Electronic Supplementary Material (ESI) for Environmental Science: Nano. This journal is © The Royal Society of Chemistry 2024

Supporting Information

Portable visual assay of anthrax biomarker based on lanthanide coordination polymer nanoparticles and smartphone-integrated mini-device

Shengnan Yin^a*, Tianlun Xu^b

a, Institute for Advanced Study, Shenzhen University, Shenzhen 518060

b, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou,

310058, China

*Corresponding Author. E-mail: snyin0204@163.com

Table of contents

- 1. Figure S1 Particle size measured by DLS.
- 2. Figure S2 EDS spectra of LML-Tb³⁺-AMP NPs.
- 3. Figure S3 EDS mapping results of LML-Tb³⁺-AMP NPs.
- 4. **Figure S4** XRD pattern of LML-Tb³⁺-AMP NPs.
- 5. Figure S5 Optimization of experimental conditions.
- 6. **Figure S6** Schematic illustration of the fabrication and composition, and use of the portable detection device.
- 7. Figure S7 The RGB values recognized by smartphone APP.
- 8. Figure S8 SEM image and UV-vis spectra of LML-Tb³⁺- AMP/AG film.
- Table S1 The singlet and triplet energy levels of DPA and the lowest emission level of Tb³⁺.
- Table S2 Comparison in the sensitivity performance for DPA detection between the proposed method and the previously reported methods.
- 11. Table S3 Determination of DPA in real samples.
- 12. **Table S4** Comparison in the sensitivity performance for DPA detection between the proposed method and the previously reported smartphone-based sensing method.



Figure S1 Particle size measured by DLS



Figure S2 EDS spectra of LML-Tb³⁺-AMP NPs

Figure S3 EDS mapping results of LML-Tb³⁺-AMP NPs. (A) O, (B) P, (C) C, (D) Tb,

(E) N, (F) SEM image of LML-Tb³⁺-AMP NPs.

Figure S4 XRD pattern of LML-Tb³⁺-AMP NPs.

Figure S5 (A) Effect of pH on the fluorescence ratio (F_{545}/F_{425}) of LML-Tb³⁺-AMP in the absence and presence of DPA. (B) Effect of equilibrium time on the fluorescence ratio (F_{545}/F_{425}) in the LML-Tb³⁺-AMP system.

Figure S6 Schematic illustration of the (A) fabrication and composition, and (B) use of the portable detection device.

Figure S7 The RGB values recognized by smartphone APP (A and B) (the photograph

was taken under 254 nm UV lamp).

Figure S8. (A) SEM image of LML-Tb³⁺- AMP/AG film. (B) UV-vis spectra of LML-Tb³⁺- AMP/AG film. Inset: Image of the hydrogel sensor.

Table S1 The singlet and triplet energy levels of DPA and the lowest emission level of Tb^{3+} .

Sensitizer	$S_1(cm^{-1})$	$T_1(cm^{-1})$	ΔE_{ST} (cm ⁻¹)	ΔE_{TD-Tb} (cm ⁻¹)	$Tb^{3+}(^{5}D_{4}, cm^{-1})$
DPA	32722.6	26364.5	6358.1	5864.0	20500.5

The lowest emission levels of Ln³⁺ were obtained from ref.^[1]

S₁: Lowest excited singlet; T₁: Lowest excited triplet; ΔE_{ST} : The energy gap between S₁ and T₁; ΔE_{TD-Tb} : the energy differences between the lowest triplet excited state of sensitizer and the emission levels of Tb³⁺.

Sensing system	Mode	Linear range (µM)	LOD (nM)	Ref.
Tb ³⁺ -GMP-Eu ³⁺	Ratiometric	2-16	96	[1]
His@ZIF-8/Tb ³⁺	Turn-on	0-10	20	[2]
EBT @ CDs/Eu ³⁺	Ratiometric	0.5-110	10.6	[3]
Tb ³⁺ @ UIO-67	Ratiometric	0.3–6	36	[4]
$Fe_{3}O_{4} @ Tb^{3+}$	Turn-on	0-1	5.4	[5]
R6G/Eu-CdS@ZIF-8	Ratiometric	0.1-150	67	[6]
Tb/Eu -BTC	Ratiometric	0.05-3	4.9	[7]
g-C ₃ N ₄ -Eu ³⁺ -Cit	Ratiometric	0.1-15	13	[8]
LML-Tb ³⁺ -AMP	Ratiometric	0.01–10	3.4	This work

 Table S2 Comparison in the sensitivity performance for DPA detection between the

 proposed method and the previously reported methods.

Samples	Added	Found (µM)	Recovery (%)	RSD (%)
Lake water 1	0.00	ND^{a}		
	0.50	0.51	110.0	2.8
	5.00	5.12	103.7	0.4
Lake water 2	0.00	ND ^a		
	0.50	0.49	97.9	1.6
	5.00	5.01	100.2	0.8

Table S3 Determination of DPA in real samples

^a Not detected.

Sensing system	Mode	Linear range	LOD	Ref.
EBT @ CDs/Eu ³⁺	Ratiometric	0-12µM	0.68µM	[3]
g-C ₃ N ₄ -Eu ³⁺ -Cit	Ratiometric	0-20μΜ	2.5µM	[8]
ТЬ-РТА-ОН	Ratiometric	0-40 µM	0.48µM	[9]
Tb-GSH-CuNCs	Turn-on	0.5-70µM	0.5µM	[10]
Tb ³⁺ @JUC-505	Turn-on	0-100μΜ	2.17µM	[11]
HAp:Tb-EDTA	Ratiometric	0.1-500 μΜ	0.5µM	[12]
UiO-66-NH ₂ /Eu	Ratiometric	0-35µM	0.52µM	[13]
Eu-MOF@Tb	Ratiometric	_	2μΜ	[14]
LML-Tb ³⁺ -AMP	Ratiometric	0–100 µM	0.24µM	This work

Table S4 Comparison in the sensitivity performance for DPA detection between the

 proposed method and the previously reported smartphone-based sensing method.

References

[1] N. Gao, Y. F. Zhang, P. C. Huang, Z. H. Xiang, F. Y. Wu and L. Q. Mao, Perturbing

tandem energy transfer in luminescent heterobinuclear lanthanide coordination polymer

nanoparticles enables real-time monitoring of release of the anthrax biomarker from bacterial pores, *Anal. Chem.*, 2018, **90**, 7004–7011.

[2] L. Guo, M. Liang, X. Wang, R. Kong, G. Chen, L. Xia, and F, Qu, The role of lhistidine as molecular tongs: a strategy of grasping Tb³⁺ using ZIF-8 to design sensors for monitoring an anthrax biomarker on-the-spot, *Chem. Sci.*, 2020, **11**, 2407-2413.

[3] Q. Zhou, Y. Fang, J. Li, D. Hong, P. Zhu, S. Chen and K. Tan, A design strategy of dual-ratiomentric optical probe based on europium-doped carbon dots for colorimetric and fluorescent visual detection of anthrax biomarker, *Talanta*, 2021, **222**, 121548.

[4] X. Zhang, W. Zhang, G. Li, Q. Liu, Y. Xu and X. Liu, A ratiometric fluorescent probe for determination of the anthrax biomarker 2,6-pyridinedicarboxylic acid based on a terbium(III)–functionalized UIO-67 metal-organic framework, *Microchim. Acta*, 2020, **187**, 122.

[5] T. M. Koo, M. J. Ko, B. C. Park, M. S. Kim and Y. K. Kim, Fluorescent detection of dipicolinic acid as a biomarker in bacterial spores employing terbium ion-coordinated magnetite nanoparticles, *J. Hazard. Mater.*, 2021, **408**, 124870.

[6] X. Q. Li, J. J. Luo, L. Deng, F. H. Ma and M. H. Yang, In situ incorporation of fluorophores in zeolitic imidazolate framework-8 (ZIF-8) for ratio-dependent detecting

a biomarker of anthrax spores, Anal. Chem., 2020, 92, 7114-7122.

[7] M. Wu, Z. W Jiang, P. Zhang, X. Gong and Y. Wang, Energy transfer-based ratiometric fluorescence sensing anthrax biomarkers in bimetallic lanthanide metalorganic frameworks, *Sensor Actuat. B-Chem.*, 2023, **383**, 133596.

[8] M. Yuan, Y. Jin, L. Yu, Y. M. Bu, M. T. Sun, C. Yuan and S. H. Wang. Europiummodified carbon nitride nanosheets for smartphone-based fluorescence sensitive recognition of anthrax biomarker dipicolinic acid, *Food Chem.*, 2023, **398**, 133884.

[9] L. Yu, L. X. Feng, L. Xiong, S. Li, S. Wang, Z. Y. Wei and Y. X. Xiao, Portable visual assay of Bacillus anthracis biomarker based on ligand-functionalized dualemission lanthanide metal-organic frameworks and smartphone-integrated minidevice, *J. Hazard. Mater*, 2022, **434**, 128914.

[10] S. Pu, C. Shi, C. Lv, K. Xu, X. Hou and L. Wu, Tb³⁺-based off-on fluorescent platform for multicolor and dosage-sensitive visualization of bacterial spore marker, *Anal.Chem.*, 2023, **95**, 8137-8144.

[11] Y. Liu, M. Wang, Y. Hui, L. Sun, Y. Hao, H. Ren, H. Guo and W. Yang, Polyarylether-based COFs coordinated by Tb³⁺ for the fluorescent detection of anthraxbiomarker dipicolinic acid, *J. mater. Chem. B*, 2023, DOI: 10.1039/d3tb02070c. [12] C. Lv, S. Pu, L. Wu and X. Hou, Self-calibrated HAp:Tb-EDTA paper-based probe with dual emission ratio fluorescence for binary visual and fluorescent detection of anthrax biomarker, *Talanta*, 2024, **266**, 124979.

[13] P. Huo, Z. Li, R. Yao, Y. Deng, C. Gong, D. Zhang, C. Fan and S. Pu, Dual-ligand lanthanide metal–organic framework for ratiometric fluorescence detection of the anthrax biomarker dipicolinic acid, *Spectrochim Acta A*, 2022, **282**, 121700.

[14] Y. Xu, X. Shi, F. Ran, Z. Zhang, J. Phipps, X. Liu and H. Zhang, Differential sensitization toward lanthanide metal–organic framework for detection of an anthrax biomarker, *Microchim. Acta*, 2022, **190**, 27.