Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2016

Supporting Information

A lanthanide(III) metal-organic framework exhibiting ratiometric luminescent temperature sensing and tunable white light emission

Lan-Lan Wu,[b] Junfang Zhao,[a] Hui Wang,[a] Jingyuan Wang*,[a]

a. Technical Institute of Physics and Chemistry of the Chinese Academy of Sciences, 29 Zhongguancun East Road, Haidian District, Beijing, 100190, P. R. China.
E-mail: jywang@mail.ipc.ac.cn

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

*Corresponding author

Email: jywang@mail.ipc.ac.cn (Jingyuan Wang)

Experimental Section

All reagents and solvents were obtained from commercial source and used without further purification.

Synthesis of EuL

$Eu(NO_3)_3 \cdot 6H_2O$ (22.3 mg, 0.05 mmol) and **H_2L** (15 mg, 0.05 mmol) were dissolved in mixed solvents of DMF (1 mL) and ethanol (3 mL) in a 15 mL Teflon-lined stainless-steel autoclave and heated at 120 °C for 72 h. After it was cooled to room temperature, colorless block crystals suitable for X-ray diffraction analysis were collected, washed with ethanol (yield: 73%). Elemental analysis for $C_{21}H_{19}N_7O_9Eu$ (665.39) (%): calcd: C, 37.91; H, 2.88; N, 14.74; Found: C, 37.89; H, 2.83; N, 14.67. **TbL** was **s**ynthesized similar to **EuL,** except for the use of $Tb(NO_3)_3 \cdot 6H_2O$ as the reagent. And the codoped compounds were also synthesized similar to **EuL,** except for the use of the mixture of $Eu(NO_3)_3 \cdot 6H_2O$ and $Tb(NO_3)_3 \cdot 6H_2O$.

General Methods

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449F3 TG/DTA instrument under air atmosphere. The samples were heated from room temperature to 800 °C with a heating rate of 10 °C/min. 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) with the step of 0.02°. 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. The fluorescence excitation and emission spectra were recorded at room temperature with a Hitachi F-4500 spectrophotometer equipped with a 150 W Xenon lamp as an excitation source. The photomultiplier tube (PMT) voltage was 700 V, the scan speed was 1200 nm/min. The temperature-dependent properties of the phosphors were measured with an Horiba Jobin–Yvon Fluorolog-3 FL3-211 spectrometer equipped with a 450 W xenon lamp as the excitation source. The luminescence decay curves were obtained by using a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) with a tunable laser (pulse

width 4 ns, gate 50 ns) as the excitation source (Continuum Sunlite OPO).

X-ray crystallography

The X-ray intensity data for **EuL** and **TbL** were collected on a Bruker SMART APEX-II CCD diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) operating at 1.5 kW (50 kV, 30 mA) at room temperature. Data integration and reduction were processed with SAINT software.[S1] Multiscan absorption corrections were applied with the SADABS program.[S2] The 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.[S3] All non-hydrogen atoms were refined with anisotropic temperature parameters. All hydrogen atoms attached to carbon atoms were generated geometrically and refined using a riding model. The detailed crystallographic data and structure refinement parameters are summarized in Table S1. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number: 1430036 for **EuL** and 1430037 for **TbL**.

References

S1 SAINT, Program for Data Extraction and Reduction, Bruker AXS, Inc., Madison, WI, 2001.

S2 G. M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany 1996.

S3 (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.

Table S1. Crystal and Structure Refinement Data for **EuL** and **TbL.**

compound	**EuL** (squeezed)	**TbL** (squeezed)
Empirical formula	$C_{21}H_{19}N_7O_9Eu$	$C_{21}H_{19}N_7O_9Tb$
Formula weight	665.39	672.35
T, K	293(2)	273(2)
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a/Å	28.110(4)	28.282(4)
b/Å	13.7799(16)	13.5640(18)
c/Å	14.3362(17)	14.509(2)
α/deg	90	90
β/deg	100.267(3)	100.155(3)
γ/deg	90	90
V/ Å^3	5464.3(11)	5478.8(13)
Z	8	8
D_{calc}/g cm^{-3}	1.618	1.630
μ/mm^{-1}	2.355	2.640
F(000)	2632	2648
Reflections collected	16350	16466
Independent reflections	5205 (R_{int} = 0.0842)	5230 (R_{int} = 0.0712)
R_1[a], wR_2[b] [I > 2σ(I)]	0.0602, 0.1595	0.0510, 0.1390
R_1[a], wR_2[b] (all data)	0.0871, 0.1744	0.0736, 0.1527
Goodness on F^2	1.080	1.056

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b]$wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\ \Sigma[w(F_o^2)^2]^{1/2}$

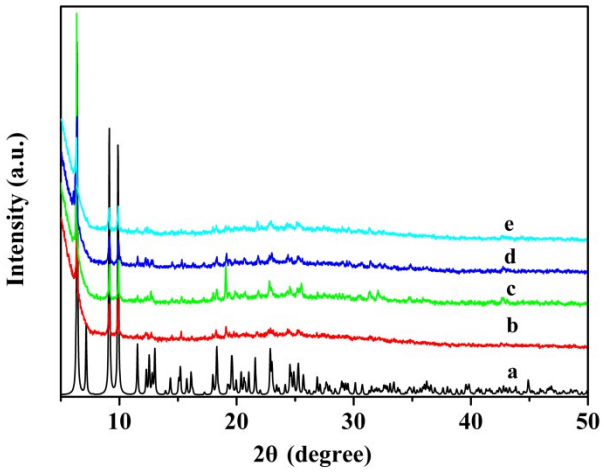

Fig. S1 PXRD patterns of the compounds: (a) simulated **EuL**, (b) **EuL**, (c) **TbL**, (d) $\mathbf{Eu_{0.0878}Tb_{0.9122}L}$, (e) $\mathbf{Eu_{0.0748}Tb_{0.9252}L}$.

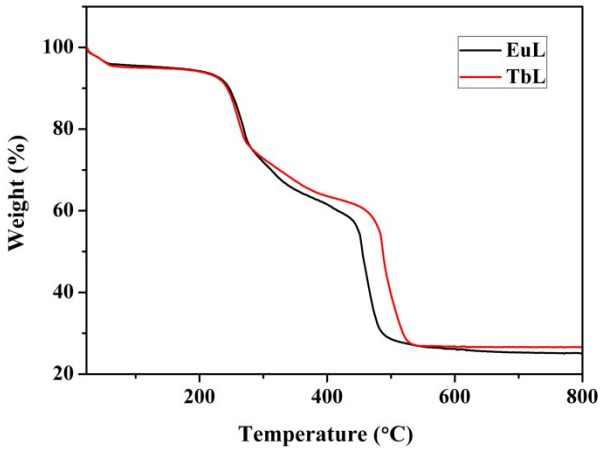

Fig. S2 The TGA curve of **EuL** and **TbL.**

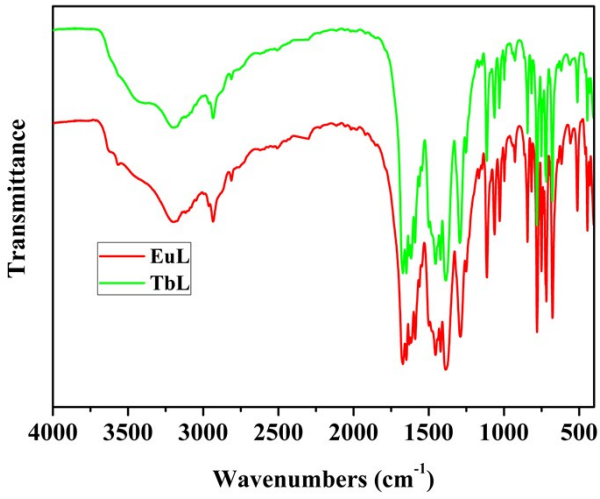

Fig. S3 IR spectrum of the compounds.

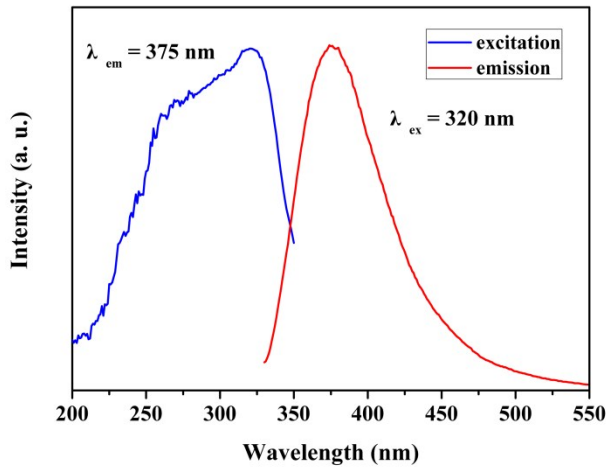

Fig. S4 Excitation and emission spectra of $\mathbf{H_2L}$ at room temperature**.**

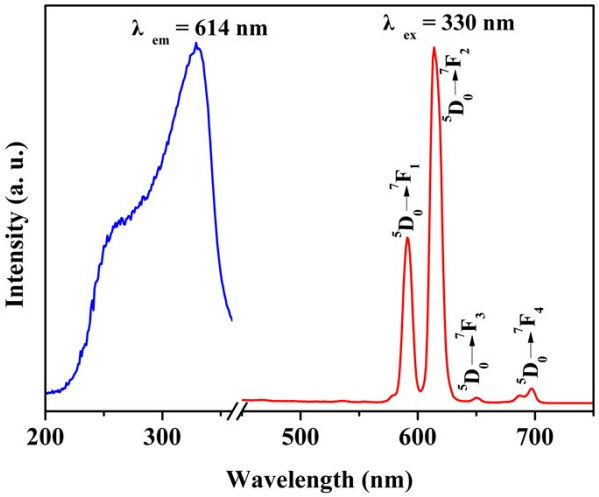

Fig. S5 Excitation and emission spectra of **EuL** at room temperature.

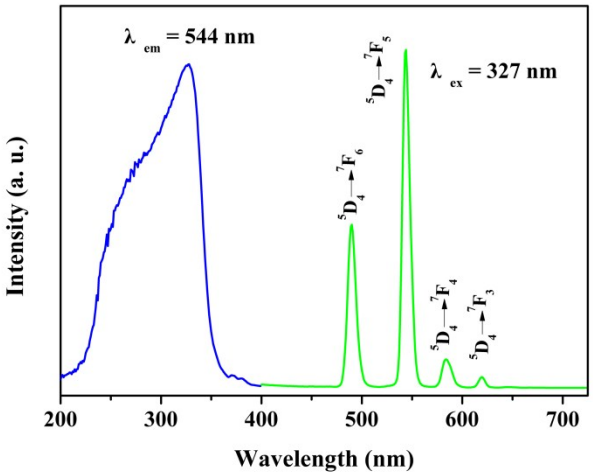

Fig. S6 Excitation and emission spectra of **TbL** at room temperature.

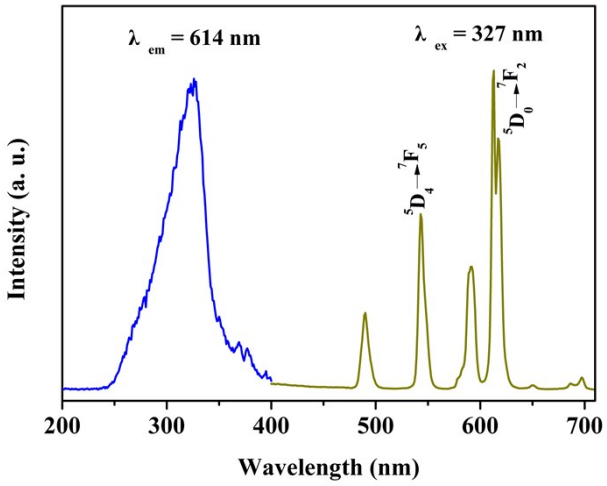

Fig. S7 Excitation and emission spectra of $\mathbf{Eu_{0.0878}Tb_{0.9122}L}$ at room temperature.

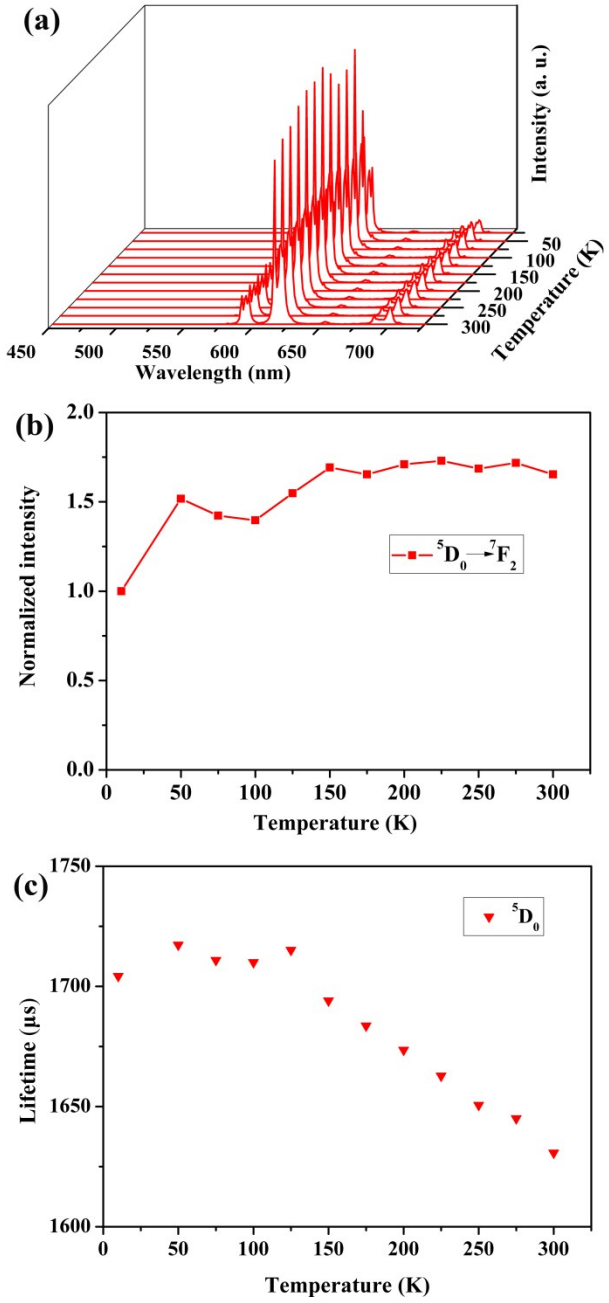

Fig. S8 (a) Emission spectra of **EuL** recorded between 10 and 300 K excited at 323 nm; (b) temperature dependence of normalized intensities of $^5D_0 \rightarrow {}^7F_2$ transitions in **EuL**; (c) temperature dependence of the $^5D_0$ lifetime for **EuL.** The decay curves are monitored at 614 nm and excited at 323 nm.

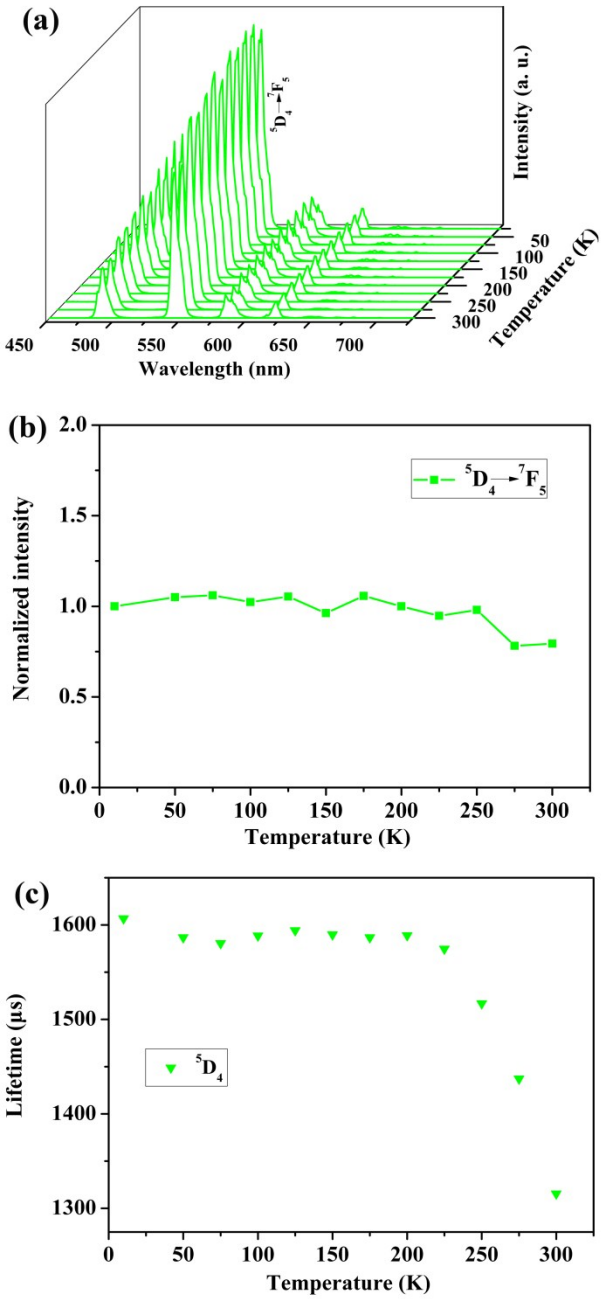

Fig. S9 (a) Emission spectra of **TbL** recorded between 10 and 300 K excited at 325 nm; (b) temperature dependence of normalized intensities of $^5D_4 \rightarrow {}^7F_5$ transitions in **TbL**; (c) temperature dependence of the $^5D_4$ lifetime for **TbL.** The decay curves are monitored at 544 nm and excited at 325 nm.

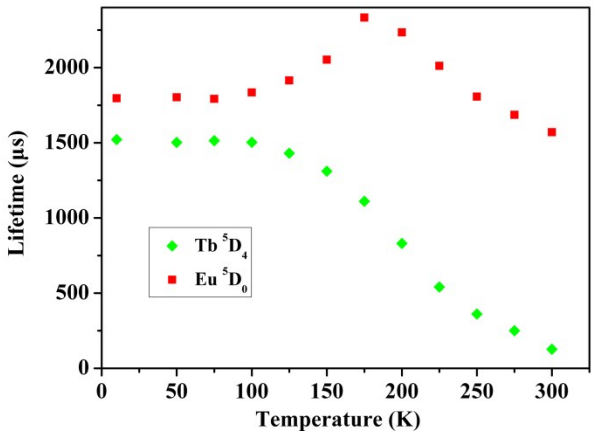

Fig. S10 Temperature dependence of the $^5D_4$ (Tb^{3+}) and $^5D_0$ (Eu^{3+}) lifetime for **$Eu_{0.0878}Tb_{0.9122}L$.** The decay curves are monitored at 544 nm and 614 nm, respectively, and excited at 325 nm.

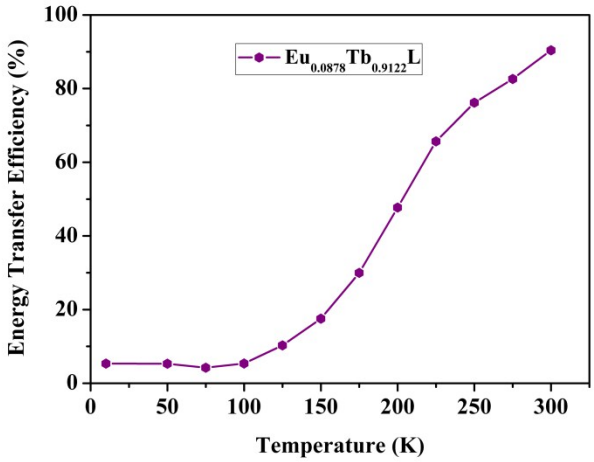

Fig. S11 Temperature dependence of the Tb^{3+}-to-Eu^{3+} energy transfer efficiency in **$Eu_{0.0878}Tb_{0.9122}L$.**

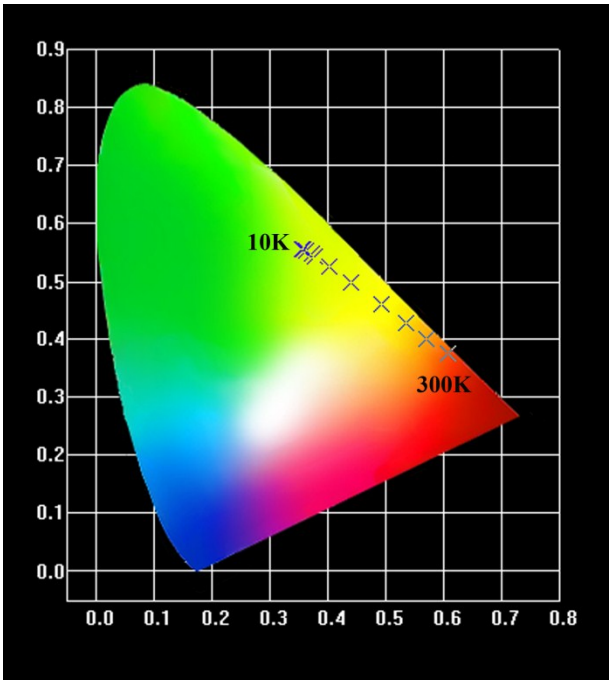

Fig. S12 CIE chromaticity diagram showing the temperature-dependent luminescence color of $\mathbf{Eu_{0.0878}Tb_{0.9122}L}$.

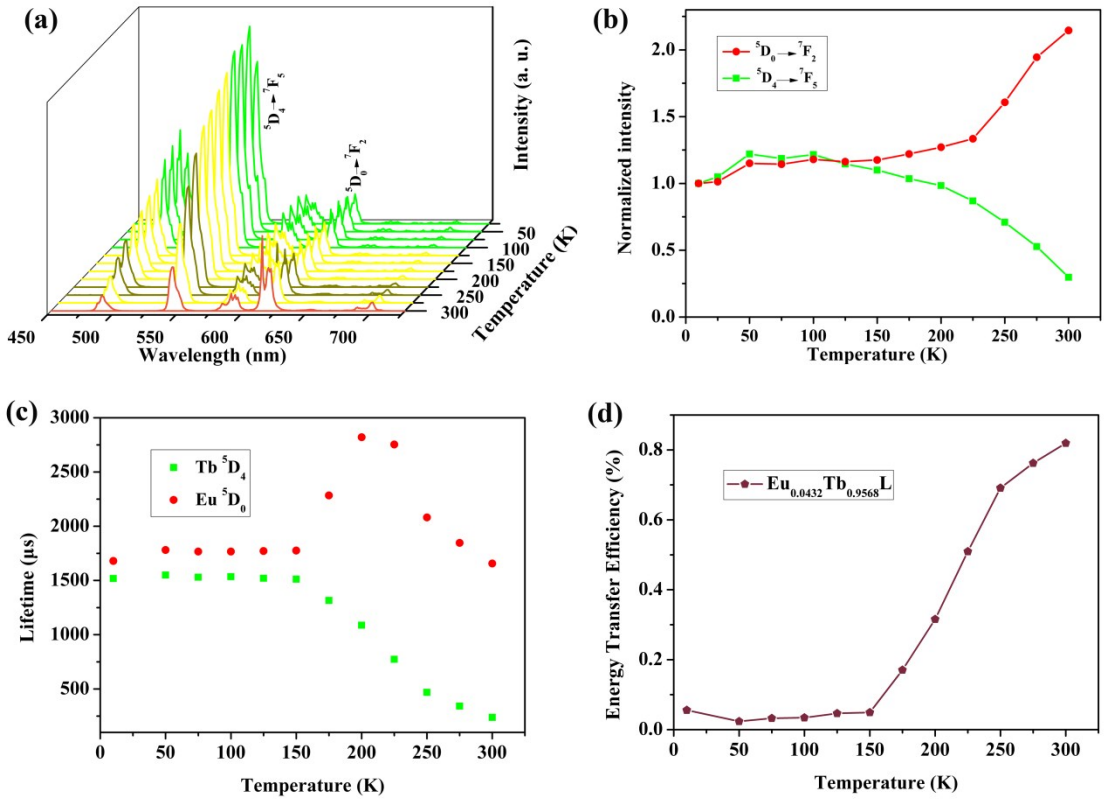

Fig. S13 (a) Emission spectra of $\mathbf{Eu_{0.0432}Tb_{0.9568}L}$ recorded between 10 and 300 K excited at 325 nm; (b) temperature dependence of normalized intensities of $^5D_0 \rightarrow {}^7F_2$ and $^5D_4 \rightarrow {}^7F_5$ transitions in $\mathbf{Eu_{0.0432}Tb_{0.9568}L}$; (c) temperature dependence of the $^5D_4$

(Tb^{3+}) and $^5D_0$ (Eu^{3+}) lifetime for **$Eu_{0.0432}Tb_{0.9568}L$**; (d) temperature dependence of the Tb^{3+}-to-Eu^{3+} energy transfer efficiency in **$Eu_{0.0432}Tb_{0.9568}L$.** The decay curves are monitored at 544 nm and 614 nm, respectively, and excited at 325 nm.

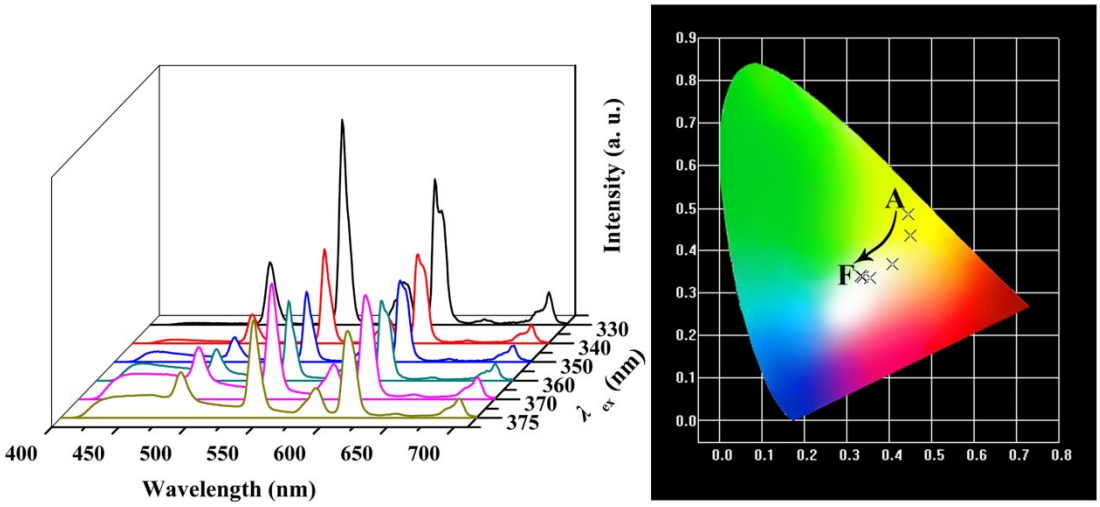

Fig. S14 (a) Solid-state emission spectra of compound **$Eu_{0.0831}Tb_{0.9169}L$** with excitation wavelength varying from 330 to 375 nm; (b) the CIE chromaticity diagram for the compound **$Eu_{0.0831}Tb_{0.9169}L$** (A → F: excitation wavelength from 330 to 375 nm).