Supporting Information

Dual-Ligand Europium-Based Metal-Organic Frameworks and Hydrogels for Sensitive Ratiometric Fluorescent Detection of Tetracyclines in Food

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To verify the accuracy of the TCs analysis method established in this study, the research further employed HPLC to detect the TCs content in real samples. The specific chromatographic conditions were set as follows: the column used was a Hypersil GOLD column (specifications: 100 nm × 2.1 mm, 1.9 μm); the mobile phases for gradient elution were divided into Phase A (containing 5 mmol/L ammonium acetate, 0.1% (v/v) formic acid, and 2% (v/v) methanol) and Phase B (pure methanol), with the detailed gradient elution procedure referring to Table S1; meanwhile, the flow rate was set at 0.3 mL/min, the column temperature at 35 °C, the sample injection volume at 10.0 μL, and the detection wavelength of the UV-Vis detector was 350 nm.

The Stern-Volmer equation was used to verify whether the fluorescence quenching is static or dynamic. If the result is greater than 10, it is static quenching; otherwise, it is dynamic quenching. The equation is as follows:

$$\frac{F_0}{F} = 1 + K_{sv}C_q = 1 + K_q\tau_0 C_q$$

In equation(1)： F_0 and F are the fluorescence intensities of NH_2-BDC-Eu-DPA before and after the addition of DOX, TC, and OTC, respectively; K_{SV} is the Stern-Volmer constant (dynamic quenching constant) / (L/mol); C_q is the concentration of DOX, TC, and OTC / (mol/L); τ_0 is the average fluorescence lifetime of NH_2-BDC-Eu-DPA / s; K_q is the dynamic fluorescence quenching rate constant / (L/(mol · s)).

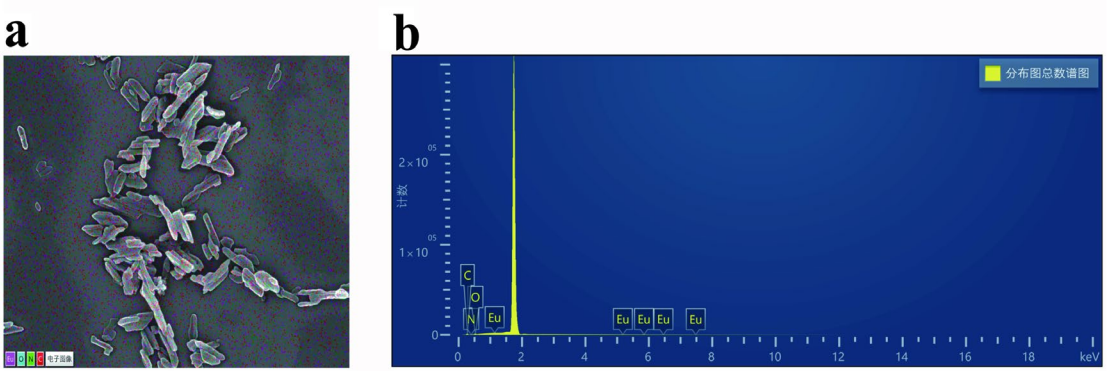

Fig. S1. EDS layer images of NH_2-BDC-Eu-DPA (a), and total distribution maps of various elements (b).

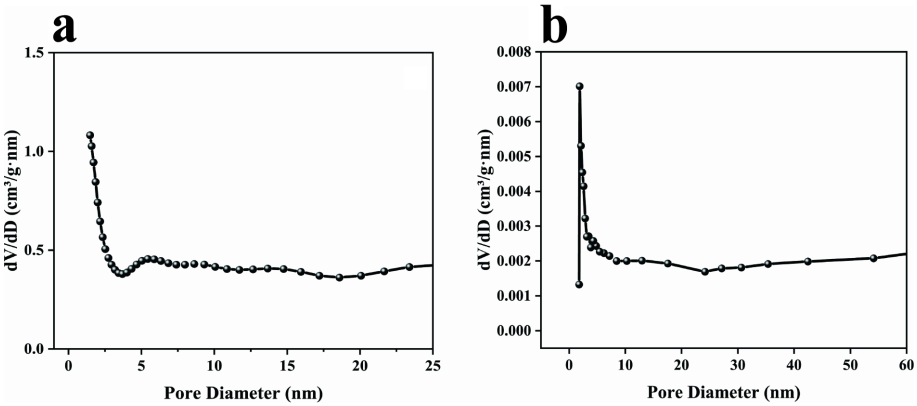

Fig. S2. Density functional theory (DFT) pore size distribution (a) and Barrett-Joyner-Halenda (BJH) pore size distribution (b) of NH_2-BDC-Eu-DPA.

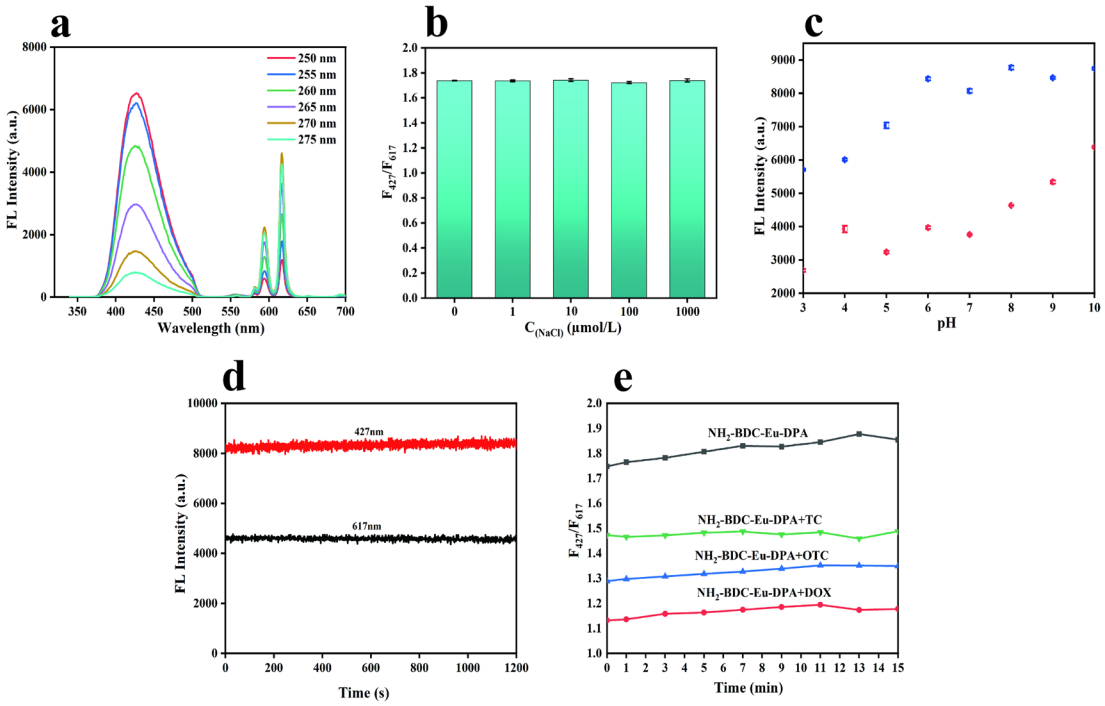

Fig. S3. Fluorescence spectra of NH_2-BDC-Eu-DPA under different excitation wavelengths (a); the fluorescence intensity of NH_2-BDC-Eu-DPA at different NaCl concentrations (b); the fluorescence intensity of NH_2-BDC-Eu-DPA under different pH conditions (c); the fluorescence stability of NH_2-BDC-Eu-DPA fluorescent material upon continuous xenon lamp irradiation for 20 min (d); the reaction stability between NH_2-BDC-Eu-DPA and TCs (e).

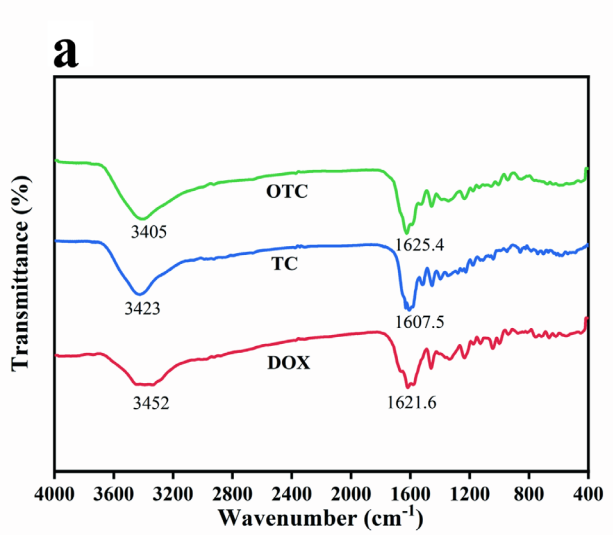

Fig. S4. FT-IR spectra of DOX, TC and OTC.

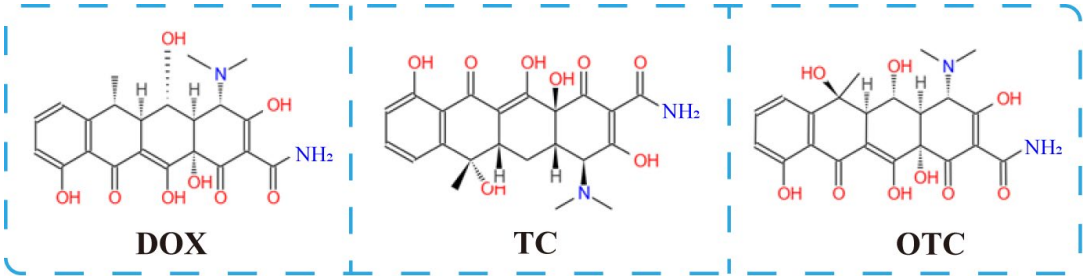

Fig. S5. Chemical structures of DOX, TC, and OTC.

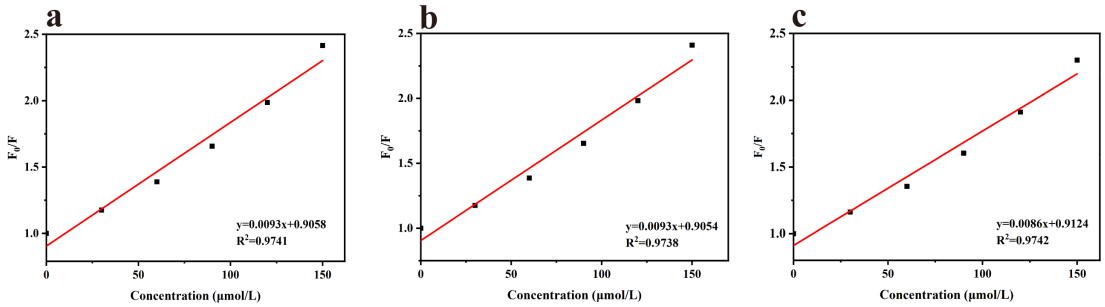

Fig. S6. Linear plots of Ksv for DOX, TC, and OTC.

Table S1 Gradient Elution Program for the Analysis of DOX, TC and OTC

Time (min)	A (%,v/v)	B (%,v/v)
0	95	5
2	85	15
5	60	40
7	5	95
7.1	95	5
9	95	5

Table S2 Total distribution spectrum of various elements in NH_2-BDC-Eu-DPA

Total atlas of distribution maps				
Elements	Line system type	Wt%	Wt% Sigma	At%
C	K-line system	51.40	2.42	62.73
N	K-line system	8.75	3.49	9.6
O	K-line system	29.61	1.69	27.12
Eu	L-line system	10.24	1.76	0.99
Total amount		100.00		100.00

Table S3 Fluorescence lifetimes and χ^2 at 427 nm and 617 nm for NH_2-BDC-Eu-DPA before and after adding DOX, TC, and OTC

Samples	Parameters	Em 427 nm	Em 617 nm
NH_2-BDC-Eu-DPA	FL lifetime	14.9 ns	456.9 μs
	χ^2	1.08	1.11
NH_2-BDC-Eu-DPA	FL lifetime	14.9 ns	458.7 μs
+DOX	χ^2	1.07	1.04
NH_2-BDC-Eu-DPA	FL lifetime	15.0 ns	455.6 μs
+TC	χ^2	1.02	0.99
NH_2-BDC-Eu-DPA	FL lifetime	14.9 ns	444.1 μs
+OTC	χ^2	1.00	1.03

297 **Table S4** Comparison of reported methods for DOX, TC, and OTC detection

Methods	Materials	Linear range	LOD	Applications	TCs	References
Fluorescence and colorimetry	O-CDs/ Ca@Mu	1.0~35.0 μM	325 nM	Water	DOX	1
Fluorescence	OVA-Ce/Ni NCs	0.2~80 μM	51 nM	Milk and fish	DOX	2
Fluorescence	Ln-Cu complexes	0-500 μmol/L	0.92 μmol/L	Water	DOX	3
Fluorescence and colorimetry	R-CDs	0~150 μM	460 nM	Water	TC	4
Fluorescence	CRSSs-NH2@N-CDs	0.5~60 μM	390 nM	Milk	TC	5
Fluorescence	MoS_2/CdTe	0.1~1.0 μmol/L	6.74 nmol/L	Milk	TC	6
Fluorescence	W-CDs	0.0067~21 μM	2.96 nM	Water	OTC	7
photoelectrochemistry sensor	$ZnIn_2S4$/rGO	100 fM ~50 nM	61.2 fM	Water	OTC	8
Fluorescence	B-CDs	0.2~60 μg/L	0.1 μg/L	Tea drinks	OTC	9
Fluorescence	NH_2-BDC-Eu-DPA	1-200 μmol/L	31.0 nmol/L	Milk and pork	DOX	This work
		1-200 μmol/L	29.7 nmol/L		TC	
		1-200 μmol/L	35.1 nmol/L		OTC	

298

References

1 A. A. F. Aal, M. A. Mahmoud, H. A. Rageh, R. M. Elmasry, A. Y. B. Jardan, M. M. E. Wekil and H. A. Ali, *Talanta Open.*, 2025, **11**, 100438.

2 H. Chen, H. Yang, Y. Zheng, Y. Li, J. Hu, X. Yang and Y. Wang, *Food Chem.*, 2025, **482**, 144074.

3 W. Liu, K. Shao, W. Yao and E. Gao, *J. Mol. Struct.*, 2025, **1328**, 141262.

4 Q. Fu, C. Long, L. Qin, Z. Jiang, T. Qing, P. Zhang and B. Feng, *J. Environ. Pollut.*, 2021, **283**, 117109.

5 M. Yuan, J. An, G. Zhang, Y. Hu, M. Luo, Y. Shi and Y. Liu, *J. Ceram. Int.*, 2022, **48**, 4047-4054.

6 N. Liang, X. Hu, W. Li, Y, Wang, Z. Guo, X. Huang, Z. Li, X. Zhang, J. Xiao, X. Zou and J. Shi, *Food Chem.*, 2022, **378**, 132076.

7 Z. Wang, H. Xu, L. Wang, X. Zheng, T. Zhao, B. Qu and H. Wang, *Microchem. J.*, 2025, **212**, 113398.

8 Y. Lei, B. Pan, G. Li, L. Zou and Q. Shen, *Microchem. J.*, 2025, **208**, 112336.

9 Z. Li, S. Li, L. Jiang, J. Niu, Y. Zhang, L. Nie, Q. Zhou and C. Chen, *Food Chem.*, 2024, **447**, 138998.