# **Supporting information**

# Postsynthetic Lanthanides functionalization of Nanosized Metal-organic Frameworks for Highly Sensitive Ratiometric Luminescent thermometry

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#### **Experimental section**

# Materials

All chemicals were purchased from commercial sources and used without purification.  $In(NO_3)_3 \cdot xH_2O$  (300.83 g·mol<sup>-1</sup>),  $AlCl_3 \cdot 6H_2O$ ,  $Ga(NO_3)_3 \cdot xH_2O$  (255.74 g·mol<sup>-1</sup>) and 2,2'-bipyridine-5,5'-dicarboxylic acid (H<sub>2</sub>bpydc) were purchased from Aldrich. Lanthanide chlorides were obtained from the corresponding oxides in HCl (37.5%).

### Synthesis of In(OH)(bpydc) (1)

In(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (180.5 mg, 0.6 mmol), H<sub>2</sub>bpydc (146.9 mg, 0.6 mmol), and 10 ml DMF were placed in a 20 ml Pyrex tube. The mixture was heated at 150 °C for 48 h. The resulting white powder was separated from the mixed dispersion by centrifugation and washed with DMF and acetonitrile. To remove the organic species encapsulated within the pores of the open framework, the product was washed with acetonitrile via soxhlet extraction for 24 h, followed by drying at 60 °C under vacuum for 6 h. The yield was 34% based on indium. Anal. Calcd for  $C_{12}H_7InN_2O_5 \cdot 1.4H_2O$ : C, 36.09; H, 2.82; N, 7.02. Found: C, 36.21; H, 2.67; N, 7.29.

#### Synthesis of Al(OH)(bpydc) (MOF-253, 2)

The synthesis of MOF-253 nanoparticles was accomplished in the direct analogy with the microcrystalline MOF-253 product.<sup>S1</sup> AlCl<sub>3</sub>·6H<sub>2</sub>O (144.9 mg, 0.6 mmol), H<sub>2</sub>bpydc (146.9 mg, 0.6 mmol), sodium acetate (123 mg, 1.5 mmol) and 10 ml DMF were placed in a 20 ml Pyrex tube. Noted that sodium acetate is included to reduce the size of the product, because of that sodium acetate can facilitate the deprotonation of H<sub>2</sub>bpydc ligands and enhance the nucleation rate of MOF-253. The mixture was heated at 120 °C for 12 h. The resulting white powder was separated from the mixed dispersion by centrifugation and washed with DMF and acetonitrile. To remove the organic species encapsulated within the pores of the open framework, the product was washed with acetonitrile via soxhlet extraction for 24 h, followed by he followed by drying at 60 °C under

vacuum for 6 h. The yield was 81% based on aluminum.

# Synthesis of Ga(OH)(bpydc) (COMOC-4, 3)

Nanocrystals of **3** were prepared according to the method described by Liu et  $al.^{S2}$  Ga(NO3)3·xH<sub>2</sub>O (153.4 mg, 0.6 mmol), H<sub>2</sub>bpydc (146.9 mg, 0.6 mmol), and 10 ml DMF were placed in a 20 ml Pyrex tube, and then heated at 150 °C for 48 h. This resulted in a green powdered phase in suspension. The powder color immediately changed to orange upon contact with air. The orange solid was separated from the mixed dispersion by centrifugation and washed with DMF and acetonitrile. To remove the organic species encapsulated within the pores of the open framework, the product was washed with acetonitrile via soxhlet extraction for 24 h, followed by drying at 60 °C under vacuum for 6 h. The yield was 31% based on indium.

# Synthesis of Eu<sup>3+</sup>@1 and Tb<sup>3+</sup>@1

The Compouds 1 (50 mg, 0.134 mmol), EuCl<sub>3</sub>·6H<sub>2</sub>O (49 mg, 0.134 mmol), and methanol (10 ml) were added to a 20 ml Pyrex tube and heated at 60 °C for 24 h. The solid was then filtered off and soaked in 10 ml DMF. After 24 h, the solids were washed with acetonitrile (2 × 10 mL), followed by soaking in acetonitrile for 3 d, and the solution was exchanged with fresh acetonitrile (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum. Synthesis of Tb<sup>3+</sup>@1 is similar to that of Eu<sup>3+</sup>@1 except the starting material EuCl<sub>3</sub>·6H<sub>2</sub>O was substituted by TbCl<sub>3</sub>·6H<sub>2</sub>O (50 mg, 0.134 mmol).

# Synthesis of Eu<sup>3+</sup>/Tb<sup>3+</sup>@1, Eu<sup>3+</sup>/Tb<sup>3+</sup>@2, and Eu<sup>3+</sup>/Tb<sup>3+</sup>@3

The Compouds 1 (50 mg, 0.134 mmol), EuCl<sub>3</sub>·6H<sub>2</sub>O (0.245 mg,  $6.7 \times 10^{-4}$  mmol), TbCl<sub>3</sub>·6H<sub>2</sub>O (49.62 mg, 0.133 mmol), and methanol (10 ml) were added to a 20 ml Pyrex tube and heated at 60 °C for 24 h. The solid was then filtered off and soaked in 10 ml DMF. After 24 h, the solids were washed with acetonitrile (2 × 10 mL), followed by soaking in acetonitrile for 3 d, and the solution was exchanged with fresh acetonitrile (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum.

The synthesis of  $Eu^{3+}/Tb^{3+}@2$ , and  $Eu^{3+}/Tb^{3+}@3$  was similar to that of  $Eu^{3+}/Tb^{3+}@1$  except compound 1 was replaced by 2 and 3.

# **Physical Measurements**

The elemental microanalyses (EA) were performed on a Vario ELIII elemental analyzer. ICPMS data were obtained on an X-7 series inductively coupled plasma-mass spectrometer (Thermo Elemental, Cheshire, UK). Powder X-ray diffraction patterns (PXRD) were recorded with a Bruker D8 diffractometer using CuK $\alpha$  radiation with 40 mA and 40 kV. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) were carried out on a JEOL JEM-2010F electron microscope equipped with an energy-dispersive X-ray spectrum (EDS, JEOL JXA-840) and operated at 200 kV. Thermogravimetric analysis (TGA) was measured using a Netzsch STA 449C system at a heating rate of 15 K min<sup>-1</sup> under the nitrogen protection.

# Luminescent properties characterization

The photoluminescent spectra and luminescent decay times were examined by an Edinburgh FLS920 phosphorimeter. The outer absolute luminescent quantum efficiency was determined employing an integrating sphere (150 mm diameter, BaSO4 coating) from an Edinburgh FLS920 phosphorimeter. The spectra were corrected for variations in the output of the excitation source and for variations in the detector response. The quantum yield can be defined as the integrated intensity of the luminescence signal divided by the integrated intensity of the absorption signal. The absorption intensity was calculated by subtracting the integrated intensity of the light source with the sample in the integrating sphere from the integrated intensity of the light source with a blank sample in the integrating sphere. The excitation wavelength of the measurements of the emission quantum yields was listed in Table 1. The estimated errors for quantum yields and luminescent lifetimes are within 5%.



**Figure S1**. PXRD patterns and TEM images of  $Ln^{3+}@1$  ( $Ln^{3+} = Eu^{3+}$ ,  $Tb^{3+}$ ,  $Eu^{3+}/Tb^{3+}$ ) samples. The scale bar in TEM images is 200 nm.



Figure S2. Thermogravimetric analysis of  $Ln^{3+}@1$  ( $Ln^{3+} = Eu^{3+}$ ,  $Tb^{3+}$ ,  $Eu^{3+}/Tb^{3+}$ ) samples.



**Figure S3**. (a) Emission spectra ( $\lambda_{ex} = 318$  nm) and (b) luminescent lifetimes ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ) of Eu<sup>3+</sup>@1 recorded from 10 to 60 °C; Temperature-dependent normalized (c) intensity and (d) lifetime of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of Eu<sup>3+</sup>.



**Figure S4**. (a) Emission spectra ( $\lambda_{ex} = 314$  nm) and (b) luminescent lifetimes ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ) of Tb<sup>3+</sup>@1 recorded from 10 to 60 °C; Temperature-dependent (c) normalized intensity and (d) lifetime of  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition of Tb<sup>3+</sup>.



**Figure S5.** (a) Temperature-dependent Emission spectra (10-60 °C) of the  $Eu^{3+}/Tb^{3+}@1$  product upon exposure to air. (b) temperature-dependent normalized intensity of  $Eu^{3+}$  ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ) and  $Tb^{3+}$  ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ) for  $Eu^{3+}/Tb^{3+}@2$  and (c) the dependence of  $I_{Tb}/I_{Eu}$  on temperature for  $Eu^{3+}/Tb^{3+}@1$ . The red line plotted in (c) is the linear fitted curve.



**Figure S6** The temperature-dependent emission spectra of  $Eu^{3+}/Tb^{3+}@1$  when the  $Eu^{3+}/Tb^{3+}$  feed ratio is 0.99/0.01. The inset plots the thermometric response of  $I_{Tb (544 nm)}/I_{Eu (613 nm)}$  towards temperature



**Figure S7** The temperature-dependent emission spectra of  $Eu^{3+}/Tb^{3+}@1$  when the  $Eu^{3+}/Tb^{3+}$  feed ratio is 0.999/0.001. The inset plots the thermometric response of  $I_{Tb}$  (544 nm)/ $I_{Eu}$  (613 nm) towards temperature.



**Figure S8.** The second measurement of thermal dependent luminescence of  $Eu^{3+}/Tb^{3+}@1$ : (a) Emission spectra recorded between 10 and 60 °C, (b) temperaturedependent normalized intensity of  $Eu^{3+}$  ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ) and  $Tb^{3+}$  ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ) and (c) the dependence of  $I_{Tb}/I_{Eu}$  on temperature. The red line plotted in (c) is the linear fitted curve.



**Figure S9.** The third measurement of thermal dependent luminescence of  $Eu^{3+}/Tb^{3+}@1$ : (a) Emission spectra recorded between 10 and 60 °C, (b) temperaturedependent normalized intensity of  $Eu^{3+}$  ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ) and  $Tb^{3+}$  ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ) and (c) the dependence of  $I_{Tb}/I_{Eu}$  on temperature. The red line plotted in (c) is the linear fitted curve.



**Figure S10.** The reversible changes of emission intensity ratio of  $Tb^{3+}$  (545 nm) to  $Eu^{3+}$  (613 nm) of  $Eu^{3+}/Tb^{3+}@1$  by the alternative thermo-cycles in the range of 10-60 °C.



**Figure S11**. Temperature-dependent decay time ( $\lambda_{ex} = 312 \text{ nm}$ ) of Eu<sup>3+</sup>/Tb<sup>3+</sup>@1: (a)  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of Eu<sup>3+</sup>, (b)  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition of Tb<sup>3+</sup>, and (c) normalized values.



Figure S12. The temperature-dependent emission spectra of TbCl<sub>3</sub>.  $\lambda_{ex} = 312$  nm.



Figure 13. The emission intensity ratio  $(I_{Tb}/I_{Eu})$  of  $Eu^{3+}/Tb^{3+}@1$  as a function of temperature. The plotted red line is the linear fitted curve.



Figure S14. PXRD patterns and TEM images of compound 2 and  $Eu^{3+}/Tb^{3+}@2$ . The scale bar is 50 nm.



Figure S15. PXRD patterns and TEM images of compound 3 and  $Eu^{3+}/Tb^{3+}@3$ . The scale bar is 100 nm.



**Figure S16.** (a) Emission spectra of Eu<sup>3+</sup>/Tb<sup>3+</sup>@**3** recorded between 10 and 60 °C, (b) temperature-dependent normalized intensity of Eu<sup>3+</sup> ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ) and Tb<sup>3+</sup> ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ) for Eu<sup>3+</sup>/Tb<sup>3+</sup>@**3** and (c) the dependence of I<sub>Tb</sub>/I<sub>Eu</sub> on temperature for Eu<sup>3+</sup>/Tb<sup>3+</sup>@**3**. The red line plotted in (c) is the linear fitted curve.

**Table S1.** The atomic ratio of  $Ln^{3+}$  and  $In^{3+}$  of  $Ln^{3+}@1$  samples resulted from the EDS studies.

Samples	In <sup>3+</sup>	Eu <sup>3+</sup>	Tb <sup>3+</sup>
Eu <sup>3+</sup> @1	1	0.89	
Tb <sup>3+</sup> @1	1		0.69
$Eu^{3+}/Tb^{3+}@1$	1	0.91	a

<sup>a</sup> The content of  $Tb^{3+}$  in  $Eu^{3+}/Tb^{3+}$  (a) 1 is too low to be detected.

**Table S2.** The detailed ICPMS studies of  $Ln^{3+}$  (*i*) amples.

Samples	$In^{3+}(mM)$	Eu <sup>3+</sup> (mM)	Tb <sup>3+</sup> (mM)
Eu <sup>3+</sup> @1	1.653	1.486	
Tb <sup>3+</sup> @1	1.786		1.251
$Eu^{3+}/Tb^{3+}@1$	1.641	0.011	1.493

## References

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- S2 Y. Liu, R. Decadt, T. Bogaerts, K. Hemelsoet, A. M. Kaczmarek, D. Poelman, M. Waroquier, V. Van Speybroeck, R. Van Deun and P. Van Der Voort, *J. Phys. Chem. C*, 2013, **117**, 11302.