ln-doped analogies: **$Eu_xTb_{1-x}L$** were synthesized by using a mixture of $Eu(NO_3)_3 \cdot 6H_2O$ and $Tb(NO_3)_3 \cdot 6H_2O$ as the metal source through the same procedures

as **LnL**.

Crystal data for **EuL**: $C_{40}H_{36}N_6ClO_{17}Eu$, $M_r = 1060.16$, Tetragonal, space group *I4/m*, $a = 15.181(5)$ Å, $b = 15.181(5)$ Å, $c = 23.369(5)$ Å, alpha = 90, beta = 90, gamma = 90, $V = 5386(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.307$ g cm^{-3}, final $R_1 = 0.0683$ and w$R_2 = 0.2326$ ($R_{int} = 0.0966$) for 1047 independent reflections [$I>2\sigma(I)$]. CCDC   1006519.

Crystal data for **TbL**: $C_{40}H_{36}N_6ClO_{17}Tb$, $M_r = 1067.12$, Tetragonal, space group *I4/m*, $a = 15.160(5)$ Å, $b = 15.160(5)$ Å, $c = 23.388(5)$ Å, alpha = 90, beta = 90, gamma = 90, $V = 5375(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.319$ g cm^{-3}, final $R_1 = 0.0731$ and w$R_2 = 0.2638$ ($R_{int} = 0.1217$) for 2446 independent reflections [$I>2\sigma(I)$]. CCDC   1006520.

Crystal data for **GdL**: $C_{40}H_{36}N_6ClO_{17}Gd$, $M_r = 1065.45$, Tetragonal, space group *I4/m*, $a = 15.164(5)$ Å, $b = 15.164(5)$ Å, $c = 23.519(5)$ Å, alpha = 90, beta = 90, gamma = 90, $V = 5408(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.309$ g cm^{-3}, final $R_1 = 0.0644$ and w$R_2 = 0.2375$ ($R_{int} = 0.0652$) for 2337 independent reflections [$I>2\sigma(I)$]. CCDC   1006521.

X-ray crystallography

The X-ray intensity data for the two compounds was collected on a Bruker SMART APEX-II CCD diffractometer with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) operating at 1.575 kW (45 kV, 35 mA) at room temperature. Data integration and reduction were processed with SAINT software.[2] Multiscan absorption corrections were applied with the SADABS program.[3] All structures were solved by direct methods and refined employing full-matrix least squares techniques based on F^2 using the SHELXTL-97 crystallographic software package.[4] All non-hydrogen atoms were refined with anisotropic temperature parameters.
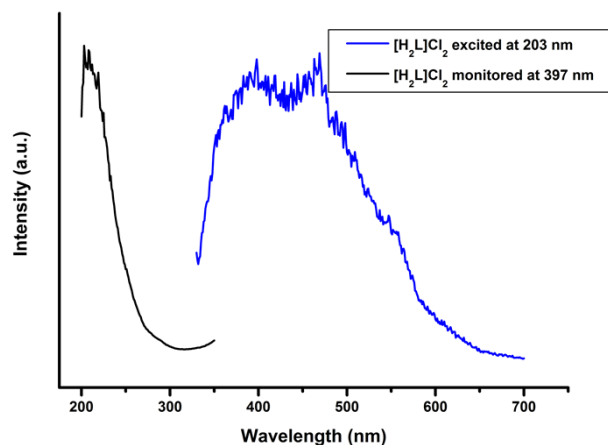
Fig. S6 Room-temperature excitation (black) and emission (blue) spectra for the free ([H$_2$L]Cl$_2$) ligand in the solid state.
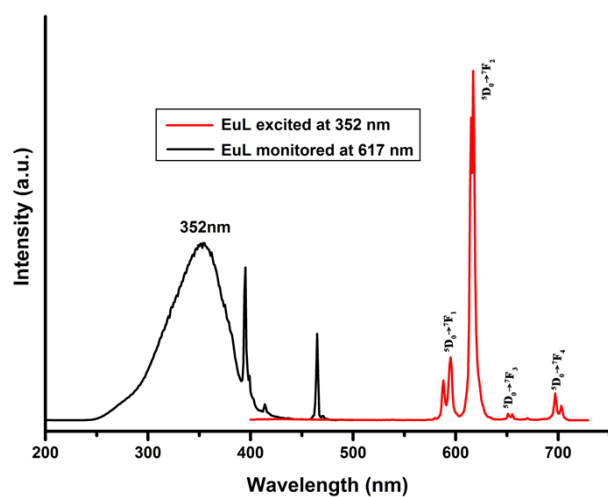

Fig. S7 Room-temperature excitation (black) and emission (red) spectra for **EuL** in the solid state.
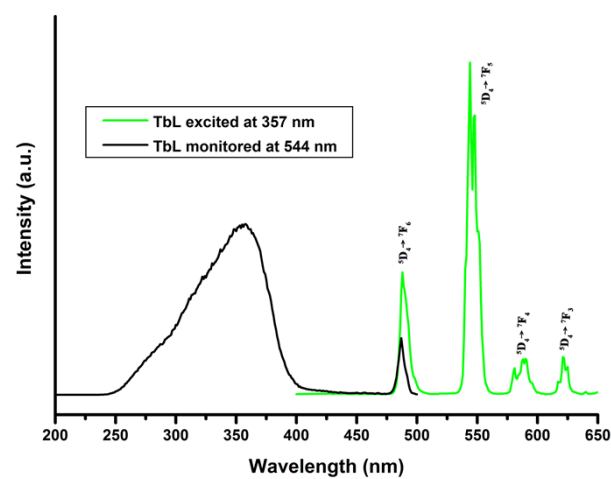

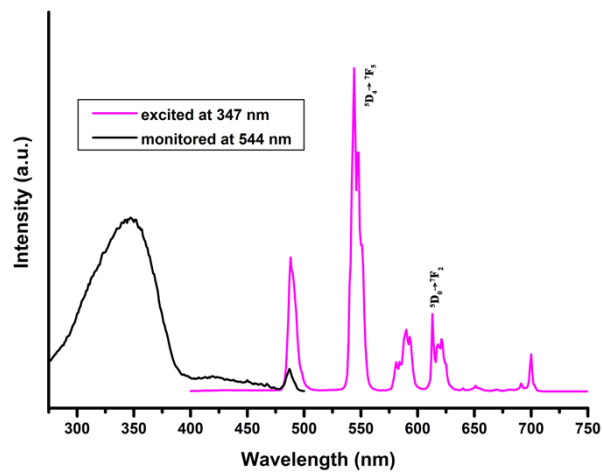**Fig. S8** Room-temperature excitation (black) and emission (green) spectra for **TbL** in the solid state.

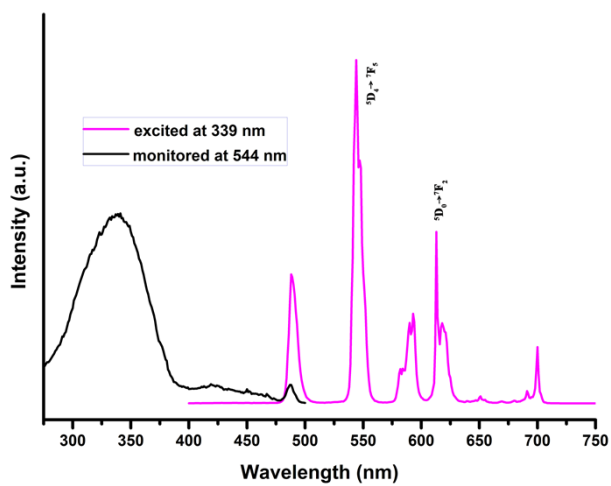**Fig. S9** Room-temperature excitation (black) and emission (pinkish red) spectra for $Eu_{0.0311}Tb_{0.9689}L$ in the solid state.

Fig. S10 Room-temperature excitation (black) and emission (pinkish red) spectra for $Eu_{0.0618}Tb_{0.9382}L$ in the solid state.

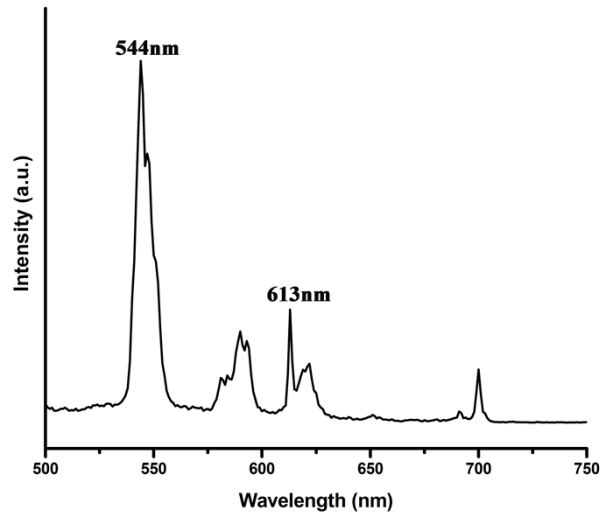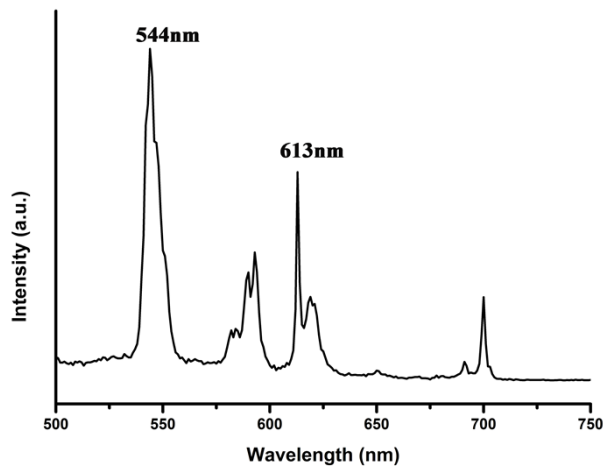**Fig. S11** Room-temperature emission spectra for $Eu_{0.0311}Tb_{0.9689}L$ in the solid state excited at 488 nm.

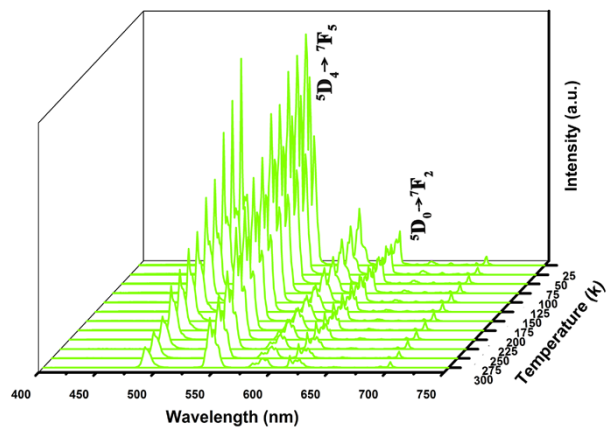**Fig. S12** Room-temperature emission spectra for $Eu_{0.0618}Tb_{0.9382}L$ in the solid state excited at 488 nm.

Fig. S13 Emission spectra of $Eu_{0.0311}Tb_{0.9689}L$ recorded between 25 K and 300 K.
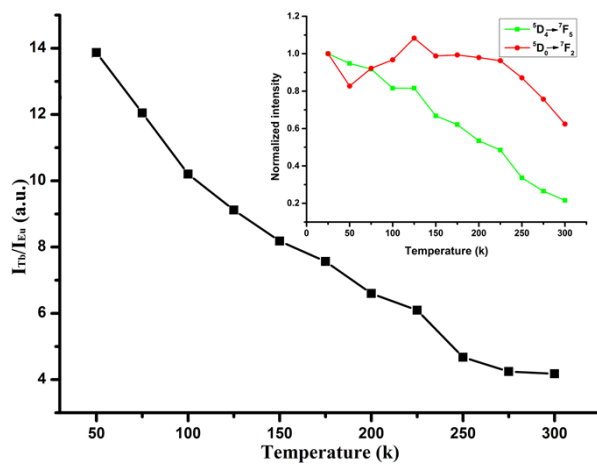
Fig. S14 Temperature-dependent intensity ratio of Tb^{3+} (544nm) to Eu^{3+} (613nm) (Inset) temperature-dependent intensity of the $^5D_4 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_2$ transition for **Eu$_{0.0311}$Tb$_{0.9689}$L** from 25K to 300 K.
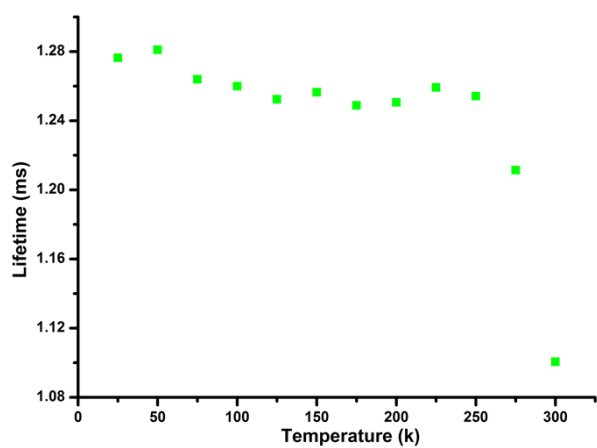

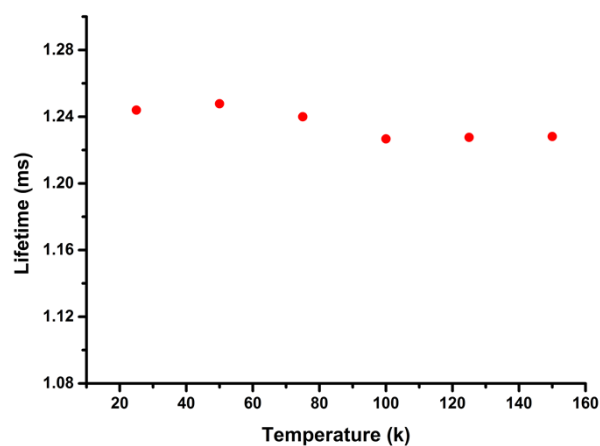**Fig. S15** Temperature-dependent of the $^5D_4$ lifetime for **TbL**.

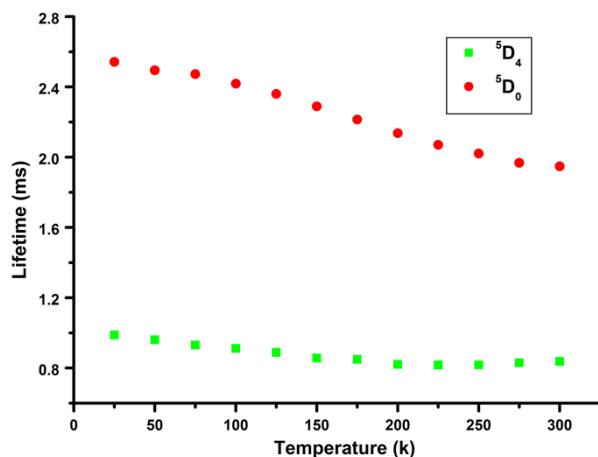**Fig. S16** Temperature-dependent of the $^5D_0$ lifetime for **EuL**.

Fig. S17 Temperature-dependent of the $^5D_4$ and $^5D_0$ lifetime for **Eu$_{0.0618}$Tb$_{0.9382}$L**.

Table S1 Energy transfer efficiency from Tb^{3+} to Eu^{3+} in **Eu$_{0.0618}$Tb$_{0.9382}$L**

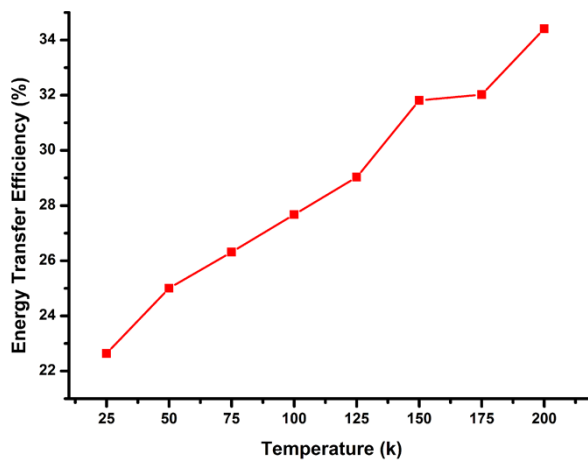| Temperature / K	25	50	75	100	125	150	175	200
Energy transfer efficiency (%)	22.64	25.00	26.32	27.67	29.03	31.81	32.03	34.41

Fig. S18 Temperature dependence of the energy transfer efficiency from Tb^{3+} to Eu^{3+} ions in **Eu$_{0.0618}$Tb$_{0.9382}$L**.

Table S2 The cell parameters of **EuL** at room temperature (293 k) and liquid nitrogen atmosphere (190K)

	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V/Å^3	M…M
At room temperature	15.181(5)	15.181(5)	23.369(5)	90	90	90	5386(3)	11.685
Liquid nitrogen atmosphere	15.056(5)	15.056(5)	23.236(5)	90	90	90	5267(3)	11.618

1 F. K. Zheng, A. Q. Wu, Y. Li, G. C. Guo, J. S. Huang, *Chin. J. Struct. Chem.*, 2005, **24**, 940.

2 *SAINT, Program for Data Extraction and Reduction;* Bruker AXS, Inc.: Madison, WI, 2001.

3 G. M. Sheldrick, *SADABS;* University of Göttingen: Göttingen, Germany, 1996.

4 (*a*) G. M. Sheldrick, *SHELXS 97, Program for the Solution of Crystal Structure;* University of Göttingen: Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *SHELXS 97, Program for the Crystal Structure Refinement;* University of Göttingen: Göttingen, Germany, 1997.