Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Tuning photoluminescence of lanthanide metal-organic framework nanospheres through ligand-induced phase transition towards sensing

Peng Zhang,[a] Nan Song,[a] Songbin Liu,[a] Qiqing Li,[a] Yu Wang,[b] and Bo Zhou[a,*]

[a] *State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques, Guangdong Engineering Technology Research and Development Center of Special Optical Fiber Materials and Devices, South China University of Technology, Guangzhou 510641, China*

[b] *International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518060, China*

Table S1~S3.

Table S1. Structure parameters of Yb/Tb/Eu-MOF and Yb/Tb/Eu-MOF·6H_2O.

Parameters	Yb/Tb/Eu-MOF	Yb/Tb/Eu-MOF·6H_2O
a (Å)	10.45	11.38
b (Å)	10.45	17.84
c (Å)	13.38	7.2
α (°)	90	90
β (°)	90	119.36
γ (°)	90	90
Ref.	S1	S2

Note:

S1. Gustafsson, M.; Bartoszewicz, A.; Martin-Matute, B.; Sun, J.; Grins, J.; Zhao, T.; Li, Z.; Zhu, G.; Zou, X., A Family of Highly Stable Lanthanide Metal-Organic Frameworks: Structural Evolution and Catalytic Activity. *Chemistry of Materials* **2010,** *22* (11), 3316-3322.

S2. Li, J.; Yuan, X.; Wu, Y.-n.; Ma, X.; Li, F.; Zhang, B.; Wang, Y.; Lei, Z.; Zhang, Z., From powder to cloth: Facile fabrication of dense MOF-76(Tb) coating onto natural silk fiber for feasible detection of copper ions. *Chemical Engineering Journal* **2018,** *350*, 637-644.

Table S2. The lifetimes of Yb/Tb/Eu-MOF samples in different solutions.

Samples	Wavelength /nm	t_1 /μs	t_2 /μs	t_3 /μs	A_1	A_2	A_3	Weighted Lifetime/μs
Eu-MOF in Ethanol	615	103	227	-	-3.5	3.5	-	330
Eu-MOF in Water	615	127	107	-	-9.3	9.3	-	234
Tb-MOF in Ethanol	545	123	1835	-	-1.2	1.3	-	1948
Tb-MOF in Water	545	112	627	-	-1.8	1.8	-	739
Yb/Tb/Eu-MOF in Ethanol	615	91	231	786	-2.7	2.5	0.3	522
Yb/Tb/Eu-MOF in Water	615	116	185	-	-5.9	5.9	-	301
Yb/Tb/Eu-MOF in Ethanol	545	117	1422	-	-1.2	1.3	-	1529
Yb/Tb/Eu-MOF in Water	545	106	542	-	-1.5	1.8	-	627

Table S3. Samples, detection temperature range (K), maximum sensitivity (S_m,$\%K^{-1}$) and its corresponding temperature T_m (K) and the references.

Samples	Range (K)	S_m ($\%K^{-1}$)	T_m(K)	Ref.
$Tb_{0.9}Eu_{0.1}L$	303-423	1.75	423	S3
$Tb_{0.9}Eu_{0.1}PIA$	100-300	3.27	300	S4
$Tb_{0.95}Eu_{0.05}FTPTC$	25-300	9.1	125	S5
$Tb_{0.9122}Eu_{0.0878}L$	75-250	4.9	250	S6
$Tb_{0.95}Eu_{0.05}CPNA$	25-300	2.55	131	S7
$CsPbBr_3$@Eu0BTC	293-393	3.9	293	S8
$Tb_{0.9975}Eu_{0.0025}$-BABDC-PBMA	0.5-240	3.61	240	S9
$Tb_{0.98}/Eu_{0.02}$-BTC	298-383	16.14	359	S10
$Tb_{0.9931}Eu_{0.0069}$-BMBDC	50-200	1.15	200	S11
$Tb_{0.98}Eu_{0.02}$-DSTP	77-275	2.4	275	S12
Yb/Tb/Eu-BTC	323-403	3.45	403	This work

Note:

S3. Yang, Y.; Wang, Y.; Feng, Y.; Song, X.; Cao, C.; Zhang, G.; Liu, W., Three isostructural Eu^{3+}/Tb^{3+} co-doped MOFs for wide-range ratiometric temperature sensing. *Talanta* **2020,** *208*, 120354.

S4. Rao, X.; Song, T.; Gao, J.; Cui, Y.; Yang, Y.; Wu, C.; Chen, B.; Qian, G., A Highly Sensitive Mixed Lanthanide Metal-Organic Framework Self-Calibrated Luminescent Thermometer. *Journal of the American Chemical Society* **2013,** *135* (41), 15559-15564.

S5. Zhao, D.; Yue, D.; Zhang, L.; Jiang, K.; Qian, G., Cryogenic Luminescent Tb/Eu-MOF Thermometer Based on a Fluorine-Modified Tetracarboxylate Ligand. *Inorganic Chemistry* **2018,** *57* (20), 12596-12602.

S6. Wu, L.-L.; Zhao, J.; Wang, H.; Wang, J., A lanthanide(III) metal-organic framework exhibiting ratiometric luminescent temperature sensing and tunable white light emission. *Crystengcomm* **2016,** *18* (23), 4268-4271.

S7. Zhao, D.; Yue, D.; Jiang, K.; Zhang, L.; Li, C.; Qian, G., Isostructural Tb^{3+}/Eu^{3+} Co-Doped Metal Organic Framework Based on Pyridine-Containing Dicarboxylate Ligands for Ratiometric Luminescence Temperature Sensing. *Inorganic Chemistry* **2019,** *58* (4), 2637-2644.

S8. Liu, J.; Zhao, Y.; Li, X.; Wu, J.; Han, Y.; Zhang, X.; Xu, Y., Dual-Emissive CsPbBr3@Eu-BTC Composite for Self-Calibrating Temperature Sensing Application. *Crystal Growth & Design* **2020,** *20* (1), 454-459.

S9. Feng, T.; Ye, Y.; Liu, X.; Cui, H.; Li, Z.; Zhang, Y.; Liang, B.; Li, H.; Chen, B., A Robust Mixed-Lanthanide PolyMOF Membrane for Ratiometric Temperature Sensing. *Angewandte Chemie-International Edition* **2020,** *59* (48), 21752-21757.

S10. Yang, X.; Zou, H.; Sun, X.; Sun, T.; Guo, C.; Fu, Y.; Wu, C.-M. L.; Qiao, X.; Wang, F., One-Step Synthesis of Mixed Lanthanide Metal–Organic Framework Films for Sensitive Temperature Mapping. **2019,** *7* (19), 1900336.
S11. Cui, Y.; Xu, H.; Yue, Y.; Guo, Z.; Yu, J.; Chen, Z.; Gao, J.; Yang, Y.; Qian, G.; Chen, B., A Luminescent Mixed-Lanthanide Metal-Organic Framework Thermometer. *Journal of the American Chemical Society* **2012,** *134* (9), 3979-3982.
S12. Wei, Y.; Sa, R.; Li, Q.; Wu, K., Highly stable and sensitive LnMOF ratiometric thermometers constructed with mixed ligands. *Dalton Transactions* **2015,** *44* (7), 3067-3074.

Figure S1~S10

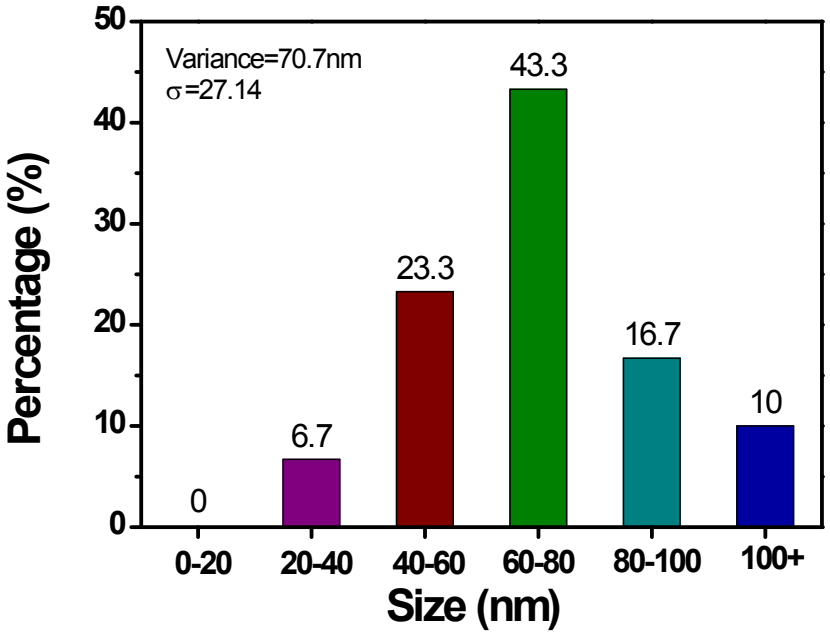

Figure S1. Size distribution of Yb/Tb/Eu-MOF nanoparticles.

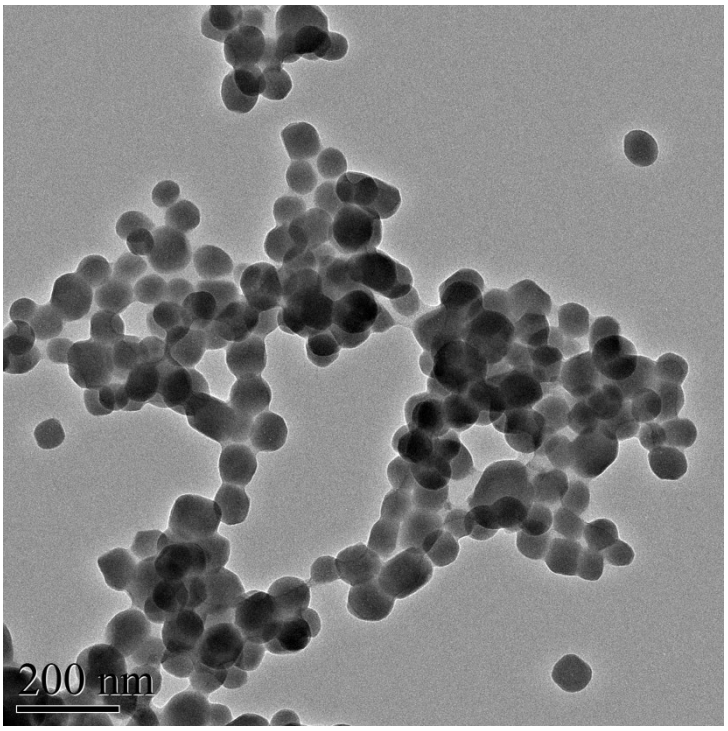

Figure S2. TEM image of MOF materials without the dropwise adding.

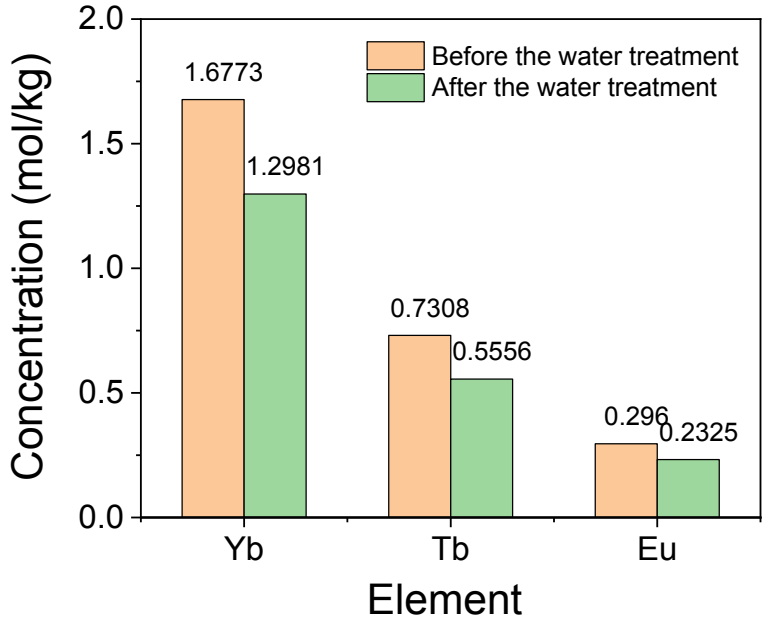

Figure S3. The concentrations of lanthanide ions of MOF materials before and after the water treatment measured by the ICP analysis.

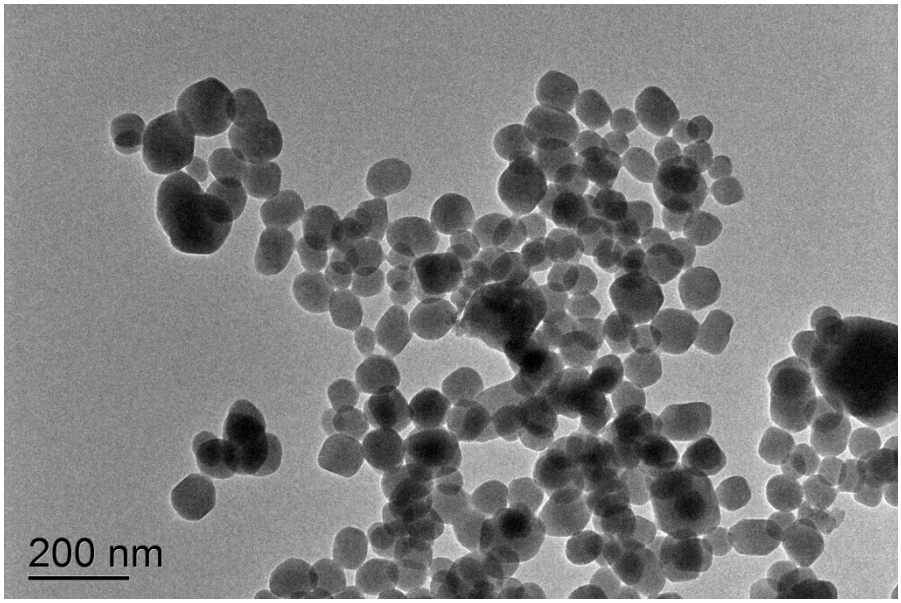

Figure S4. TEM image of Yb/Tb/Eu-MOF treated in water.

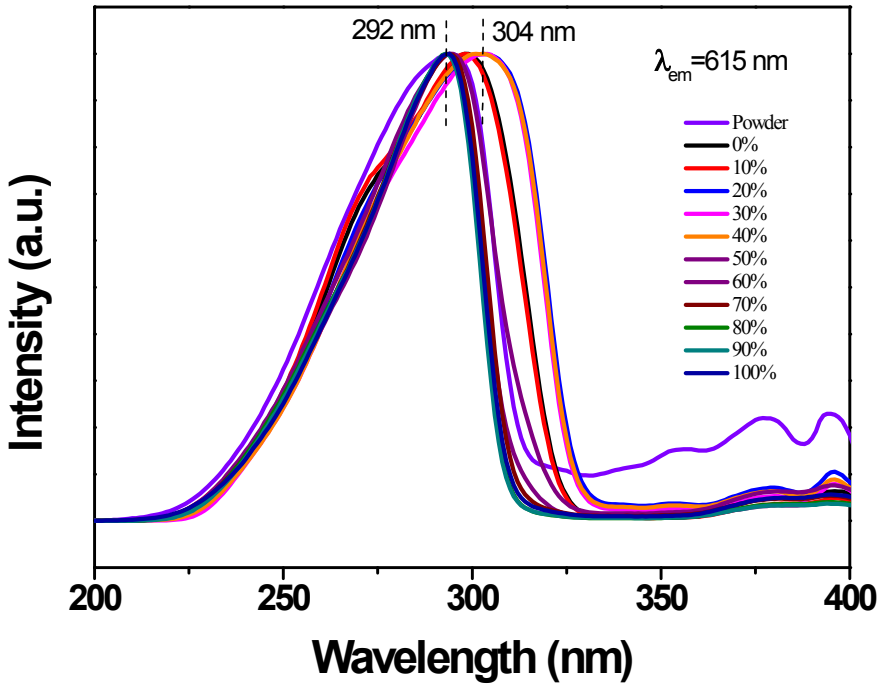

Figure S5. Excitation spectra of Yb/Tb/Eu-MOF nanospheres dispersed in water-ethanol system.

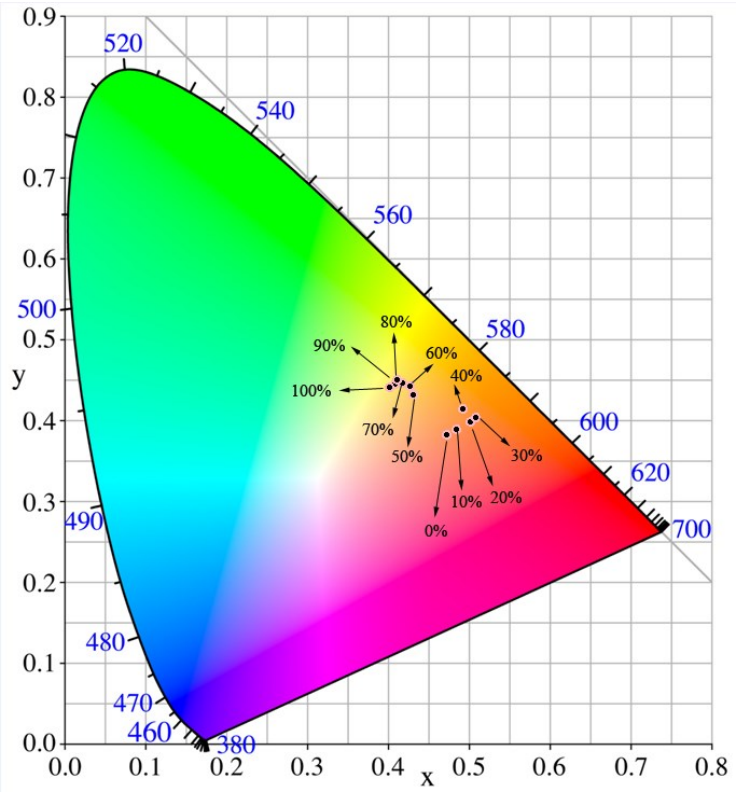

Figure S6. CIE chromaticity diagram showing the fluorescence color of Yb/Tb/Eu-MOF nanospheres treated in water-ethanol system.

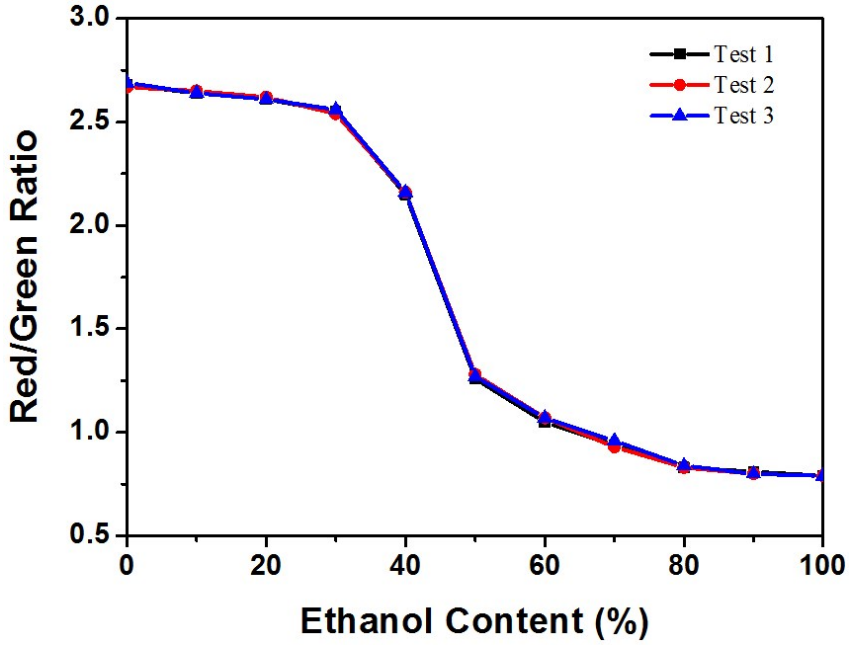

Figure S7. The reliability and reversibility of Yb/Tb/Eu-MOF nanospheres on the ethanol content.

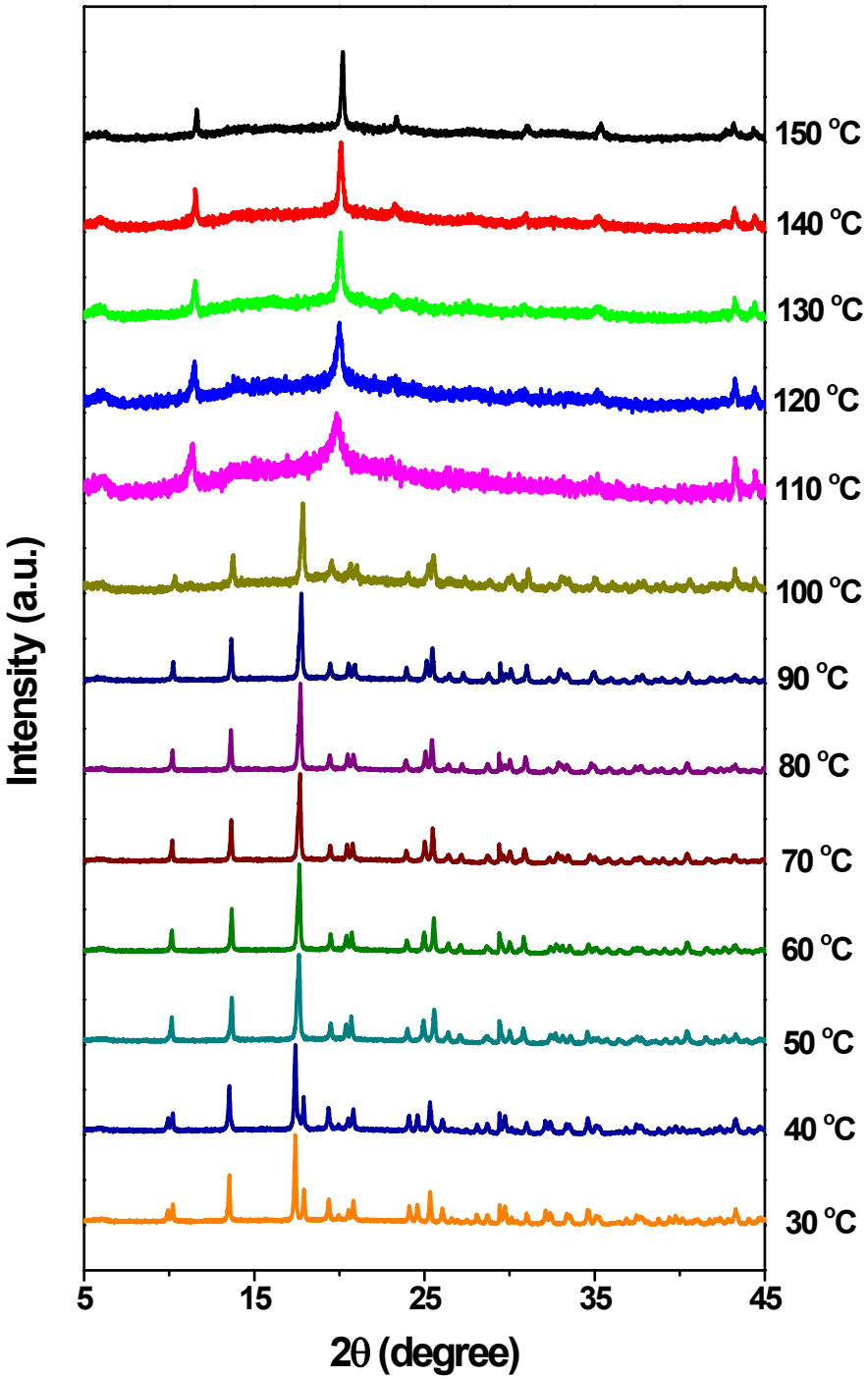

Figure S8. XRD patterns of Yb/Tb/Eu-MOF at different temperatures.

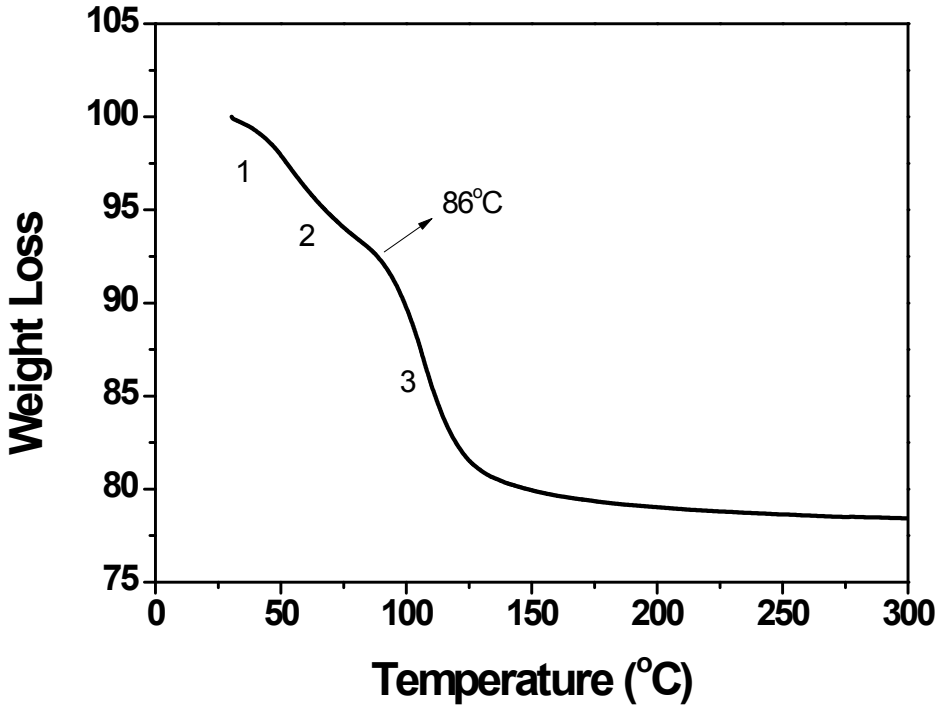

Figure S9. TGA curve of Yb/Tb/Eu-MOF · $6H_2O$

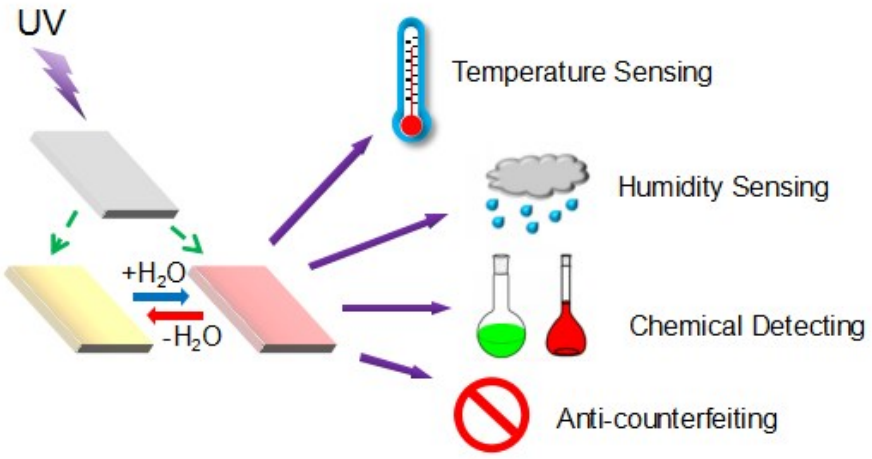

Figure S10. Potential applications of Yb/Tb/Eu-MOF.