Bifunctional color-tuning luminescent Ln@Zr-MOFs for white LEDs and sensitive, ultrafast detection of nitrobenzene in aqueous media

Mengmeng Cao[a], Chao Xia[b, *], Yunpeng Liu[a], Jinfeng Xia[c], Danyu Jiang[c], Guohong Zhou[c], Tongtong Xuan[d, *], Huili Li[a, *]

[a] *Engineering Research Center for Nanophotonics and Advanced Instrument, Ministry of Education, School of Physics and Electronic Science, East China Normal University, Shanghai 200241, China.*

[b] *Guangdong Provincial Key Laboratory of Biomedical Measurements and Ultrasound Imaging, Marshall Laboratory of Biomedical Engineering, School of Biomedical Engineering, Health Science Center, Shenzhen University, Shenzhen 518060, China.*

[c] *Key Laboratory of Transparent Optofunctional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P.R. China.*

[d] *College of Materials, Xiamen University, Xiamen 361005, Fujian, China.*

*Corresponding authors

E-mail: xiachao927@126.com (Dr. Chao Xia)

E-mail: ttxuan@xmu.edu.cn (Dr. Tongtong Xuan)

E-mail: hlli@phy.ecnu.edu.cn (Prof. Huili Li)

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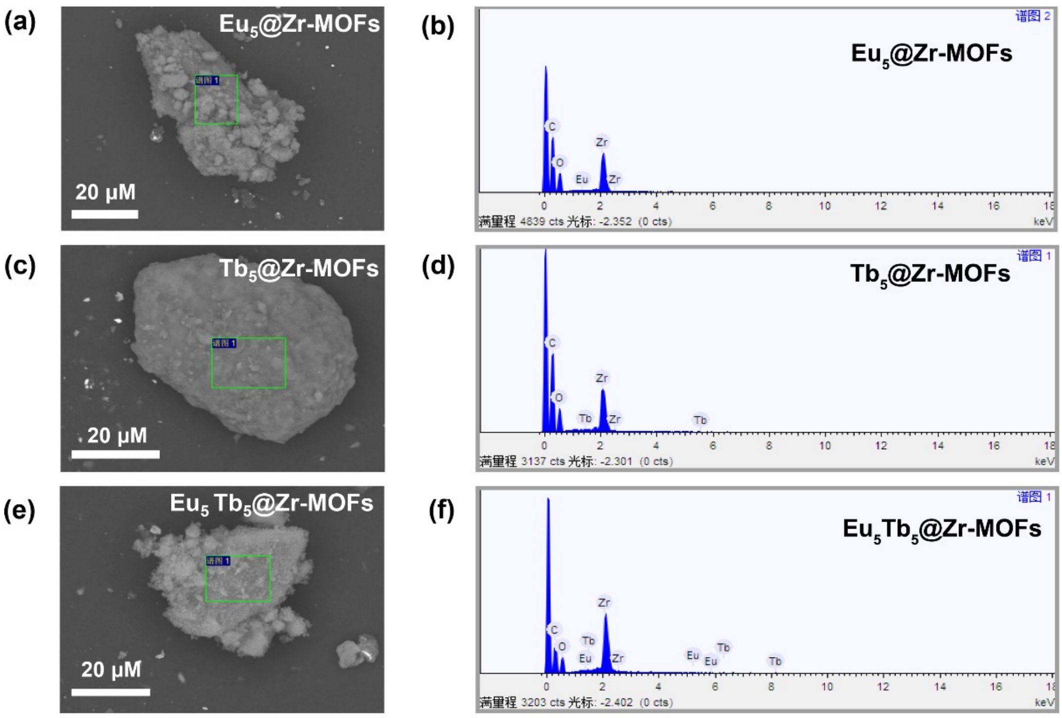

Figure S1 The SEM images and EDS spectra of Eu_5@Zr-MOFs (a, b), Tb_5@Zr-MOFs (c, d), and Eu_5Tb_5@Zr-MOFs (e, f).

Table S1 Every element content in Eu_5@Zr-MOFs, Tb_5@Zr-MOFs and Eu_5Tb_5@Zr-MOFs collected from EDS measurement.

	Eu_5@Zr-MOFs	Tb_5@Zr-MOFs	Eu_5Tb_5@Zr-MOFs
C	66.83	67.04	71.42
O	29.55	28.99	24.93
Zr	3.50	3.82	3.38
Eu	0.12	0	0.13
Tb	0	0.15	0.14

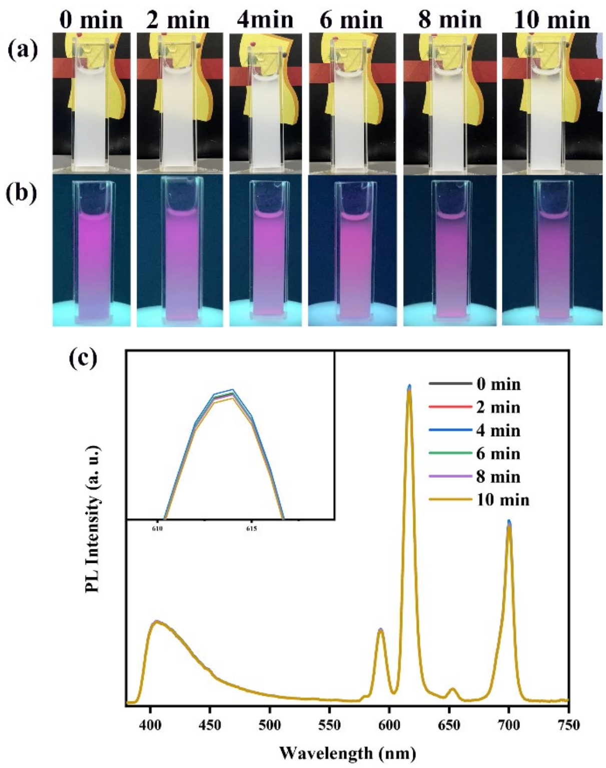

Figure S2 The photos of Eu_{10}@Zr-MOFs suspension under sunlight (a) and ultraviolet irradiation (b) as well as the corresponding emission spectra

(c) after being placed for different times.

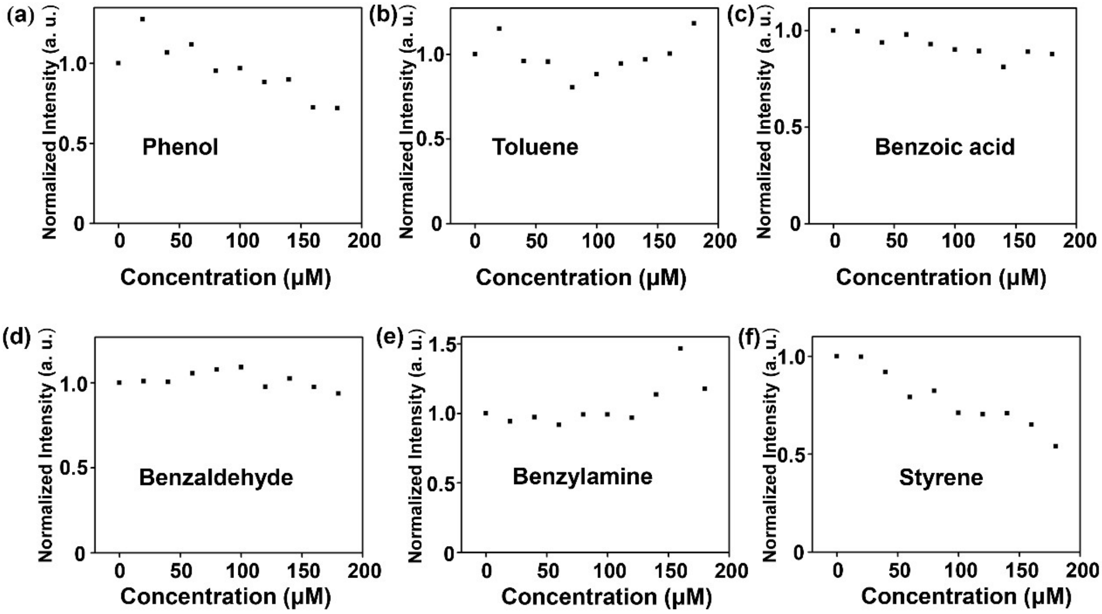

Figure S3 The variations of PL intensity for Eu_{10}@Zr-MOFs after adding different concentrations of phenol (a), toluene (b), benzoic acid (c), benzaldehyde (d), benzylamine (e), and styrene (f).

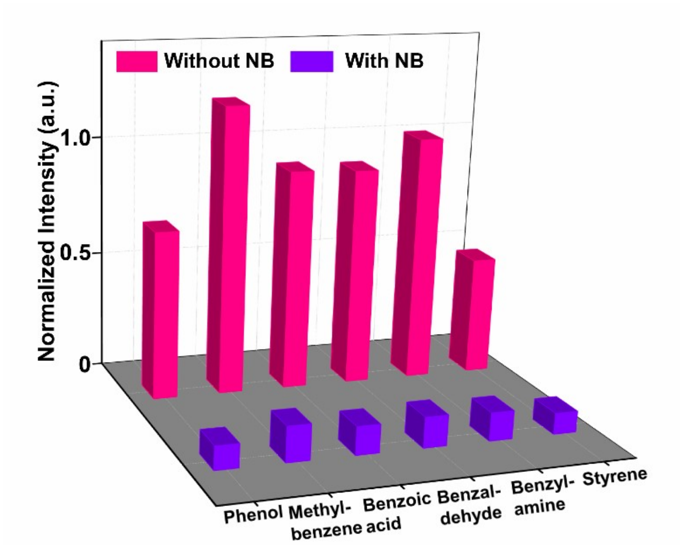

Figure S4 The luminescence intensity of Eu_{10}@Zr-MOFs suspension after adding other aromatic compounds with or without NB.

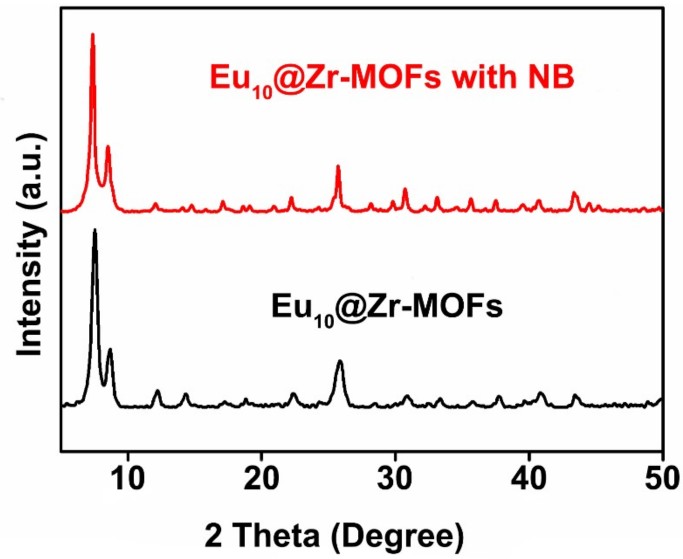

Figure S5 XRD patterns of Eu_{10}@Zr-MOFs before (black line) and after soaked in nitrobenzene solution for one day (red line).

Table S2 Performances of Ln-MOF probes for sensing NB reported in the literatures.

	K_{sv} (M^{-1})	LOD (μM)	LOQ (μM)	Refs.
$[Eu_3(bpydb)_3(HCOO)(\mu_3\text{-}OH)_2(H_2O)]$	21000	/	/	[1]
[Eu(L)1.5] n	62400	/	/	[2]
$\{[Eu_2(NSBPDC)_3(H_2O)_4]\cdot 7(H_2O)\}n$	65512	11.32	37.72	[3]
Eu-MOF	13260	~27.97 (3.44 ppm)	~93.22 (11.47ppm)	[4]
$\{[Ln_2(L2)_2(H_2O)_5]\cdot 3H_2O\}_n$ (Nd 1 and Eu 2)	1323	1.46	4.87	[5]
Tb-MOF	/	/	/	[6]
Eu_{10}@Zr-MOFs	24459.71	1.04	3.48	This work

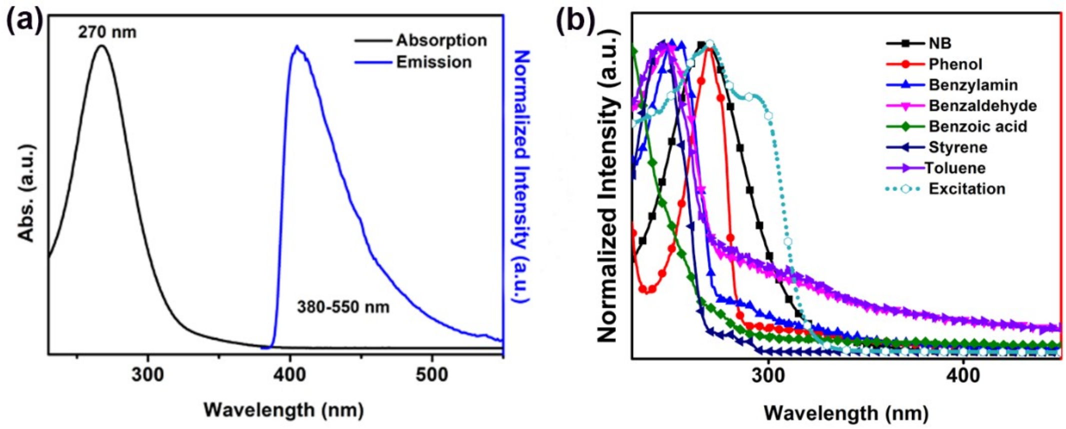

Figure S6 UV-vis absorption spectrum of NB (black line) and emission spectrum of m-H_2BDC ligands in Eu_{10}@Zr-MOFs (blue line) (a), comparison of UV-vis absorption spectra for phenol, benzine, benzaldehyde, benzoic acid, styrene, toluene and NB with excitation spectrum of Eu_{10}@Zr-MOFs (b).

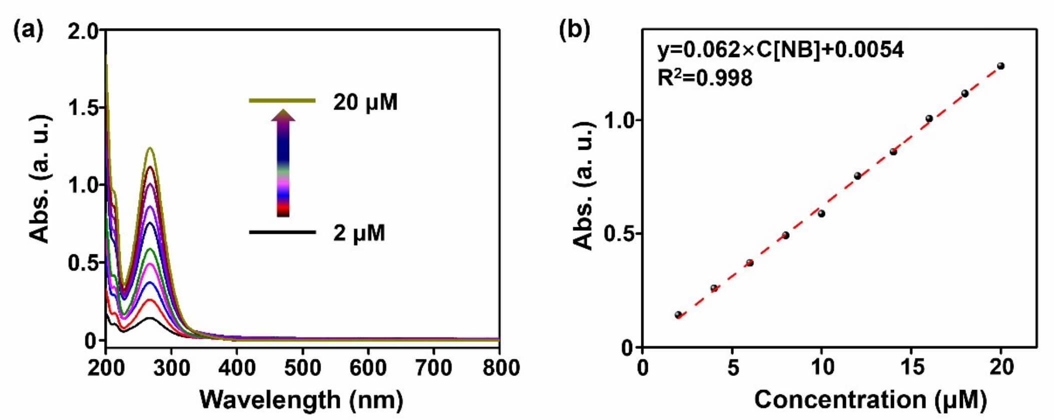

Figure S7 UV-vis absorption spectra of deionized water solutions doped with 2~20 μM NB (a) and the fitted standard curve (b).

Notes and references

1. X. Z. Song, S. Y. Song, S. N. Zhao, Z. M. Hao, M. Zhu, X. Meng, L. L. Wu and H. J. Zhang, Adv. Funct. Mater., 2014, 24, 4034-4041.
2. S. N. Zhao, X. Z. Song, M. Zhu, X. Meng, L. L. Wu, S. Y. Song, C. Wang and H. J. Zhang, RSC Adv., 2015, 5, 93-98.
3. L. L. Ren, Y. Y. Cui, A. L. Cheng and E. Q. Gao, J. Solid State Chem., 2019, 270, 463-469.
4. K. P. Bai, L. J. Zhou, G. P. Yang, M. X. Cao and Y. Y. Wang, ChemistrySelect, 2019, 4, 12794-12800.
5. Z. Sun, J. Sun, L. Xi, J. Xie, X. Wang, Y. Ma and L. Li, Cryst. Growth Des., 2020, 20, 5225-5234.
6. C. H. Zhan, D. P. Huang, Y. Wang, W. T. Mao, X. J. Wang, Z. G. Jiang and Y. L. Feng, CrystEngComm, 2021, 23, 2788-2792.