Electronic Supplementary Material (ESI) for Analytical Methods.

Metal-phenolic coordination frameworks nanozyme exhibits dual enzyme mimic activity and its application of effective colorimetric detection of biomolecules

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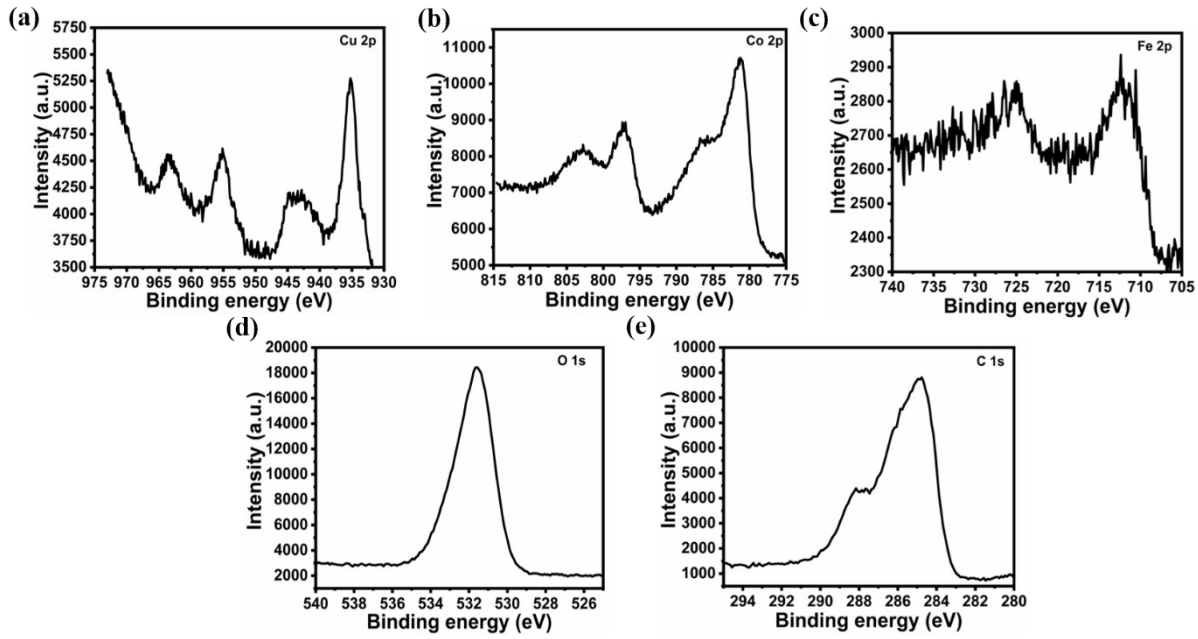

Figure S1 High-resolution XPS spectra of nanozymes showing Cu 2p, Co 2p, Fe 2p, O 1s and C 1s core energy levels.

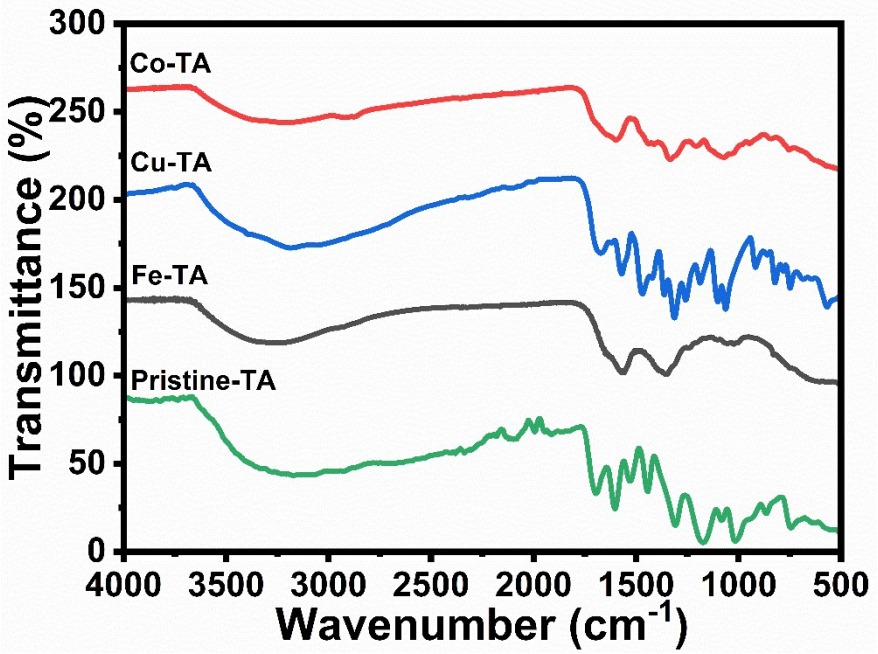

Figure S2 FT-IR spectra of Cu-TA, Co-TA, Fe-TA and Pristine-TA.

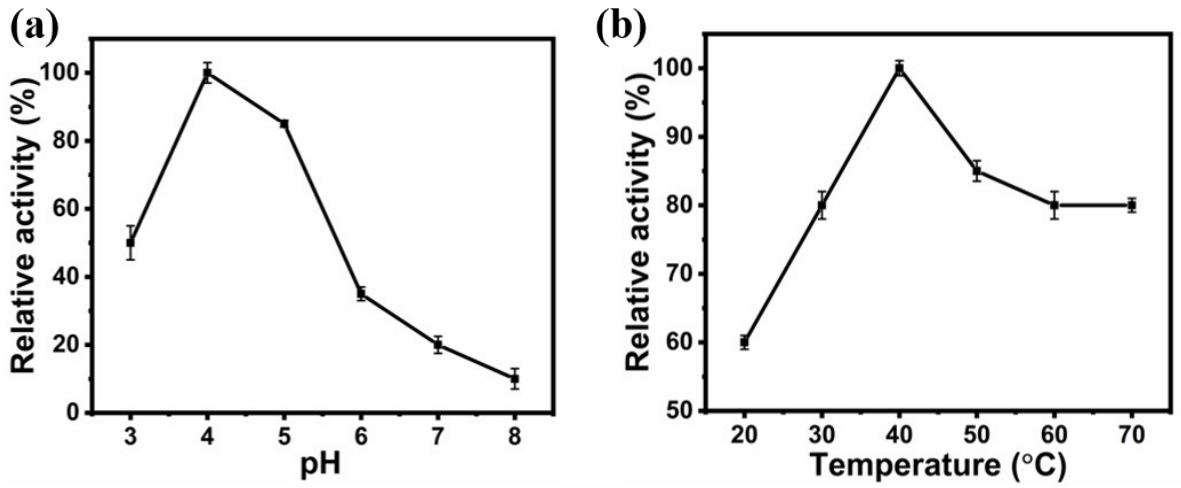

Figure S3 The effect of (a) pH and (b) temperature of the peroxidase and catalase activity of Fe-TA nanozyme.

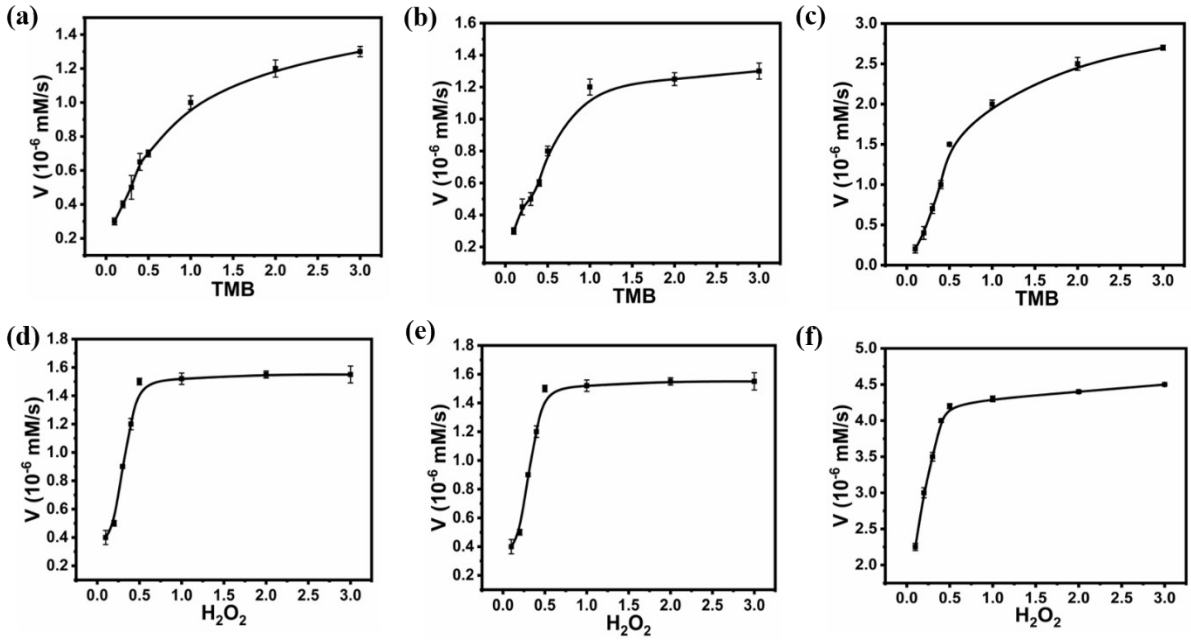

Figure S4 The Michaelis-Menten curves for different peroxidase-like nanozymes using H_2O_2 and TMB as substrates

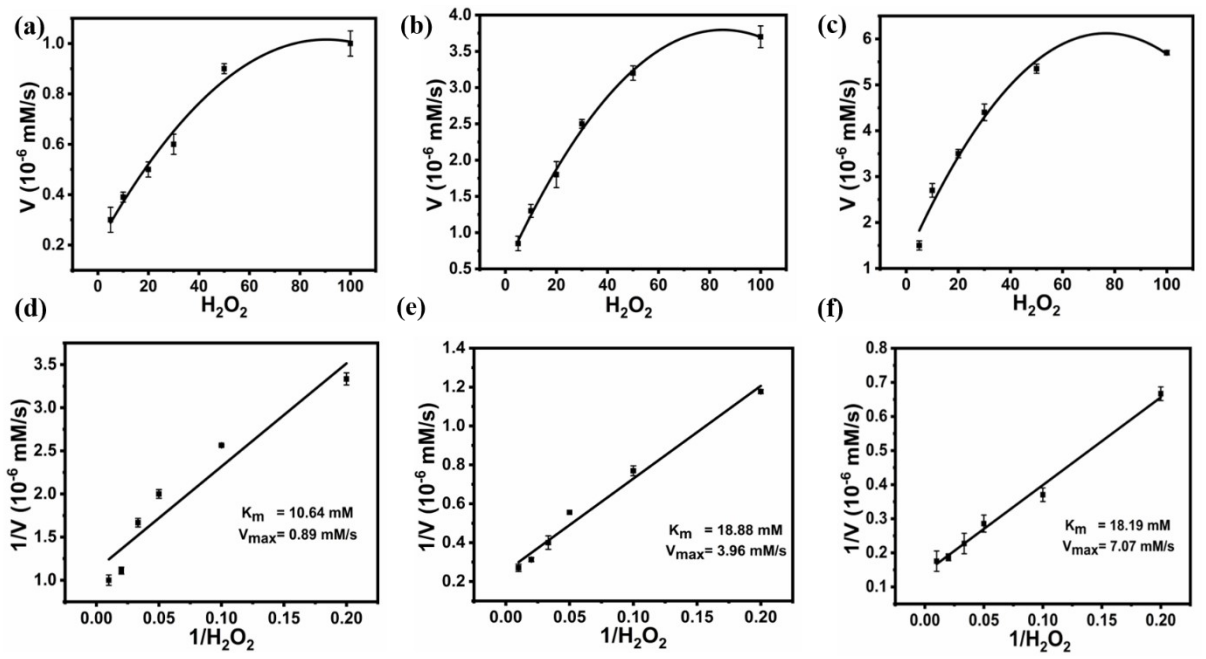

Figure S5 The Michaelis-Menten curves and double reciprocal plots for various catalase-like activities of nanozymes.

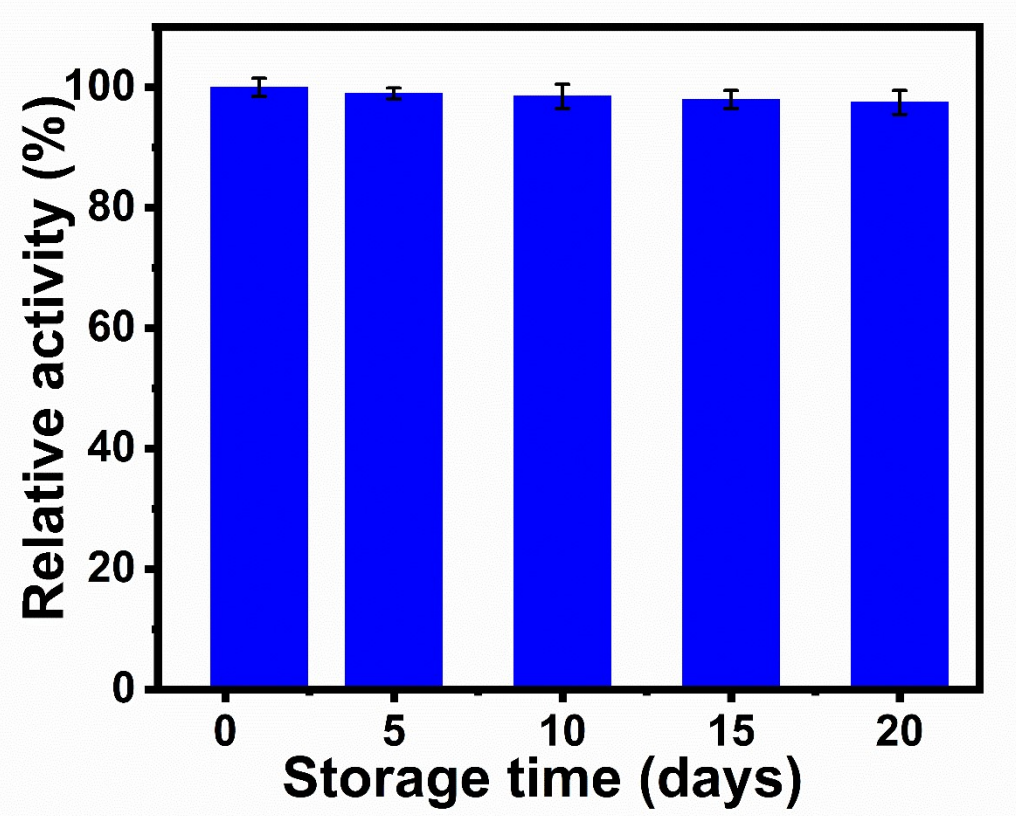

Figure S6 The remarkable stability of Fe-TA nanozyme after 21 days of storage.

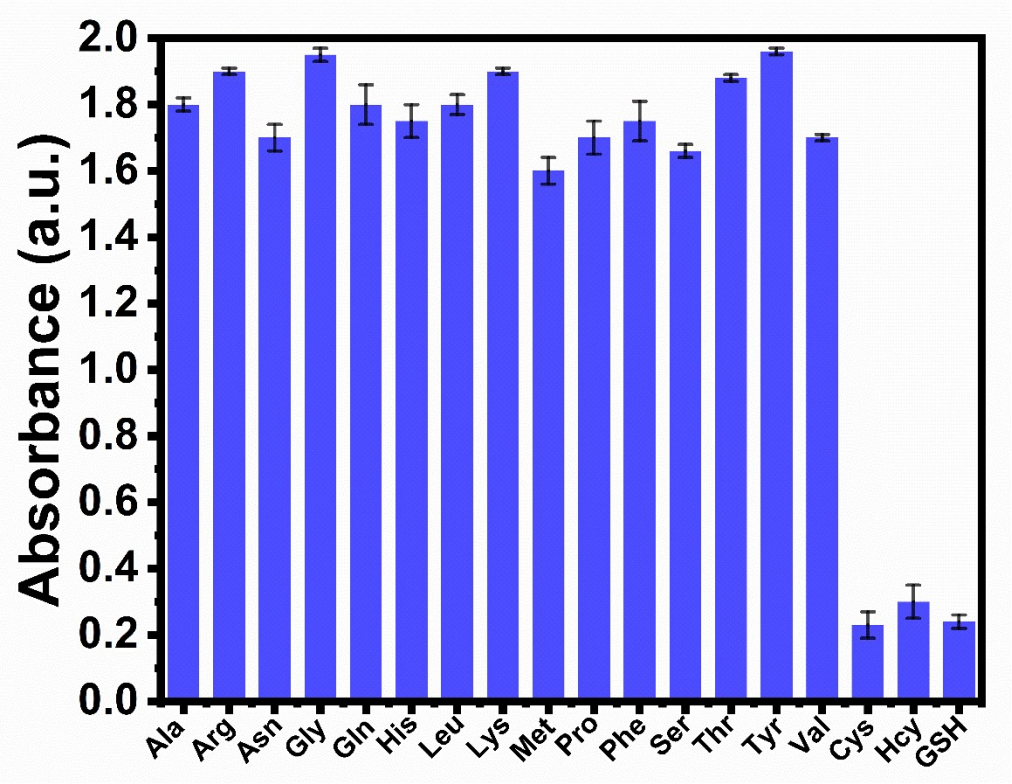

Figure S7 Selectivity performance of Fe-TA nanozyme in detecting Cys, Hcy and GSH in the presence of other possible interfering biomolecules.

Table S1 Comparison of the POD-like and CAT-like kinetic parameters of Cu-TA, Co-TA and Fe-TA nanozymes.

Enzyme mimic	MPNs	Substrate	K_m (mM)	V_{max} (Ms^{-1})
POD	Cu-TA	H_2O_2	0.261	2.04
		TMB	0.306	1.126
	Co-TA	H_2O_2	0.497	2.39
		TMB	0.248	1.251
	Fe-TA	H_2O_2	0.11	4.76
		TMB	0.348	1.651
CAT	Cu-TA	H_2O_2	10.64	0.89
	Co-TA	H_2O_2	18.88	3.96
	Fe-TA	H_2O_2	18.19	7.07

Table S2 Comparison of the linear ranges and LOD of Cys, GSH, and Hcy with previous studies.

	Materials	Method	Linear ranges (μM)	LODs (μM)	References
Cys	CeO_2/CoO	Colorimetry	5-10	3.71	[1]
	$CuMnO_2$	Colorimetry	20–300	11.26	[2]
	Pd–Fe_3O_4 DBNPs	Colorimetry	0-250	3.1	[3]
	Pt@WO_3NSs	Colorimetry	0.01–15	1.2	[4]
	$PdPt_3$-LNT NDs	Colorimetry	0–200	3.099	[5]
	Fe-TA	Colorimetry	1-2	0.382	This study
Hcy	AgNPRs	Colorimetry	0-5	0.041	[6]
	CB-CQDs	Colorimetry	0.5–20	0.6	[7]
	MnO_2 NFs-RhB	Colorimetry	0–30	0.087	[8]
	Fe^{3+}- TMB	Colorimetry	2–24	2.09	[9]
	Fe_3O_4@CuO-GO	Colorimetry	5–200	1.8	[10]
	Fe-TA	Colorimetry	2-3	0.776	This study
GSH	Hemin/GQD	Colorimetry	1-50	200	[11]
	Pd150-PCRP NPs	Colorimetry	2–300	1.65	[12]
	Fe_3O_4/CNDs	Colorimetry	0–20	0.058	[13]
	PCN-224-Mn	Colorimetry	0.5-60	0.233	[14]
	Mn_3O_4 microspheres	Colorimetry	5–60	0.889	[15]
	Fe-TA	Colorimetry	2-9	0.750	This study

Table S3 The performance of Fe-TA colorimetric sensor in spiked real water samples. (n=3)

Targets	Samples	Spiked (μM)	Found (μM)	Recovery±RSD (%)
Cys	Tap water	5	5.12	102.4±2.24
	River water	10	10.13	101.3±3.84
	Lake water	15	14.9	99.3±4.02
Hcy	Tap water	5	4.97	99.4±1.27
	River water	10	9.9	99±5.12
	Lake water	15	14.95	99.7±6.1
GSH	Tap water	5	5.02	100.4±1.98
	River water	10	9.93	99.3±3.14
	Lake water	15	15.2	101±3.55

REFERENCES

1 J. Lian, P. Liu, C. Jin, Q. Y. Liu, X. Zhang and X. Zhang, *ACS Sustainable Chemistry and Engineering*, 2020, **8**, 17540–17550.

2 Y. Chen, T. Chen, X. Wu and G. Yang, *Sensors and Actuators B: Chemical*, 2019, **279**, 374–384.

3 W. Duan, Z. Qiu, S. Cao, Q. Guo, J. Huang, J. Xing, X. Lu and J. Zeng, *Biosensors and Bioelectronics*, 2022, **196**, 113724.

4 A. Alaei, M. Hosseini, F. Nemati and H. Karimi-Maleh, *Environmental Research*, 2022, **212**, 113246.

5 Z. Ma, L. Dong, B. Zhang, B. Liang, L. Wang, G. Ma and L. Wang, *International journal of biological macromolecules*, 2022, **216**, 779–788.

6 P. Li, S. M. Lee, H. Y. Kim, S. Kim, S. Park, K. S. Park and H. G. Park, *Scientific Reports 2021 11:1*, 2021, **11**, 1–8.

7 C. Yuan, X. Qin, Y. Xu, X. Li, Y. Chen, R. Shi and Y. Wang, *Journal of Photochemistry and Photobiology A: Chemistry*, 2020, **396**, 112529.

8 H. Xue, M. Yu, K. He, Y. Liu, Y. Cao, Y. Shui, J. Li, M. Farooq and L. Wang, *Analytica Chimica Acta*, 2020, **1127**, 39–48.

9 M. Lin, Y. Guo, Z. Liang, X. Zhao, J. Chen and Y. Wang, *Microchemical Journal*, 2019, **147**, 319–323.

10 Z. Song, C. Jiang, F. Wang, L. Yu, S. Ye, P. Dramou and H. He, *Microchimica Acta*, 2021, **188**, 1–10.

11 Z. Li, X. Deng, X. Hong and S. Zhao, *Molecules 2022, Vol. 27, Page 6779*, 2022, **27**, 6779.

12 S. Li, Y. Zhao, F. Ji, R. Zheng, X. Ji, Z. Liu and L. Wang, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2022, **650**, 129617.

13 N. Luo, Z. Yang, F. Tang, D. Wang, M. Feng, X. Liao and X. Yang, *ACS Applied Nano Materials*, 2019, **2**, 3951–3959.

14 X. Lai, Y. Shen, S. Gao, Y. Chen, Y. Cui, D. Ning, X. Ji, Z. Liu and L. Wang, *Biosensors and Bioelectronics*, 2022, **213**, 114446.

15 J. Xi, C. Zhu, Y. Wang, Q. Zhang and L. Fan, *RSC Advances*, 2019, **9**, 16509–16514.