

Supplementary information

Nanoscale carbon dots-embedded metal-organic framework for turned-on fluorescent detection of water in organic solvents

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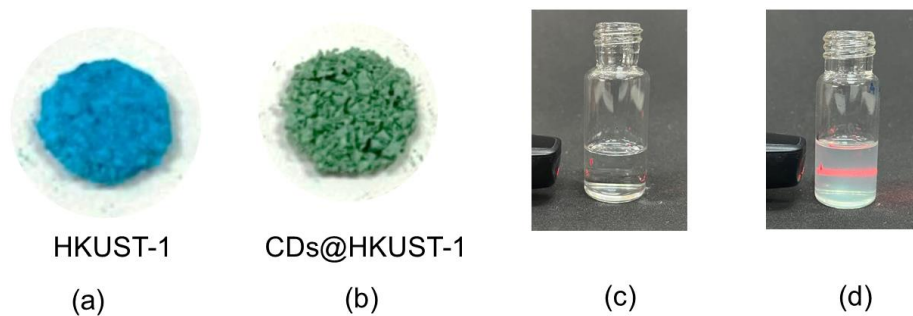


Figure S1 Photographs of (a) HKUST-1 and (b) CDs@HKUST-1. Tyndall effect of a colloidal ethanol suspension of CDs@HKUST-1 material. Ethanol solution (c) without and (d) with CDs@HKUST-1.

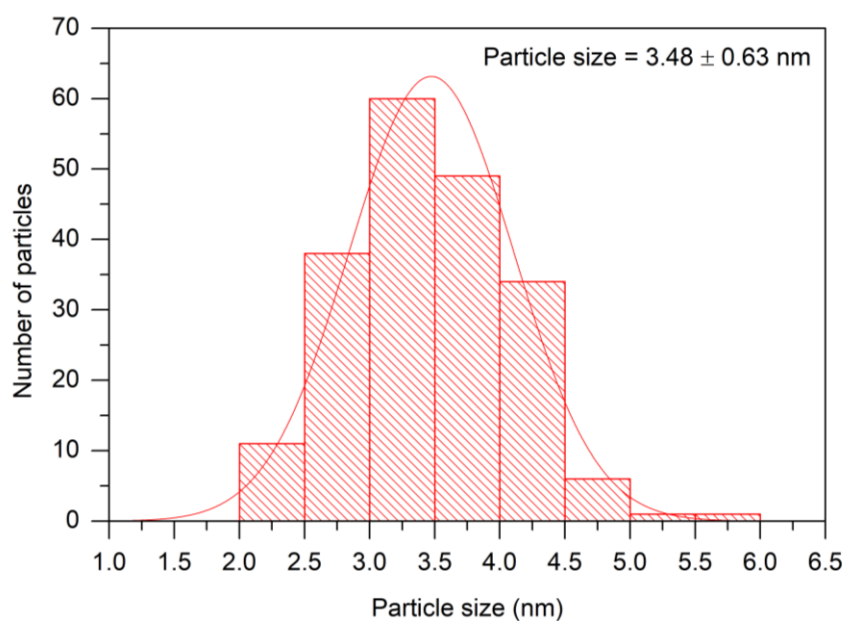


Figure S2 Size distribution histogram of CDs

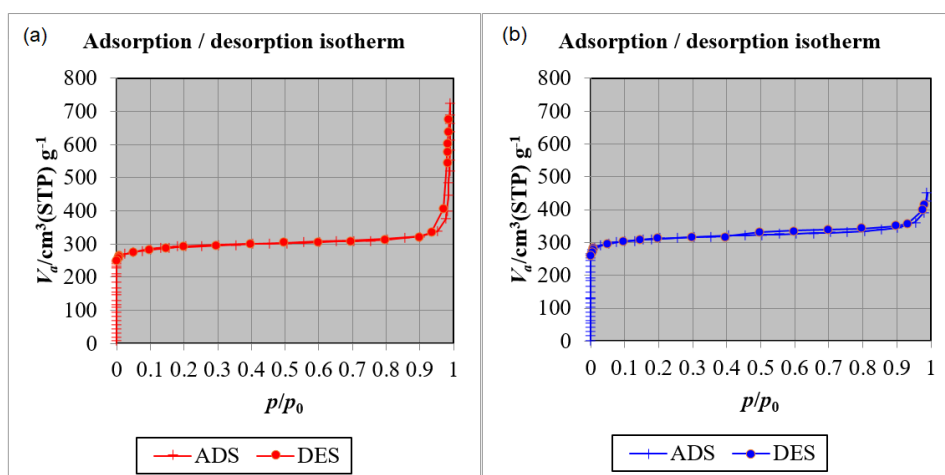


Figure S3 N_2 adsorption–desorption isotherms of (a) HKUST-1 and (b) CDs@HKUST-1

Table S1 BET surface area, total pore volume and average pore diameter of the HKUST-1 and CDs@HKUST-1

	HKUST-1	CDs@HKUST-1
BET surface area (m^2g^{-1})	1144.8	1233.2
Total pore volume ($p/p_0=0.9900$) (cm^3g^{-1})	1.0677	0.6959
Average pore diameter (nm)	3.7307	2.2571

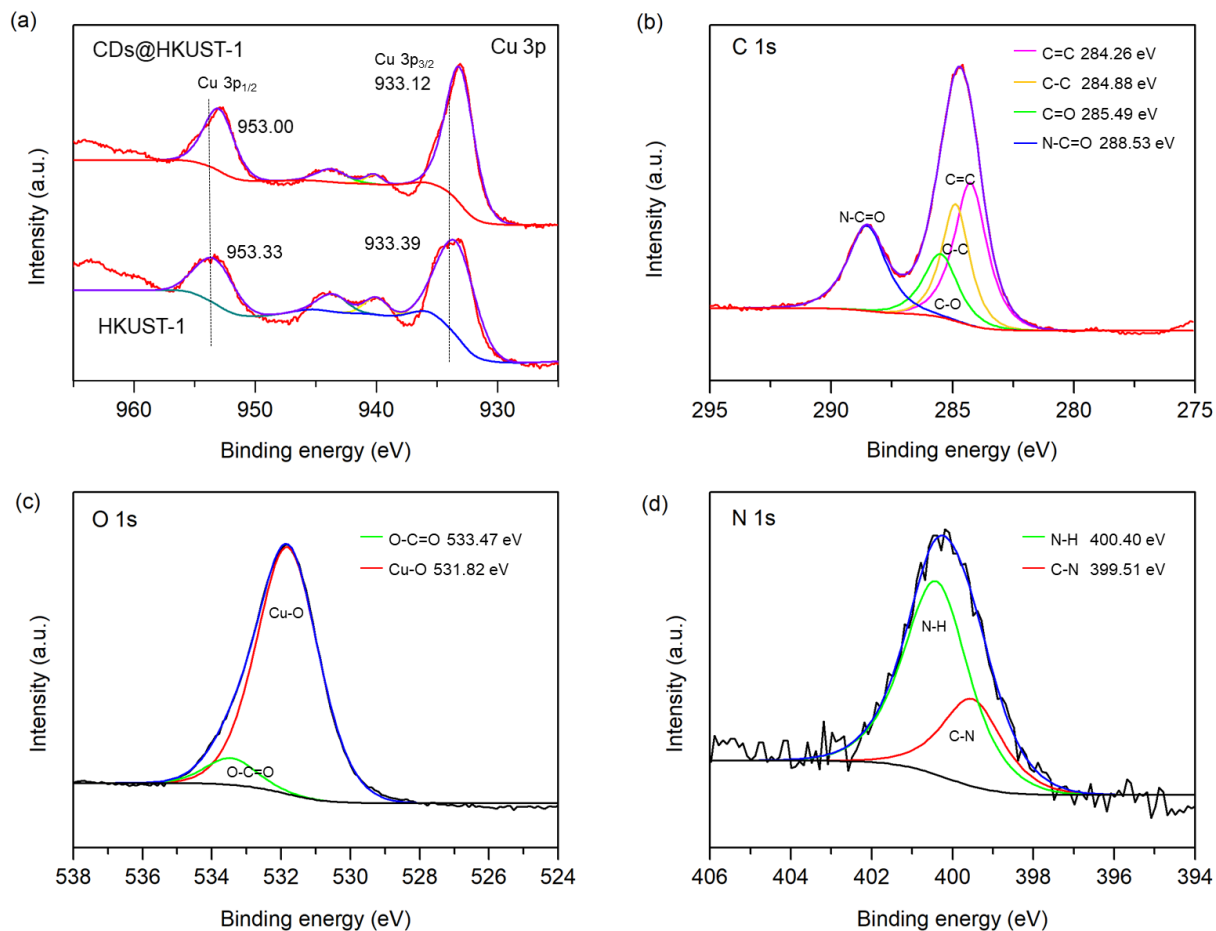


Figure S4 High-resolution XPS of (a) Cu 3p of HKUST-1 and CDs@HKUST-1, (b-d) C 1s, O 1s, and N 1s spectra of CDs@HKUST-1.

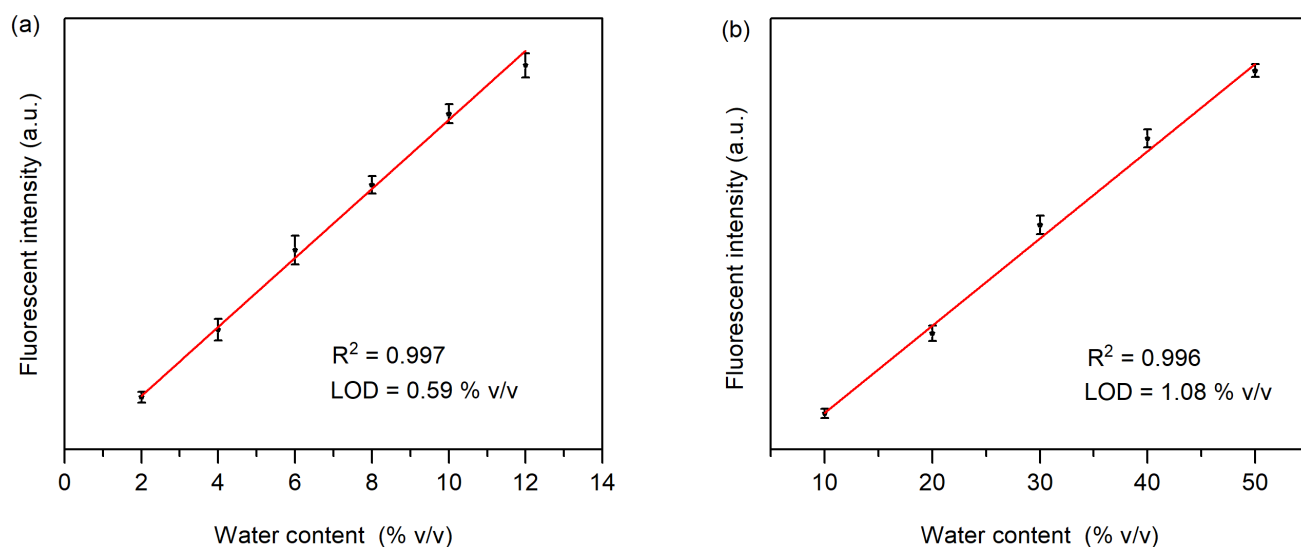


Figure S5 The linear relationship between fluorescent intensity at 450 nm of CDs@HKUST-1 in (a) ACN and (b) acetone with the incremental addition of water content.

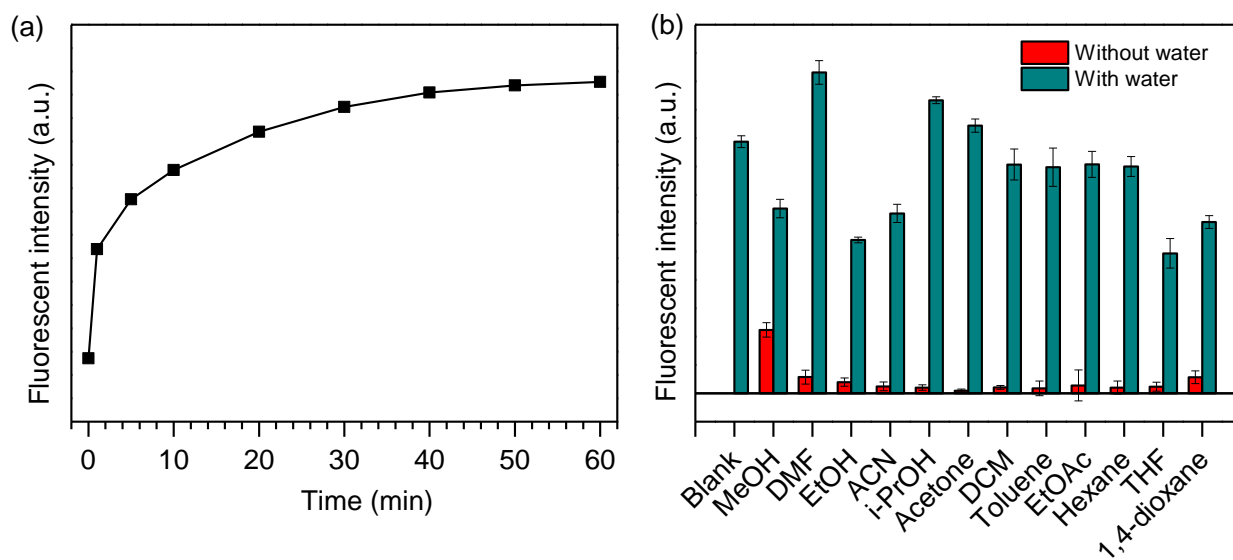


Figure S6 (a) The response speed of CDs@HKUST-1 toward water (50 %v/v) in EtOH solution. (b) Comparison of fluorescent intensity of CDs@HKUST-1 with organic solvent in the absence and presence of water (50 %v/v).

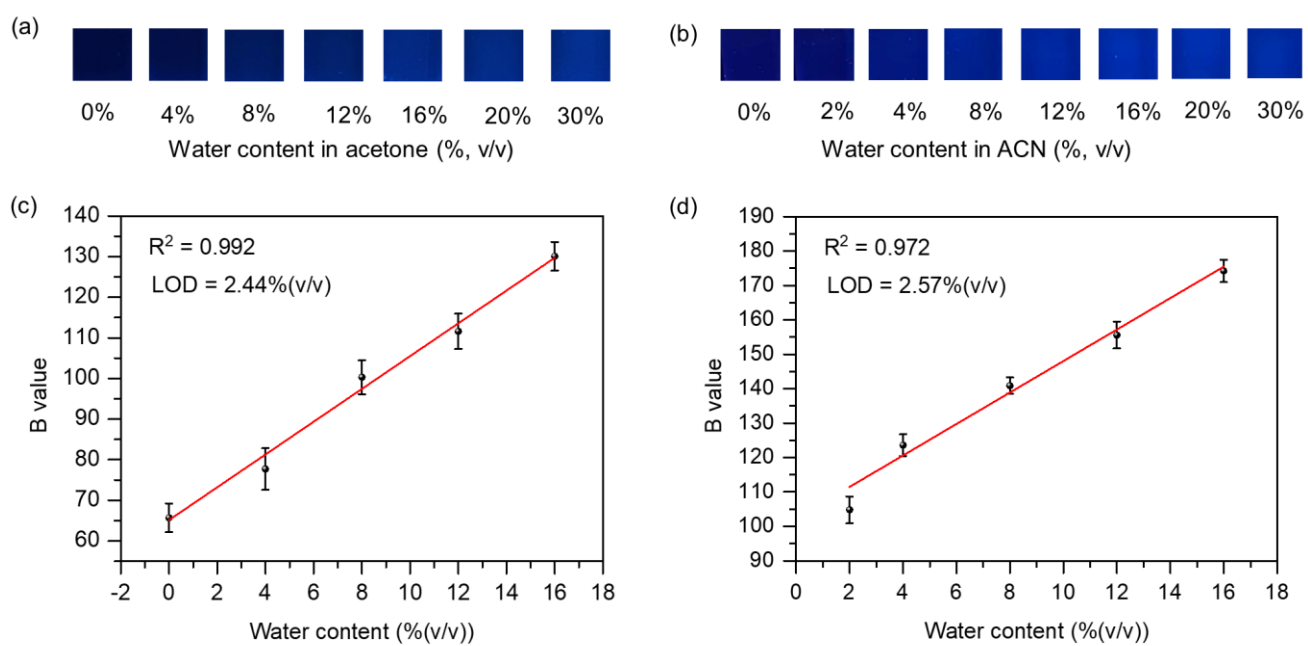


Figure S7 The digital images of fluorescence change of CDs@HKUST-1 with different water contents in (a) acetone and (b) ACN under UV light (365 nm). Linear relationship between B value and water contents in (c) acetone and (d) ACN.

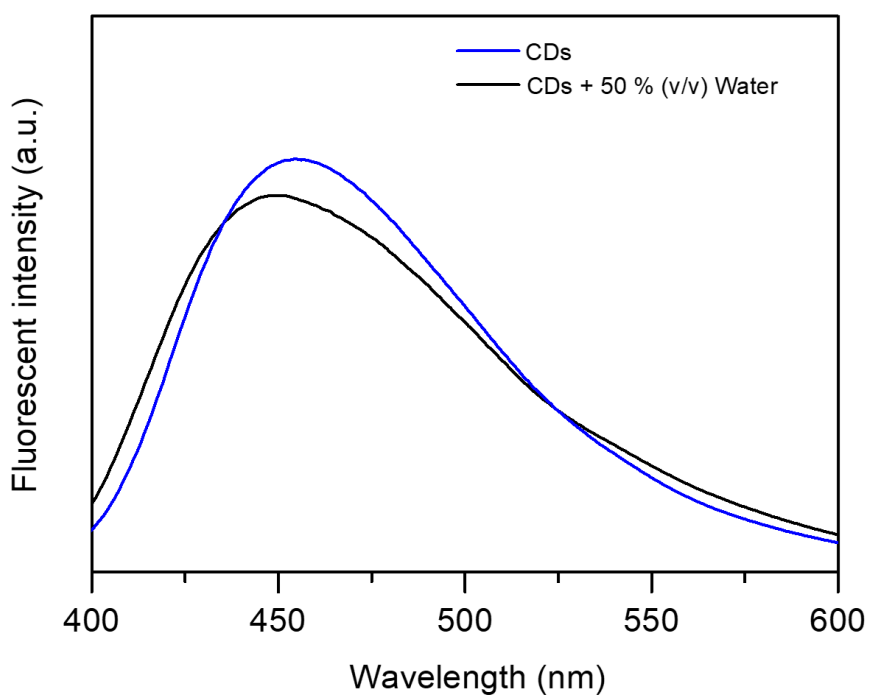


Figure S8 Fluorescent spectra of untreated CDs (blue line) and treated CDs with water (black line).

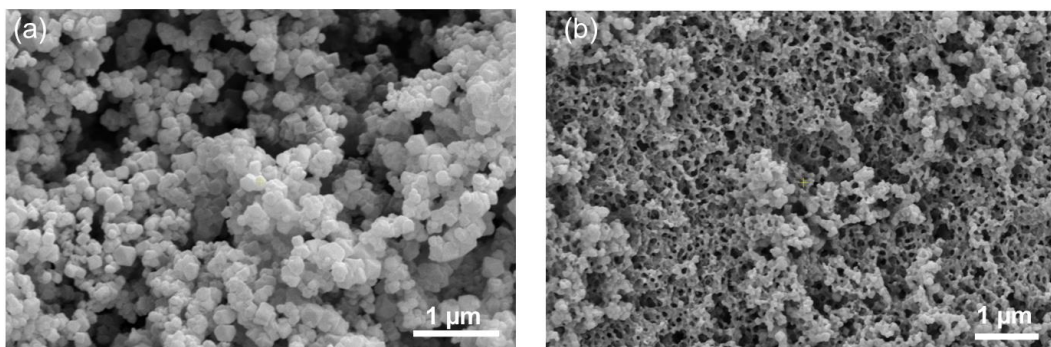


Figure S9 SEM images of (a) untreated CDs@HKUST-1 and (b) treated CDs@HKUST-1 with water.

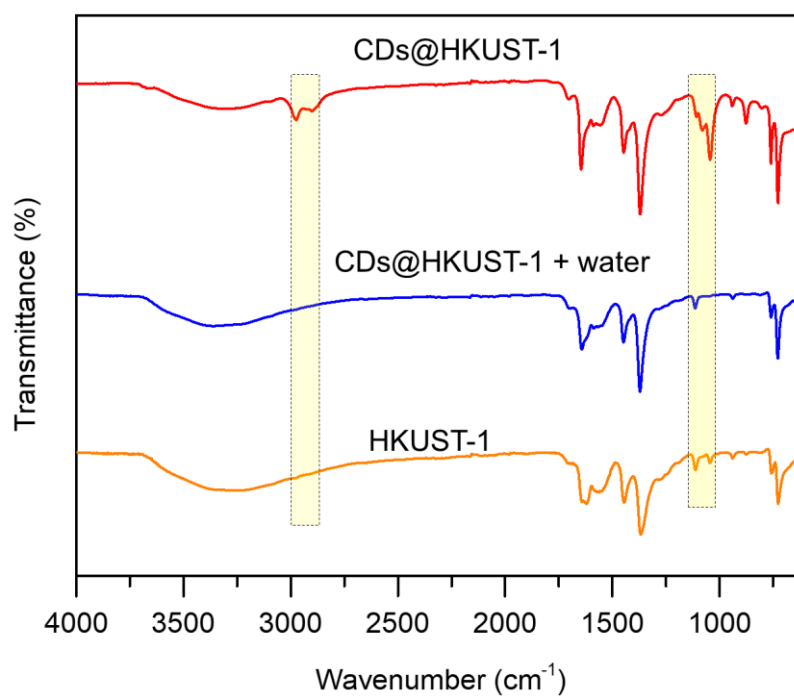


Figure S10 FT-IR spectrum of HKUST-1 and CDs@HKUST-1 before and after treatment with water.

Table S2 Calculation of LOD of CDs@HKUST-1 for water in ethanol

Blank reading	Fluorescent intensity at 450 nm
1	14630.327
2	14050.346
3	14000.756
4	14590.041
5	14300.003
6	14620.382
7	14408.012
Standard deviation (σ)	246.0342
Slope from linear equation (S)	1053.335
LOD = $3\sigma/S$	0.70 %v/v

Table S3 Comparison of the performance of fluorescent sensor of water based on MOFs

MOFs	Media	LOD (%v/v)	Detection range (%v/v)	Detection method	Ref.
Tb ³⁺ @p-CDs/MOF	DMF	0.33	0-30	Turn-off	1
Tb _{97.11} Eu _{2.89} -L1	ACN	0.04	0-2.5	Turn-off	2
MOF@Fe ₃ O ₄ /SiO ₂	Hexane	0.03	0-10	Turn-off	3
Eu ³⁺ @UiO-66- NH ₂ -IM	Ethanol	0.05	0-2	Turn-off	4
Eu _{0.02} Dy _{0.18} -MOF	Ethanol	0.1	0-0.3	Turn-off	5
AEMOF-1	THF	0.05	0-2	Turn-on	6
[Cd(py)L(H ₂ O) ₂]	Iso-propanol	0.01	0-0.36	Turn-on	7
[Cd ₂ (4,5- <i>idc</i>)(2,5- <i>tpt</i>)(H ₂ O) ₄]	DMF	0.25	0-50	Shifted emission and turn-off	8
N,S-CDs@Eu-MOF	Ethanol	-	0.19-0.82	Ratiometric sensing	9
	ACN	-	0.3-2.2		
	DMF	-	0.5-2.5		
Zn-MOF74	Acetone	0.045	0-1.5	Turn-on	10
CDs@HKUST-1	Ethanol	0.70	0-70	Turn-on	This work
	ACN	0.59	2-12		
	Acetone	1.08	10-50		

Reference

- [1] Wang, K.-M.; Du, L.; Ma, Y.-L.; Zhao, J.-S.; Wang, Q.; Yan, T.; Zhao, Q.-H. Multifunctional Chemical Sensors and Luminescent Thermometers Based on Lanthanide Metal-Organic Framework Materials. *CrystEngComm*. 2016, 18, 2690-2700.
- [2] Zhao, D.; Yue, D.; Jiang, K.; Zhang, L.; Li, C.; Qian, G. Isostructural Tb³⁺/Eu³⁺ Co-Doped Metal-Organic Framework Based on Pyridine-Containing Dicarboxylate Ligands for Ratiometric Luminescence Temperature Sensing. *Inorg. Chem*. 2019, 58, 2637-2644.
- [3] An, R.; Zhao, H.; Hu, H.-M.; Wang, X.; Yang, M.-L.; Xue, G. Synthesis, Structure, WhiteLight Emission, and Temperature Recognition Properties of Eu/Tb Mixed Coordination Polymers. *Inorg. Chem*. 2016, 55, 871-876.

- [4] Li, H.; Han, W.; Lv, R.; Zhai, A.; Li, X.-L.; Gu, W.; Liu, X. Dual-Function Mixed-Lanthanide Metal-Organic Framework for Ratiometric Water Detection in Bioethanol and Temperature Sensing. *Anal. Chem.* 2019, 91, 2148-2154.
- [5] 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, 4268-4271.
- [6] Zhao, D.; Rao, X.; Yu, J.; Cui, Y.; Yang, Y.; Qian, G. Design and Synthesis of an MOF Thermometer with High Sensitivity in the Physiological Temperature Range. *Inorg. Chem.* 2015, 54, 11193-11199.
- [7] 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. *J. Am. Chem. Soc.* 2013, 135, 15559-15564.
- [8] Othong, J.; Boonmak, J.; Kielar, F.; Youngme S. Dual Function Based on Switchable Colorimetric Luminescence for Water and Temperature Sensing in Two-Dimensional Metal–Organic Framework Nanosheets. *ACS Appl. Mater. Interfaces* **2020**, 12 (37), 41776-41784.
- [9] Gao, J.P.; Yao, R.X.; Chen, X.H.; Li, H.H.; Zhang, X.M. Blue luminescent N,S-doped carbon dots encapsulated in red emissive Eu-MOF to form dually emissive composite for reversible anti-counterfeit ink. *Dalton Trans.* **2020**, 50, 1690–1696.
- [10] Zhang, Z.; Zhong, T.; Wang, G. Zn-MOF74 as a “turn-on” fluorescent chemosensor for recognition and detection of water in acetone and Al³⁺ in ethanol with high selectivity and sensitivity. *J. Photochem. Photobiol. A.* **2022**, 431, 114052.