Dual-mode sensing platform for detection of multiple metal ions based on amine-functionalized MIL-101 (Fe) cascade Y-Shaped DNAzyme-assisted fluorescence and colorimetric analysis

A. Ravikumar[1], Emmanuel Chigozie Aham[1, 2, 3], Hui meng[1], Sanwal Aslam[1], A. Arunjegan[1], G. Tamilselvan[1], A. Anand babu Christus[4], Zhen Zhang[1*], Hongjun Zhao[5,6*]

[1]School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China.

[2]Department of Biochemistry, Faculty of Biological Sciences, University of Nigeria, Nsukka, Nigeria.

[3]Natural Science Unit, School of General Studies, University of Nigeria, Nsukka, Nigeria.

[4]Department of Chemistry, SRM Institute of Science and Technology, Ramapuram Campus, Chennai-600089, Tamil Nadu, India.

[5]Zhejiang Province Engineering Research Center for Endoscope Instruments and Technology Development, Clinical Research Centre, Department of Pulmonary and Critical Care Medicine,

[6]Quzhou People's Hospital, The Quzhou Affiliated Hospital of Wenzhou Medical University, 100 Minjiang Ave, Quzhou 324000, China.

*Corresponding author:

Email: zhangzhen@ujs.edu.cn; zhaohj_1980@163.com

Fax: +86-511-88790955

Preparation of Fe$_3$O$_4$ nanoparticles

3.6g of Sodium acetate and 1.35g of FeCl$_3$.6H$_2$O were dissolved in ethylene glycol (40 mL) with continuous stirring for 30 min, after 30 min stirring the colour will be change the yellow. The obtained yellow solution was transferred to Teflon-lined stainless-steel autoclave and heated at 200 °C for 8 h. The obtained brownish colour products washed with several times used ethanol and water and then dried in a hot air oven at 60°C at overnight.

Synthesis of Fe$_3$O$_4$@ SiO$_2$

1 mg of Fe$_3$O$_4$ nanoparticles was completely dispersed in 10 mL of ethanol solution, the mixture was sonicated for half an hour. 3 ml of tetraethyl orthosilane (TEOS) was added, and pH was adjusted to upto 10 by addition of ammonium hydroxide and the mixture was stirred for 24 hours. The obtained Fe$_3$O$_4$@SiO$_2$ were separated by centrifugation and several times washed with ethanol and distilled water and dried for overnight at 60°C.

(a)

500 nm

(b)

1 μm

(c)

Fe$_3$O$_4$-SiO$_2$
Fe$_3$O$_4$

Transmittance (%)

Wavenumber (cm^{-1})
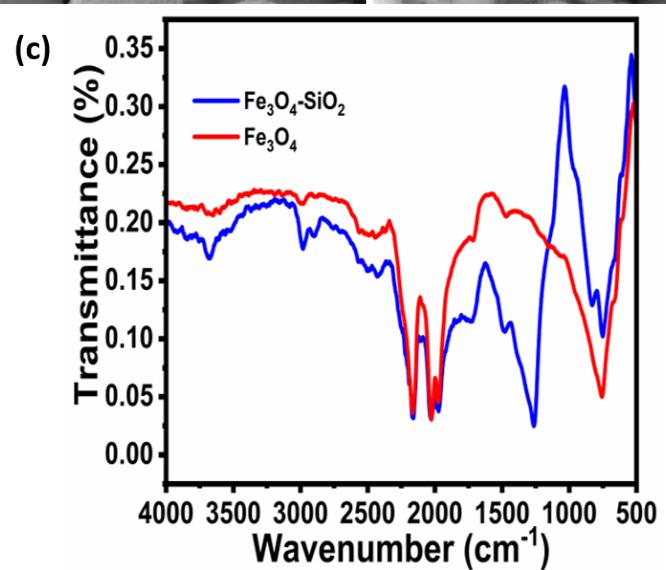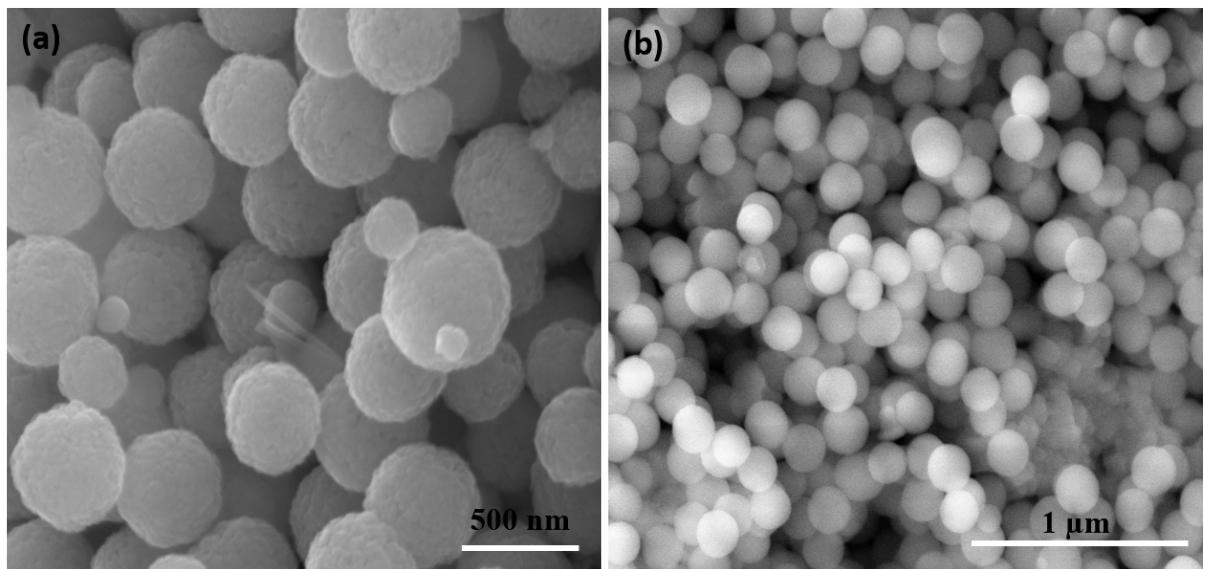
Figure S1. (a) SEM images of Fe_3O_4; (b) SEM images of $Fe_3O_4@SiO_2$; (c) FT-IR spectra of Fe_3O_4 and $Fe_3O_4@SiO_2$;
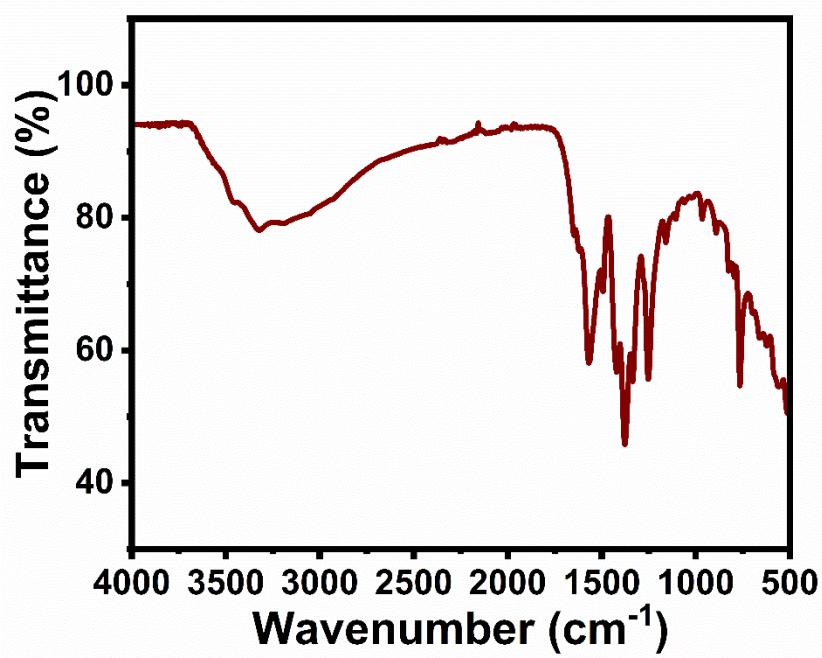
Figure S2. FTIR spectra of NH_2-MIL-101 (Fe).
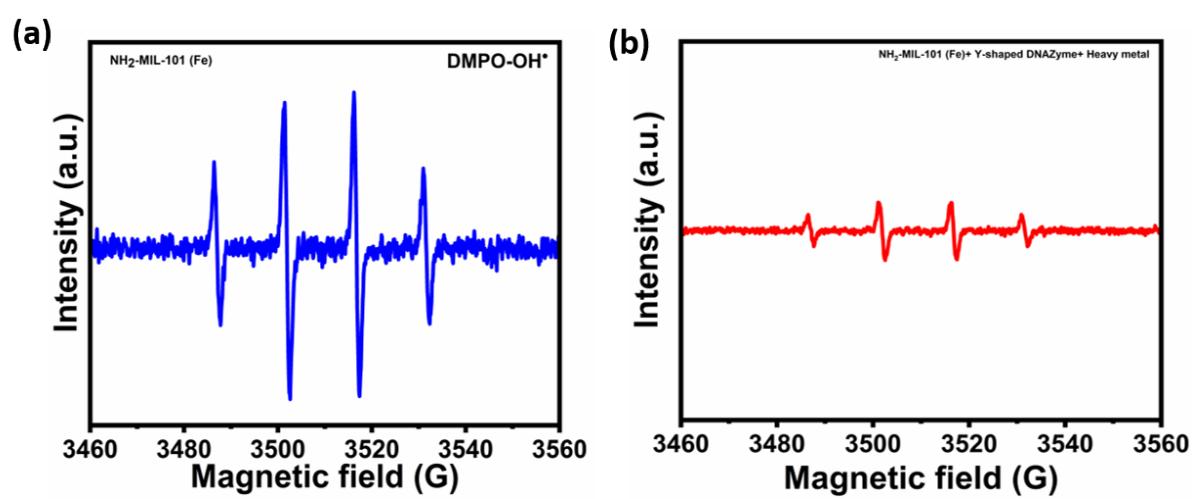
Figure S3. EPR spectra of NH_2-MIL-101 (Fe) and NH_2-MIL-101 (Fe)+Y-Shaped DNAzyme with heavy metals.
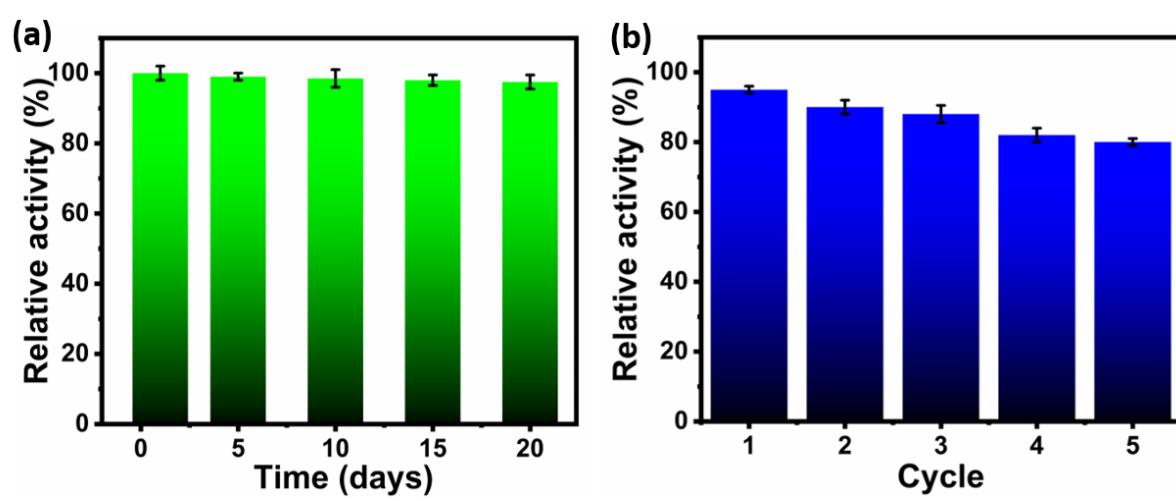
Figure S4. The stability and reproducibility analysis of NH$_2$-MIL-101 (Fe).
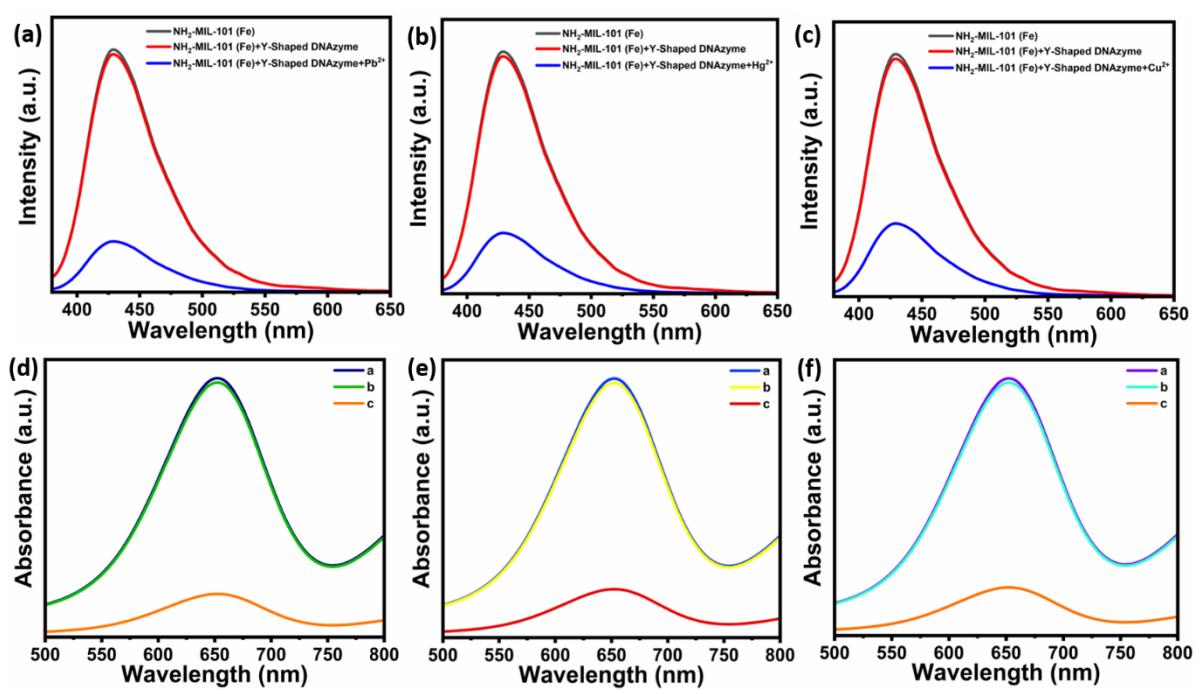
Figure S5. (a, b, c) Fluorescence intensity of Pb^{2+}, Hg^{2+} and Cu^{2+} ions in various conditions; (d, e, f) UV absorbance intensity of Pb^{2+}, Hg^{2+} and Cu^{2+} ions in various conditions [a- NH_2-MIL-101(Fe), b- NH_2-MIL-101(Fe) and Y-shaped DNAzyme, c- NH_2-MIL-101(Fe), Y-shaped DNAzyme and target metal ions].
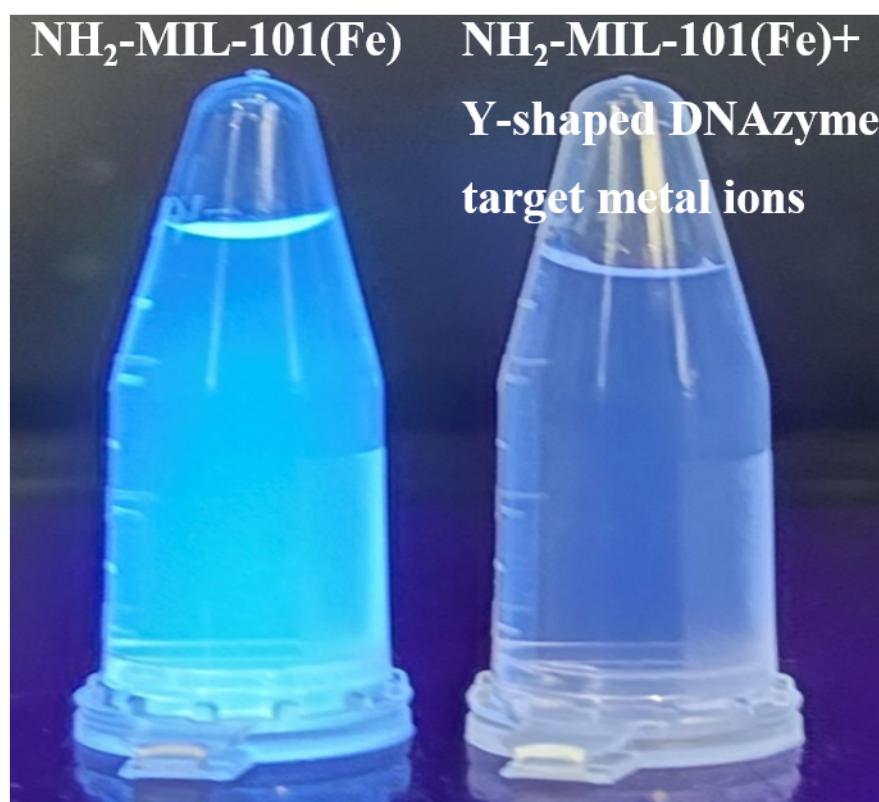
Figure S6. Photo images of without metal ions and with metal ions in NH2-MIL-101 (Fe)+Y-shaped DNAzyme.
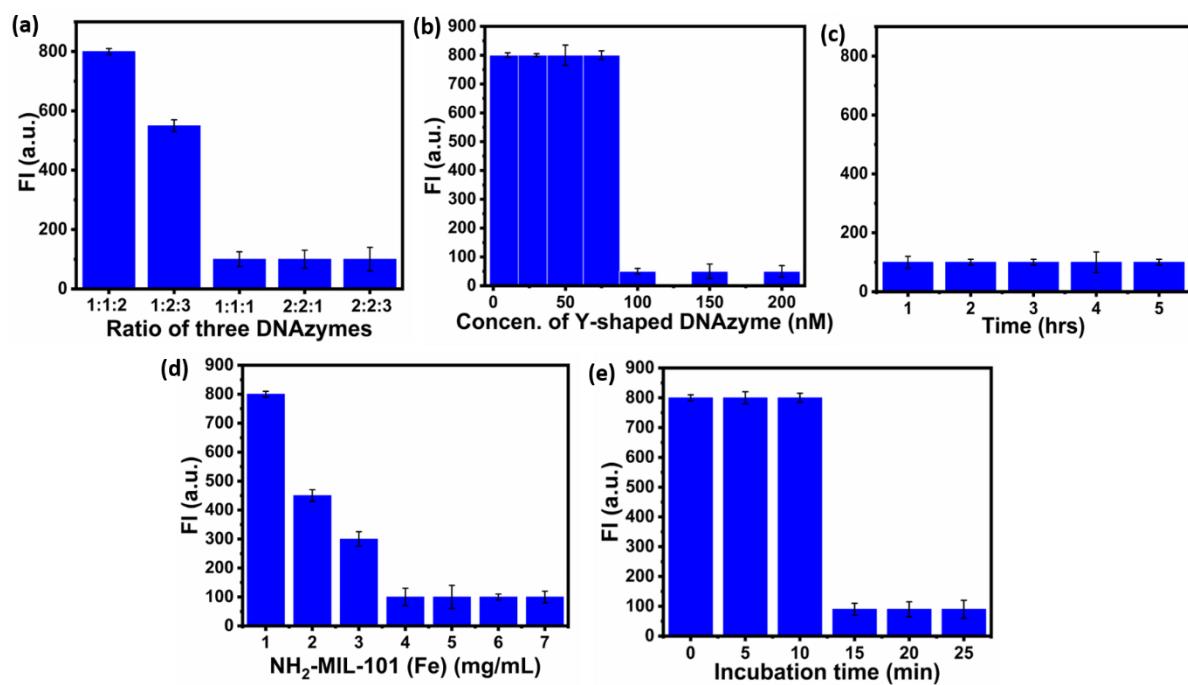
Figure S7. Optimization of reaction condition of NH$_2$-MIL-101 (Fe) on fluorescence intensity. (a) Ratio of three DNAzyme; (b) Concentration of Y-shaped DNAzyme; (c) Stability for Y-shaped dNAzyme; (d) Concentrations of NH$_2$-MIL-101 (Fe): (e) Incubation time. The error bars are standard deviations obtained from three independent measurements.
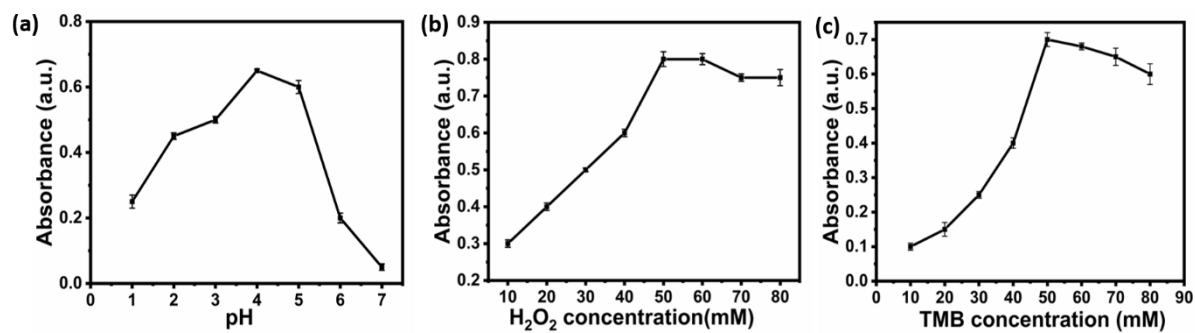
Figure S8. Optimization of reaction condition of peroxidase like activity of NH$_2$-MIL-101 (Fe). (a) Effect of reaction pH; (b) H$_2$O$_2$ concentration; (c) and TMB concentration.
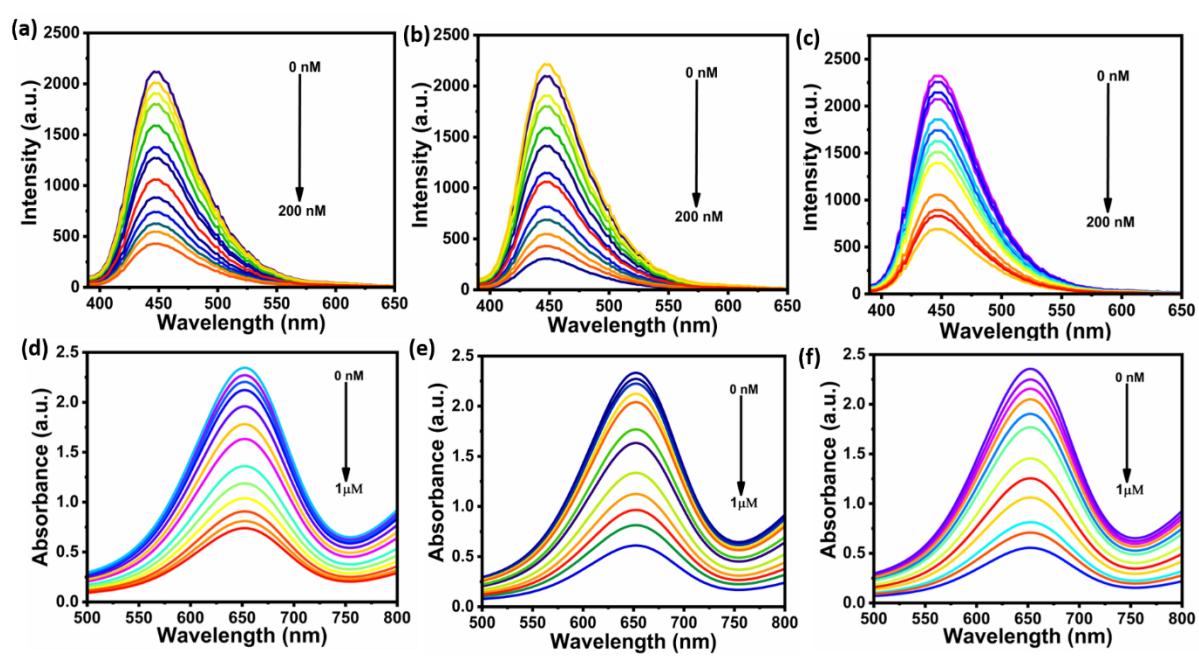
Figure S9. (a, b, c) Fluorescence spectra of NH$_2$-MIL-101 (Fe) in the presence of different concentration of Pb^{2+}, Hg^{2+} and Cu^{2+} ions. (d, e, f) Colorimetric spectra of NH$_2$-MIL-101 (Fe) in the presence of different concentration of Pb^{2+}, Hg^{2+} and Cu^{2+} ions.

**Table S1.** Comparison of the proposed method and the current dual-mode assays for detection of Pb^{2+}, Hg^{2+} and Cu^{2+} ions.

Metal ions	Methods	Materials	Linear range	Detection limit	Ref.
Pb^{2+}	Fluorescence/ Colorimetry	G-quadruplex-hemin complex	1.5-20 nM/0.5-10 nM	1.29/0.16 nM	1
	Electrochemical /colorimetry	AuNCs@COFs	0.01-5000/1-1000 nM	7.9/560 nM	2
	Fluorescence/ Colorimetry	Rh6G	0.05-6/1-5 nM	20/25 nM	3
	Fluorescence/ Colorimetry	Ti$_3$C$_2$@PtPd NPs	0.1-1/0.5-1 nM	23/74 nM	4
	Fluorescence/ Colorimetry	Y-shaped DNAzyme/NH$_2$-MIL-101 (Fe)	0-200 nM	0.21/0.43 nM	This work
Hg^{2+}	Fluorescence/ Colorimetry	ZGO:Mn NRs	5 to 400 μM	0.215/0.225 μM	5
	Fluorescence/ Colorimetry	R6G-NH$_2$	5-300/1-200 μM	1.5/5.1 μM	6

	Method	Material	Linear range	LOD	Ref.
	Fluorescence/ Colorimetry	CDs/AuNCs	0-130 nM	6.5/3.7 nM	7
	Electrochemical/ Colorimetry	GO-AuNPs	10-60/0.001-60 μM	3.33 μM	8
	Fluorescence/ Colorimetry	Y-shaped DNAzyme/NH$_2$-MIL-101 (Fe)	0-200 nM	0.23/0.57 nM	This work
Cu^{2+}	Fluorescence/ Colorimetry	N/S CDs	5 to 400 μM	0.215/0.225 μM	9
	Fluorescence/ Colorimetry	GSH-AuNCs	1.0–10 μM	0.547/0.458 μM	10
	Fluorescence/ Colorimetry	Peptide	0-60 μM	1.42/2.64 nM	11
	Fluorescence/ Colorimetry	ZTM	0.1-5/5-50 μM	5.61/4.96 nM	12
	Fluorescence/ Colorimetry	Y-shaped DNAzyme/NH$_2$-MIL-101 (Fe)	0-200 nM	0.37/0.99 nM	This work

Table S2. Detection of Pb^{2+}, Hg^{2+} and Cu^{2+} ions added in real samples (n = 3).

Metal ions		Dual mode sensor		Recovery (%)		RSD (%)	
		FL	CL	FL	CL	FL	CL
Lake water	Pb^{2+}						
		1.02	1	102	100	2.4	2.2
	2	1.98	2.02	99	101	5.5	2.7
	3	2.9	3.12	96	104.	4.6	8.2
	Hg^{2+}	1	1.02	1.03	102	103	5	5.6
	2	2.1	1.91	105	95.5	3.4	4.3
	3	3.02	3.05	100.6	101	5.6	2.2
	Cu^{2+}	1	0.98	1.06	98	106	2.9	3.2
	2	2.05	2.14	102.5	107	1.1	3.7
	3	3.03	3.1	101	103	4.1	5.3
River water	Pb^{2+}	1	1	0.99	100	99	2	1.2
	2	2.04	2.12	102	106	3.4	1.9
	3	2.93	2.95	97.6	98.3	3.7	2.2
	Hg^{2+}	1	1.07	1.01	107	101	4.2	4.6
	2	2	1.98	100	99	3.4	4.2
	3	2.97	3.08	99	102	2.1	3.2
	Cu^{2+}	1	0.99	1.06	99	106	1.35	2.9
	2	1.9	2.05	95	102.5	8.9	1.1

| | 3 | 2.81 | 2.99 | 97 | 99.6 | 6.5 | 2.7 |

REFERENCES

1. T. Ye, H. Chen, L. Bai, M. Yuan, H. Cao, L. Hao, X. Wu, F. Yin, F. Xu, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2024, **309**, 123807.

2. L. Li, W. Zhao, Y. Wang, X. Liu, P. Jiang, L. Luo, T. You, *Journal of Hazardous Materials,* 2023, **457**,131558.

3. X. Xie, M. Pan, L. Hong, K. Liu, J. Yang, S. Wang, S. Wang, *J Agric Food Chem.* https://doi.org/10.1021/acs.jafc.1c02568.

4. Z. Suo, L. Zhang, Z. Zhang, R. Liang, H. Shen, X. Chen, Y. Liu, M. Wei, B. He, H. Jin, *Food Chemistry*, 2024, **12**, 141845.

5. M. Zhang, H. Yin, L. Wan, H. Gao, S. Liu, Y. Liu, *Carbon Letters,* 2024, **11**, 1-10.

6. Z. Li, S. Liang, C. Zhang, L. Zhou, F. Luo, Z. Lou, Z. Chen, X. Zhang, M. Yang, *Microchimica Acta,* 2024, **191(7)**, 423.

7. Y. An, L. Li, L. Li, Y. Sun, B. Li, P. Wang, *J. Hazard. Mater.,* 2024, **465**, 133192.

8. J. Hou, J. Pei, Y. Kairong, B. Tong, Z. Shuang, L. Longwen, W. Li, *ACS Appl. Mater. & Interfaces,* 2022, **14 (11)**, 13848-13857.

9. Y. Gao, J. Zhang, J. Guo, Z. Shao, Y. Ming, L. He, Q. Chen, K. Zhang, *Microchemical Journal,* 2024, **200**, 110492.

10. J. Chen, C. Zhang, L. Yi, F. Duan, Y. Gu, K. Ge, X. Fan, *Food Chemistry: X*, 2024, 101958.

11. H. Cai, Y. Shao, L. Yan, H. Yu, Q. Hu, Y. Wang, X. Tu, *Analytical Methods*, 2024, **11**, 45-49.

12. Q. Diao, Z. Bu, R. Feng, X. Chen, J. Liu, Z. Tang, H. Liang, Q. Tian, S. Li, X. Niu, *Sensors and Actuators B: Chemical,* 2025, **422**, 136598.