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One-step growth of lanthanoid metal-organic framework (MOF) films under solvothermal conditions for temperature sensing

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Experimental section.

Materials and methods

5-hydroxy-1,2,4-benzenetricarboxylic acid (H_4**L**) and bulk crystals of TbH**L** and GdH**L** were made following previously reported procedures.[1] Gd_2O_3 and $TbCl_3$•6H_2O, were purchased from Sigma Aldrich and were used without further purification. The excitation and emission spectra were measured on a Shimadzu RF-5301PC spectrofluoriphotometer. X-ray powder diffraction patterns were recorded with a Philips PW 1050 diffractometer using Cu Kα radiation (λ = 1.542 Å). The morphology of the pellet and the films were investigated using a FEI NOVA nano SEM 200 scanning electron microscopy. The lifetime of the terbium emission was measured in a Tektronix DPO4054 digital oscilloscope. A nanosecond (~3 ns) Nd:YAG laser equipped with EKSPLA NTB342B-SH-SFG, which enables spectral tuning range from 225 to 2500 nm, was used as the excitation source. The collected luminescence was dispersed in a Carl Zeiss M20 grating monochromator and amplified by a Hamamatsu R928P photomultiplier. The time resolution of the setup was ~10 ns. The Gd_2O_3 pellets were made using a SPECAC Ltd. Speca press with 10 tons pressure. The pellets were sintered in a GSL 1700X tube furnace.

Preparation of Gd_2O_3 pellet and *Ln*HL film

Gd_2O_3 substrates were made by putting about 40 mg Gd_2O_3 powder into the sample model of Speca press (diameter 12.5 mm) and pressing with 10 tons pressure for 10 min. Then, these substrates were transferred to a tube furnace and heated at 1500 °C for 15 h to make it mechanically stronger.

LnH**L** films were prepared by an in situ hydrothermal synthesis method. The hydrothermal solution was made by dissolving *Ln*Cl_3•6H_2O (0.05 mmol, *Ln* = Tb, Gd) and H_4**L** (33.9 mg, 0.15 mmol) in a mixture of ethanol (5 ml) and water (5 ml). This solution together with the Gd_2O_3 substrate was placed in a 20 ml teflon-lined stainless steel vessel. The vessel was closed and put into an oven and kept at 130 °C for 15 h, then slowly cooled down to room temperature. The *Ln*H**L** film on Gd_2O_3 substrate was washed five times with H_2O and five times with ethanol.

Table S1. CIE coordinates of luminescence emission of $Gd_{0.9}Tb_{0.1}H\mathbf{L}$ at different temperatures.

Temperature (K)	X	Y
110	0.2465	0.3552
130	0.2504	0.3726
150	0.2578	0.3942
170	0.2685	0.4187
190	0.2801	0.4462
210	0.2872	0.4639
230	0.2921	0.4804
250	0.2941	0.4904
270	0.2962	0.4969

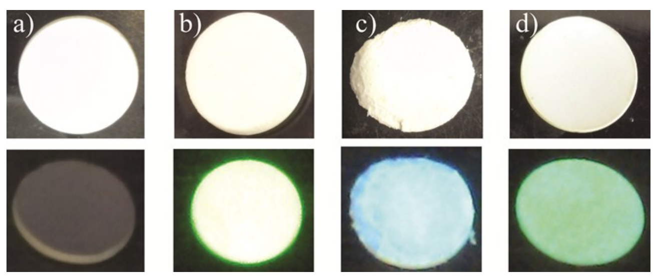

Figure S1. Pictures of a) Gd_2O_3 substrate; b) TbH**L** film on Gd_2O_3 substrate; c) GdH**L** film on Gd_2O_3 substrate. d) $Gd_{0.9}Tb_{0.1}H\mathbf{L}$ film on Gd_2O_3 substrate. Top row: under ambient light; Bottom row: under 366 nm UV light.

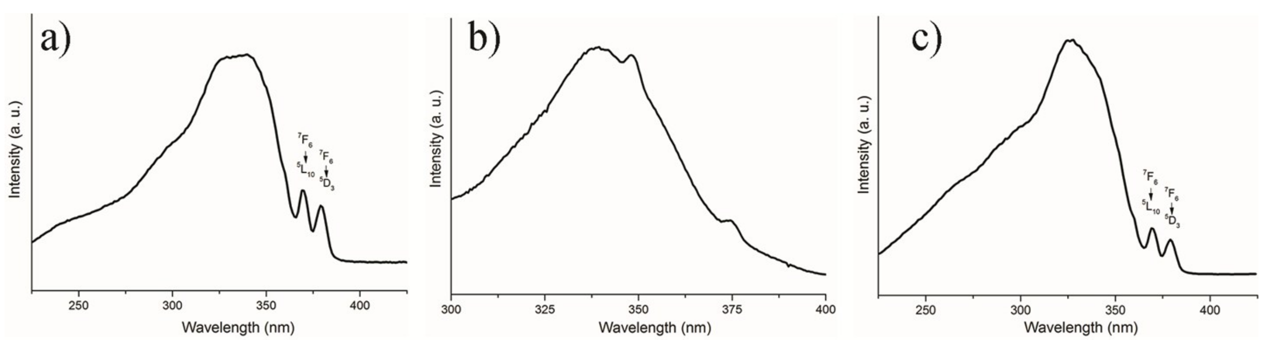

Figure S2. Excitation spectra of a) TbH**L** film on Gd_2O_3 substrate (monitored at 541 nm); b) GdH**L** film on Gd_2O_3 substrate (monitored at 475 nm). c) $Gd_{0.9}Tb_{0.1}H\mathbf{L}$ film on Gd_2O_3 substrate (monitored at 541 nm).

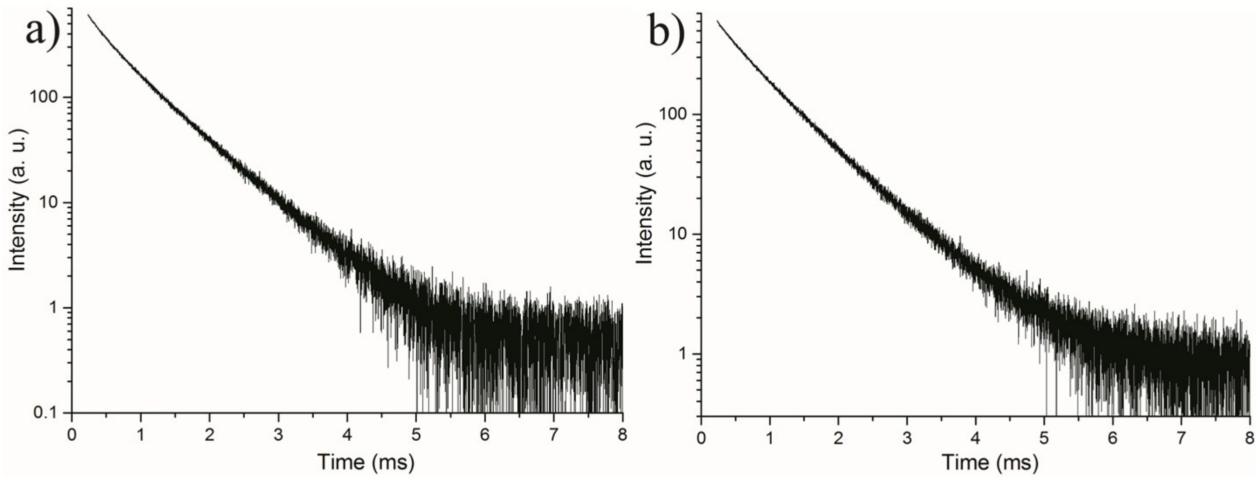

Figure S3. Luminescence decay curves of the 541 nm emission (Tb^{III}, $^5D_4 \rightarrow {}^7F_5$ transition) in a) TbHL film and b) $Gd_{0.9}Tb_{0.1}HL$ film. (λ_{exc}=325 nm)

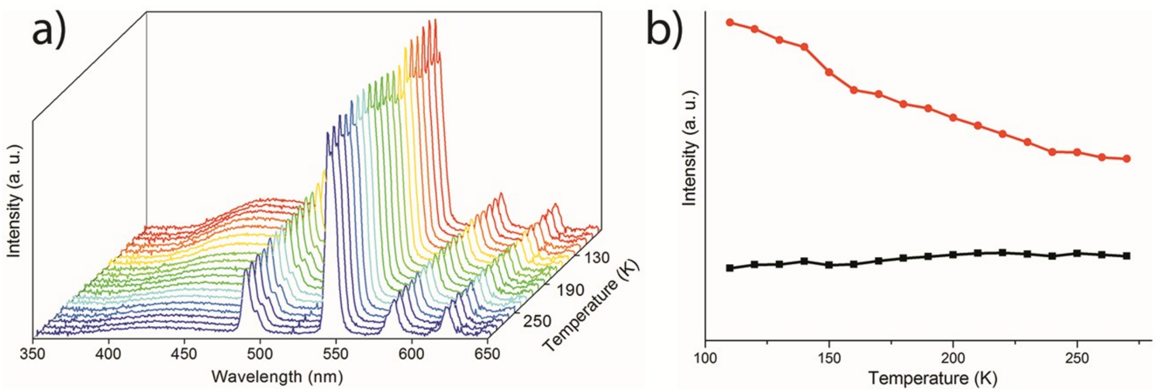

Figure S4. a) Emission spectra of the $Gd_{0.9}Tb_{0.1}H\mathbf{L}$ film in the temperature range of 110 -270 K (λ_{ex} = 325 nm). b) Temperature dependent luminescence intensity of the $^5D_4 \rightarrow {}^7F_5$ (black, Tb^{III} at 541 nm) transition and the total emission intensity from 350 nm to 650 nm (red) in the $Gd_{0.9}Tb_{0.1}H\mathbf{L}$ film (λ_{ex} = 325 nm).

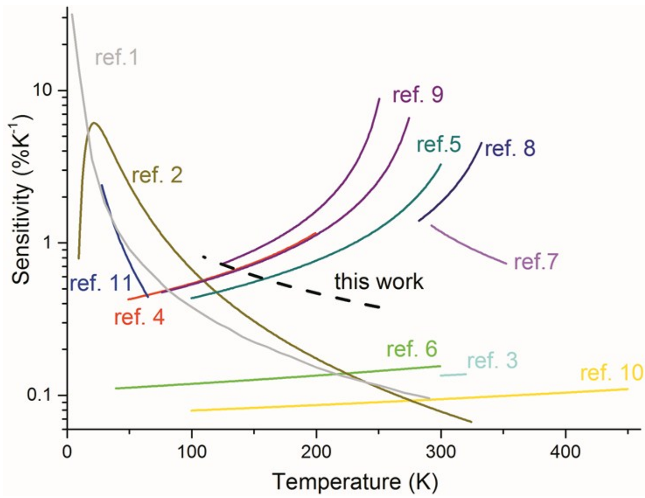

Figure S5. Overview of relative sensitivity of MOFs ratiometric thermometer reported in this work and in literature.[1-11]

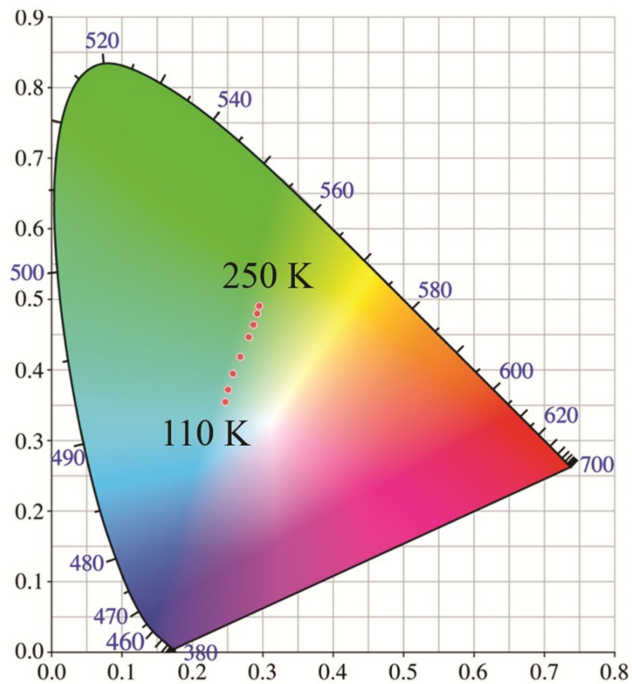

Figure S6. The luminescence colors of $Gd_{0.9}Tb_{0.1}H\mathbf{L}$ film from 110 K to 250 K in CIE chromaticity diagram.

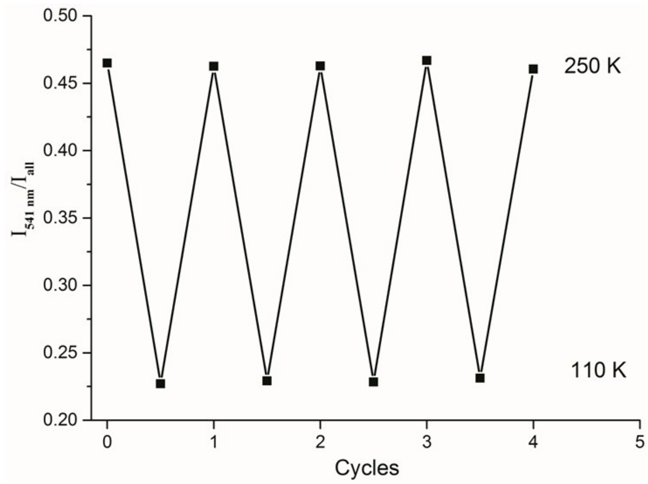

Figure S7. The reversible emission intensity ratio changes in the $Gd_{0.9}Tb_{0.1}H$**L** film after a number of temperature cycles.

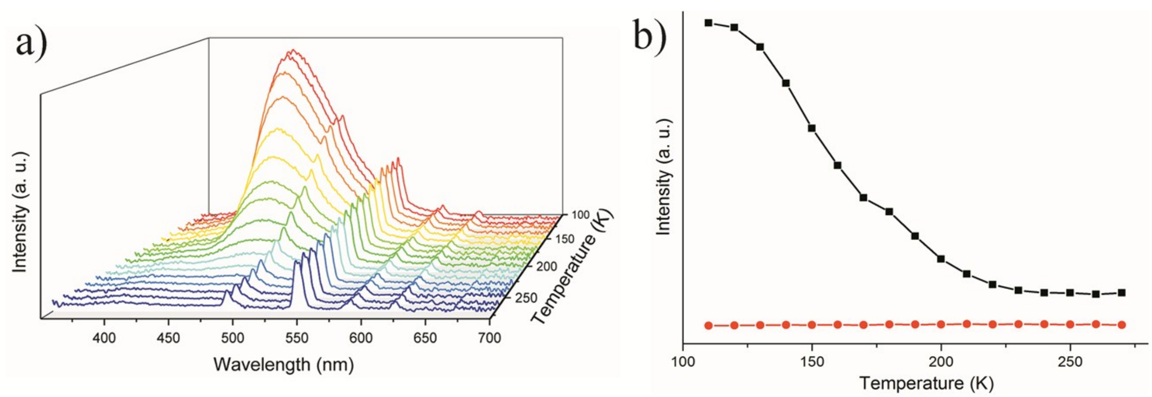

Figure S8. a) Emission spectra of $Gd_{0.99}Tb_{0.01}H$**L** film in the temperature range of 110 -270 K (λ_{ex} = 325 nm). b) Temperature dependent luminescence intensity of the $^5D_4 \rightarrow {}^7F_5$ (red, Tb^{III} at 541 nm) transition and the total emission intensity of from 350 nm to 650 nm (black) in the $Gd_{0.99}Tb_{0.01}H$**L** film (λ_{ex} = 325 nm).

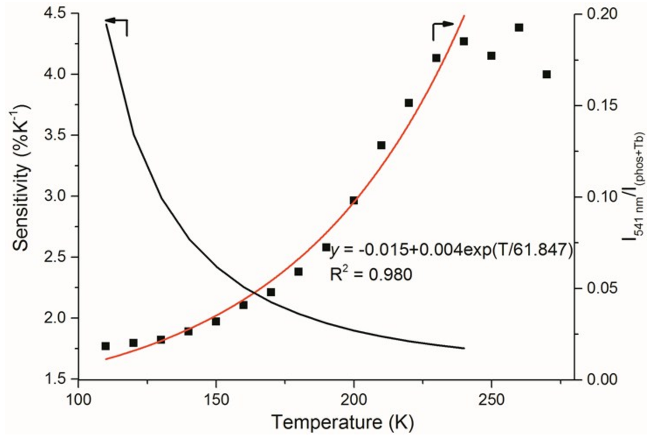

Figure S9. The emission intensity ratio of $I_{541\ nm}$ (Tb, $^5D_4 \rightarrow {}^7F_5$, 541 nm) and $I_{(phos+Tb)}$ (the emission intensity from 350 nm to 650 nm) for the $Gd_{0.99}Tb_{0.01}H\mathbf{L}$ film as a function of temperature (black squares) with the fitting curve (red line; R^2=0.980) and the relative sensitivity curve (black line, left axis).

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