Electronic Supplementary Information

A stable two-fold interpenetrated 3D Zn(II) MOF for fluorescence sensing of uric acid and tryptophan

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1. Materials and measurements

All chemical reagents were purchased commercially without any further purification. The FT-IR spectra were recorded from KBr pellets on a Nicolet Magna-IR 560 Infrared spectrometer in the 4000-400 cm^{-1} region. The solid diffuse reflectance UV–Vis spectra were recorded on a UH4150 spectrophotometer. The thermogravimetric analyses (TGA) were investigated on a standard TG-DTA analyzer under nitrogen flow at a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data were collected with a Bruker D8 Advance diffractometer using a Cu target (λ = 1.54060 Å) in the range of 5 to 50°. The fluorescence spectra of **1** were collected with a Hitachi F-4600 spectrophotometer at room temperature.

2. X-ray Crystallography

The single crystal X-ray diffraction measurement for **1** was determined on a Bruker D8 Quest diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The structures were solved by direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-2018. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms bound to carbon atoms were calculated theoretically. In this heavy-atom structure, the refinement was completed with no allowance for the ethanol hydrogen atoms in the model. The Crystal data and structure refinements for **1** are listed in Table S1. Selected bond distances and angles are listed in Table S2.

Table S1. Crystal data and structure refinements for **1**

Identification code	**1**
Empirical formula	$C_{98}H_{90}N_{16}O_{17}Zn_4$
Formula weight	2025.33
Temperature / K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$

a (Å)	17.9836(9)
b (Å)	17.9846(8)
c (Å)	14.1550(7)
α (°)	90
β (°)	97.572(2)
γ (°)	90
V (Å^3)	4538.2(4)
Z	2
ρ_{calc} (g/cm^3)	1.482
μ/mm^{-1}	1.123
R_{int}	0.0467
Reflections collected	76211
Data/restraints/parameters	7980/3/626
Goodness-of-fit on F^2	1.016
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0376 wR_2 = 0.0997
Final R indexes [all data]	R_1 = 0.0492 wR_2 = 0.1072
Largest diff. peak/hole/e Å^{-3}	0.829/-0.580
CCDC	2411183

Table S2. Selected Bond Lengths (Å) and Bond Angles (°) for **1**

Zn1-N1	2.037(2)	Zn2-N8	2.009(2)	Zn2-O5	1.923(2)
Zn1-N4	2.035(2)	Zn1-O1	1.9834(18)	Zn2-O7	1.909(2)
Zn2-N5	2.022(3)	Zn1-O3	1.960(2)		
N4-Zn1-N1	101.95(10)	O3-Zn1-N4	105.79(10)	O5-Zn2-N8	104.37(11)
O1-Zn1-N1	105.72(9)	O3-Zn1-O1	120.50(10)	O7-Zn2-N5	105.74(11)
O1-Zn1-N4	115.38(9)	N8-Zn2-N5	102.25(11)	O7-Zn2-N8	115.46(10)
O3-Zn1-N1	105.51(10)	O5-Zn2-N5	100.28(12)	O7-Zn2-O5	125.37(11)

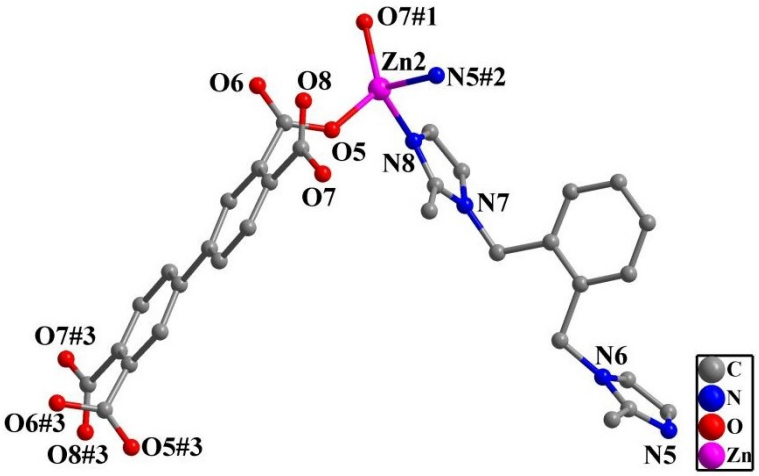


Fig. S1. The coordination environment of Zn2 center, [Symmetry codes: #1: x, 0.5 – y, –0.5 + z; #2: – x, –0.5 + y, 1.5 – z; #3: 1 – x, 1 – y, 2 – z.].

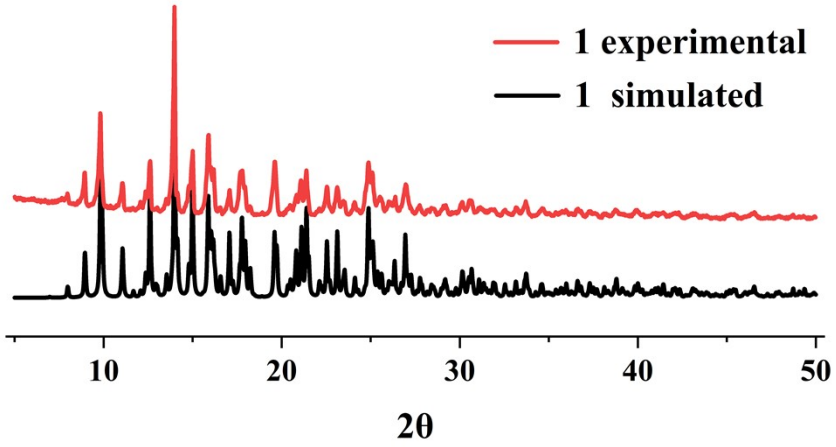


Fig. S2. The PXRD of **1**.

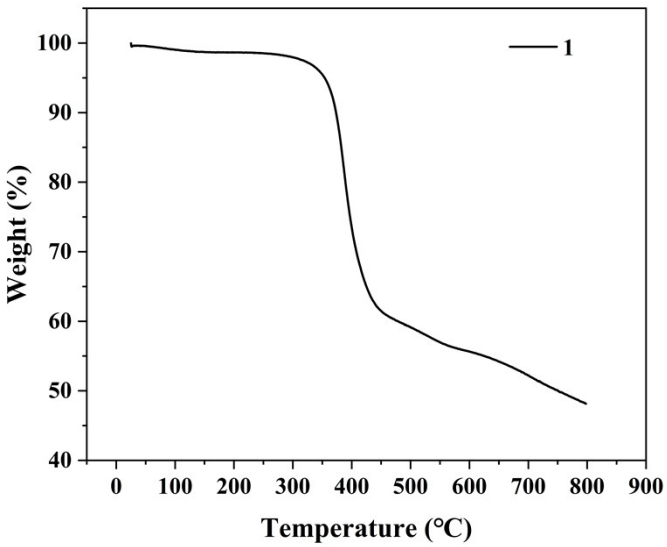


Fig. S3. The TGA diagram of **1**.

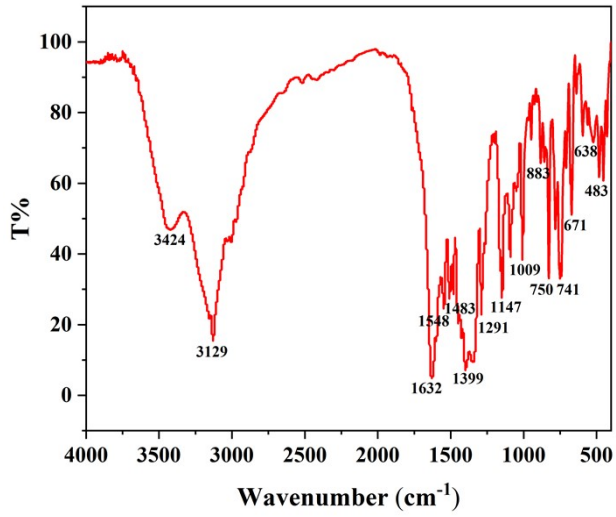


Fig. S4. IR of **1**.

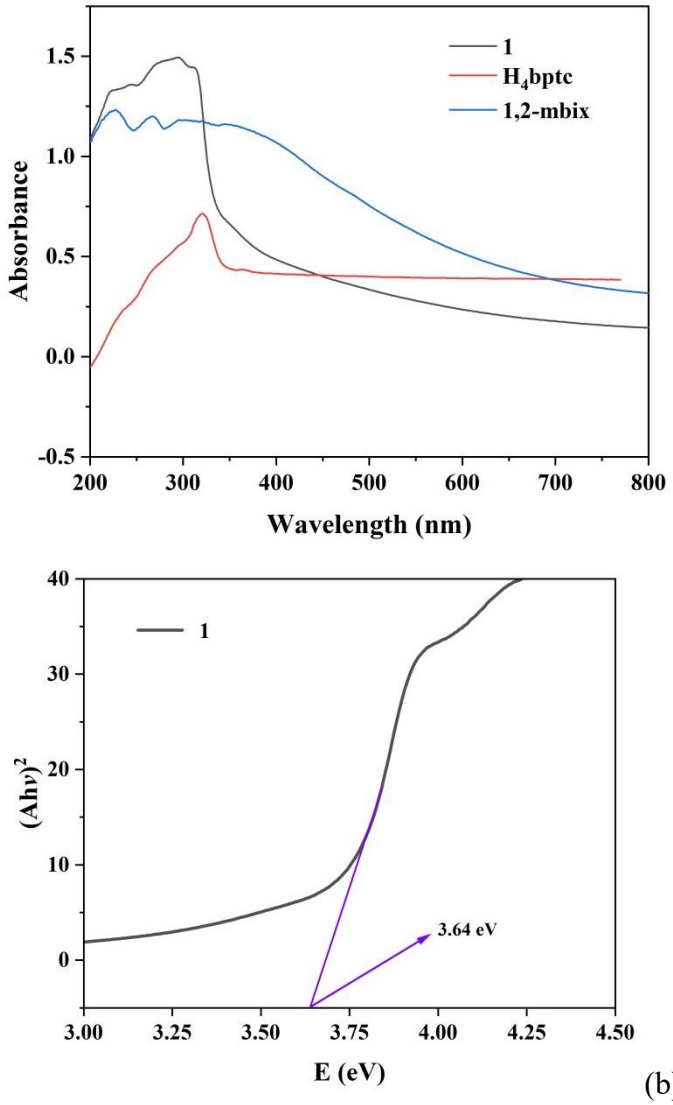
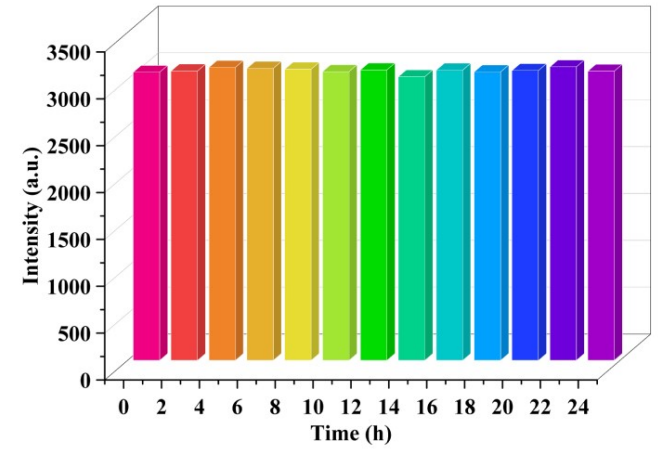
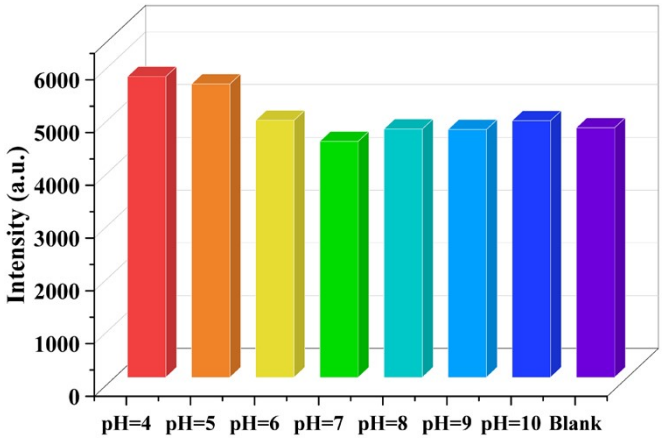


Fig. S5. (a) UV-vis absorption spectra in the solid state of H_4bptc, 1,2-mbix and **1**; (b) Diffuse reflectance spectra of **1**.



(a)



(b)

Fig. S6. The emission intensities of **1** after immersed in water for different time (a) and at different pH values (b).

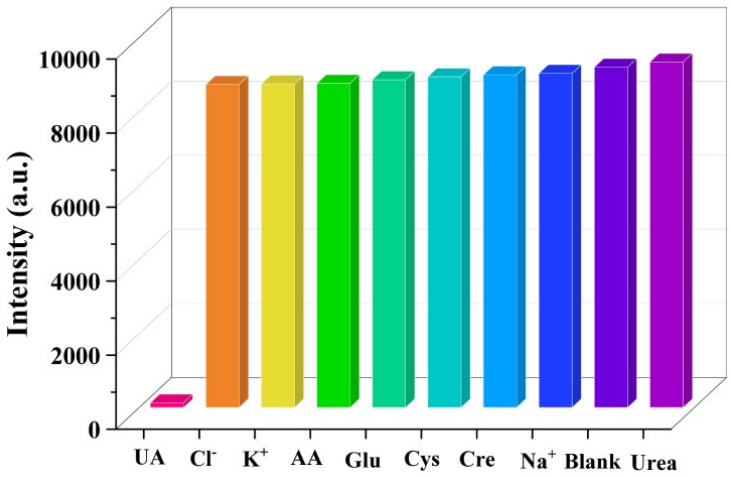


Fig. S7. The emission intensities of **1** treated with various biological metabolites.

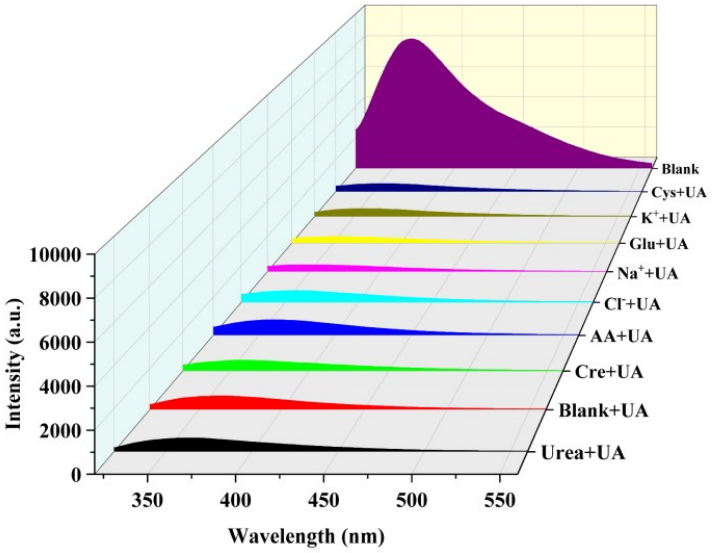


Fig. S8. Emission response of **1** in the presence various biological metabolites.

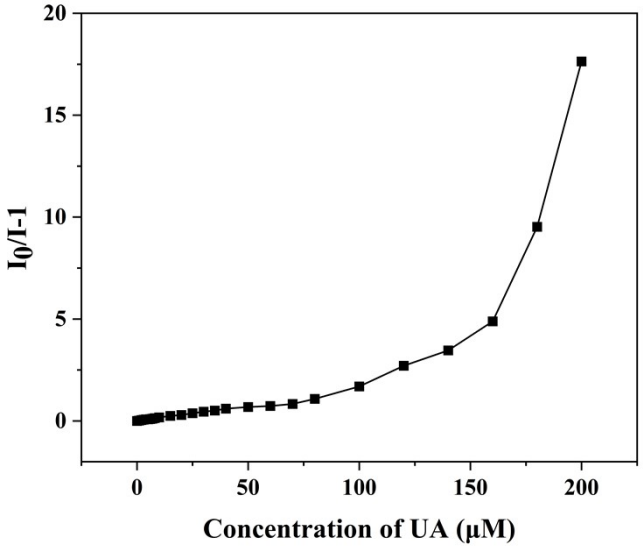


Fig. S9. *S-V* plot of **1** toward UA.

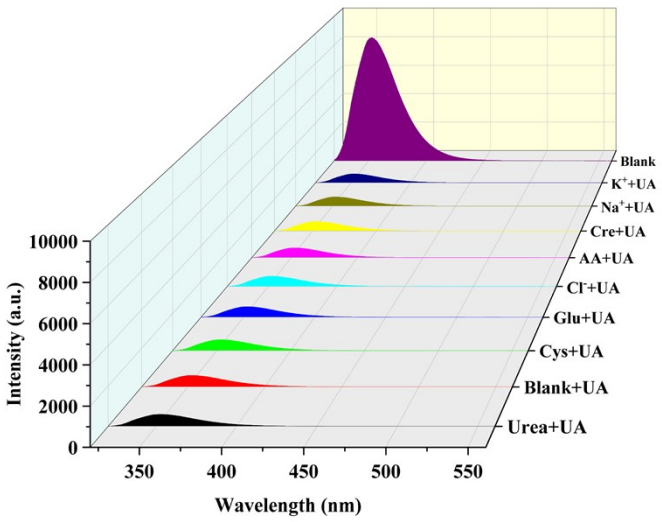


Fig. S10. Emission response of **1** in the presence various biological metabolites in serum samples.

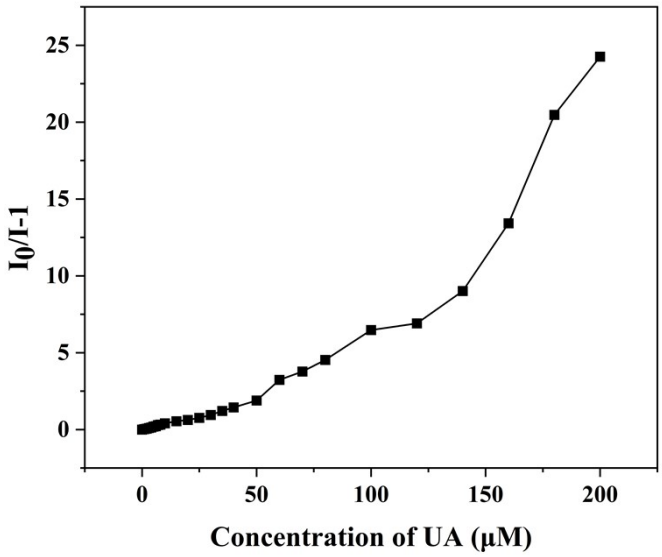


Fig. S11. *S-V* plot of **1** toward UA in serum sample.

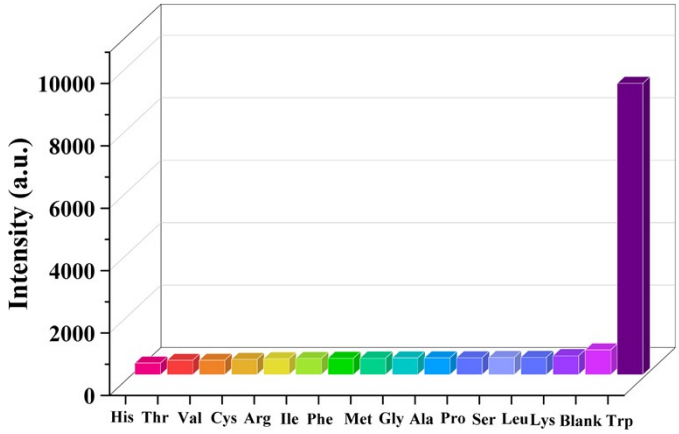


Fig. S12. The emission intensities of **1** treated with various amino acids.

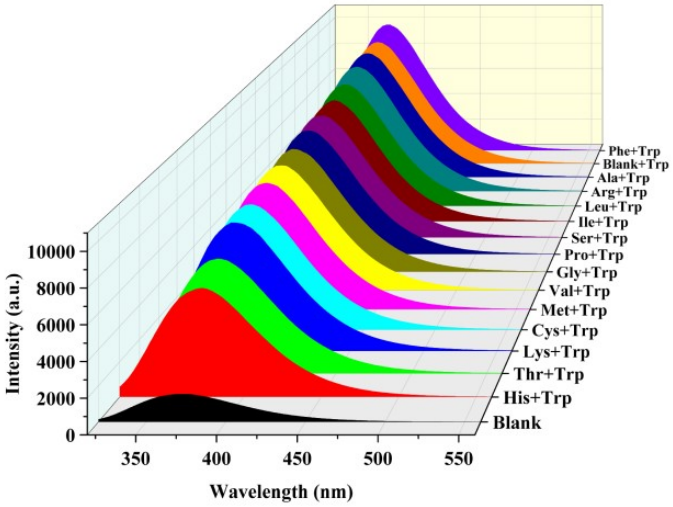


Fig. S13. Emission response of **1** in the presence various amino acids.

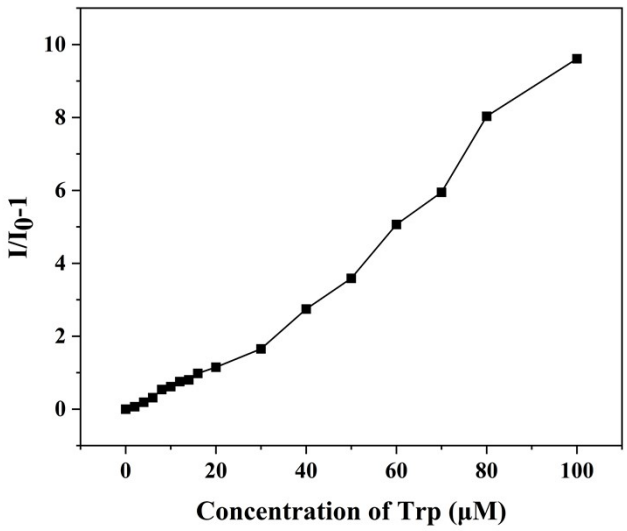


Fig. S14. *S-V* plot of **1** toward Trp.

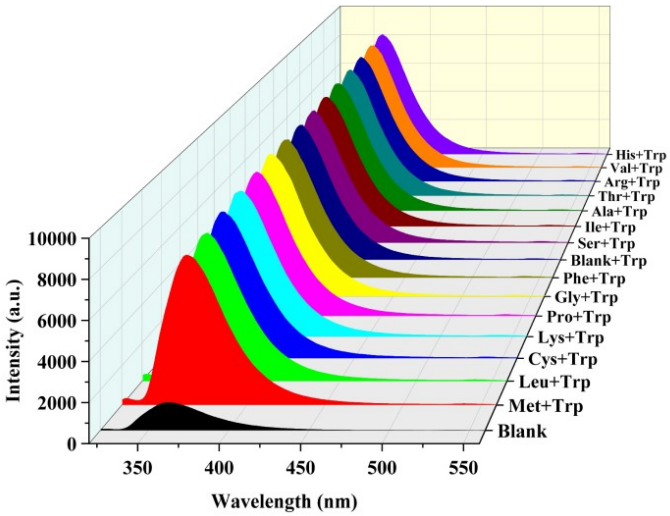


Fig. S15. Emission response of **1** in the presence various amino acids in milk sample.

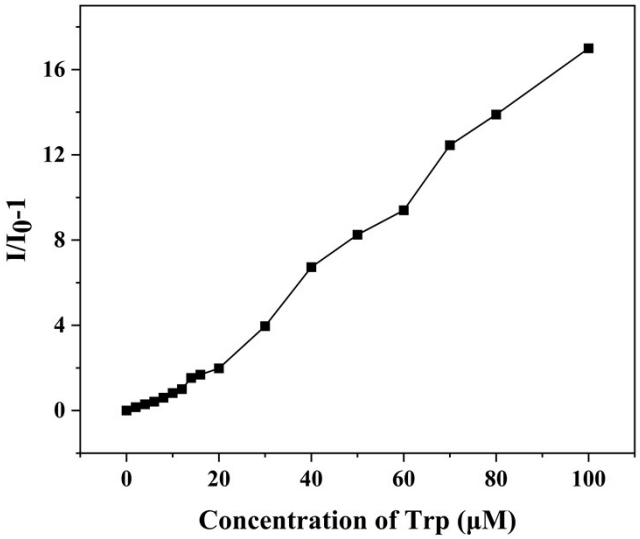
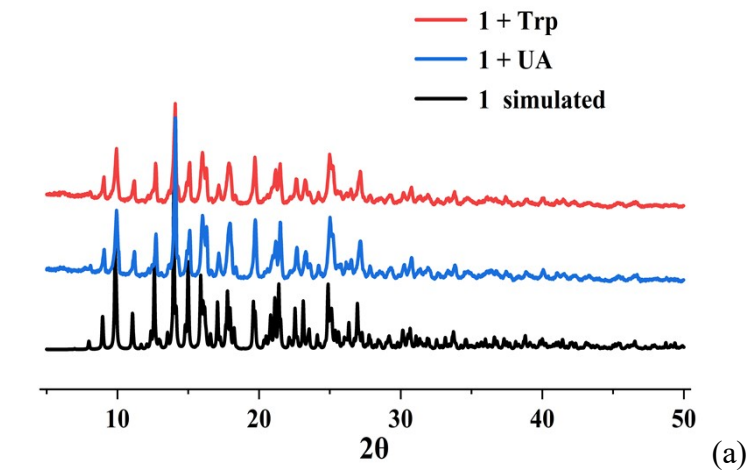
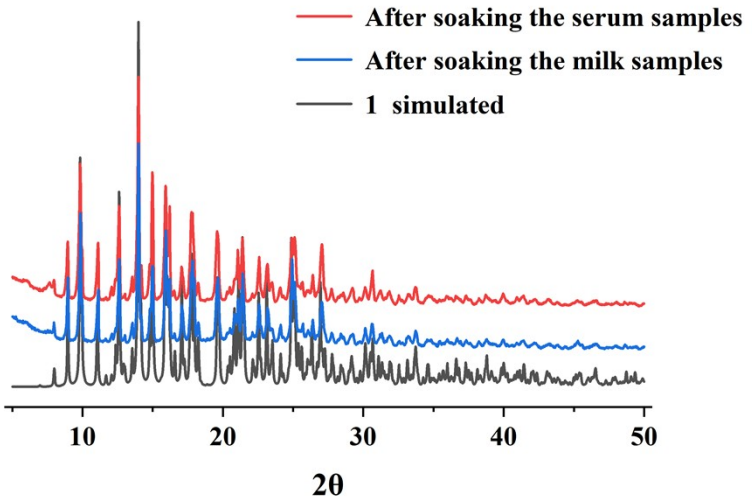


Fig. S16. *S-V* plot of **1** toward Trp in milk sample.



(a)



(b)

Fig. S17. The PXRD patterns of **1** after luminescence sensing experiments with UA and Trp aqueous solutions (a), and after soaking in serum and milk samples (b).

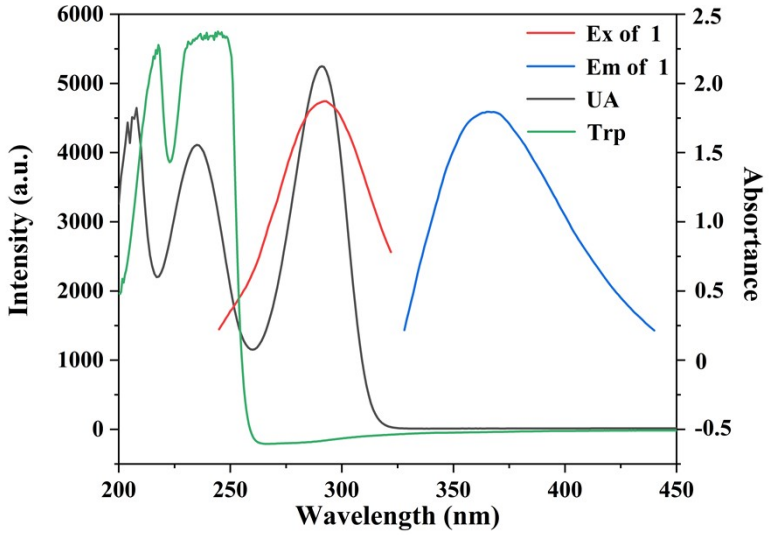


Fig. S18. Excitation spectra and emission spectra of **1**, UV spectra of UA and Trp.

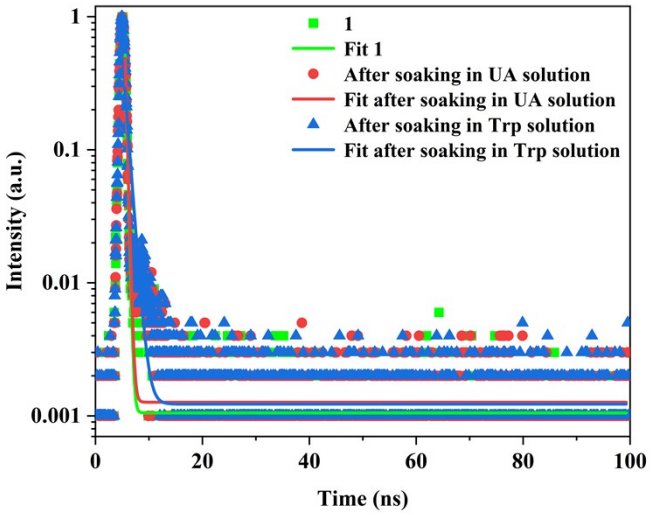


Fig. S19. The fluorescence lifetime of **1** before and after immersed in UA and Trp solutions.

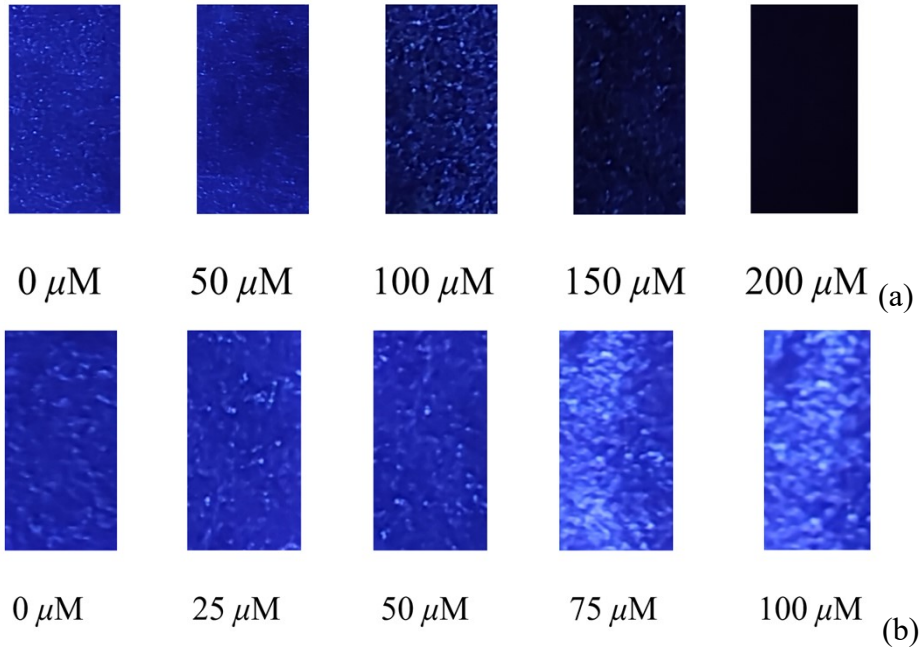
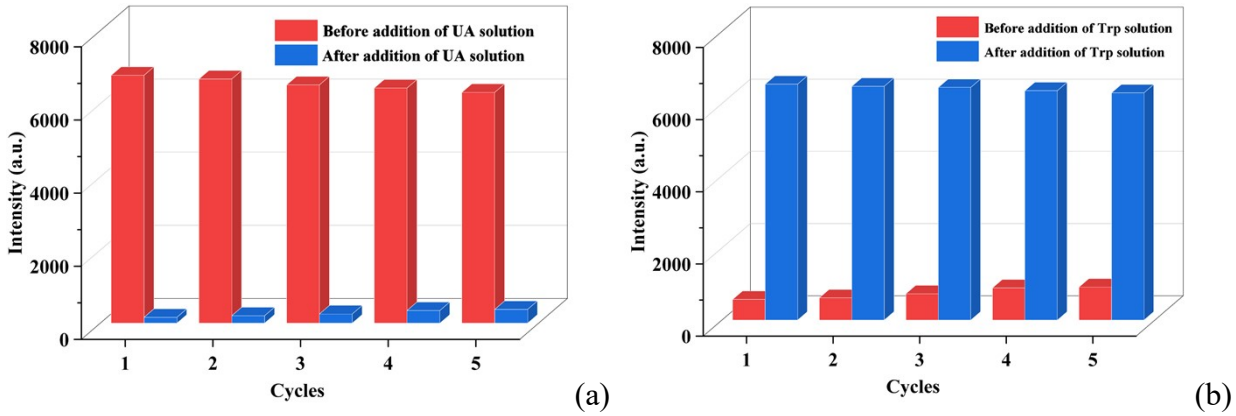


Fig. S20. Luminescent films of **1** with different concentrations of Trp and UA treatment under UV light.



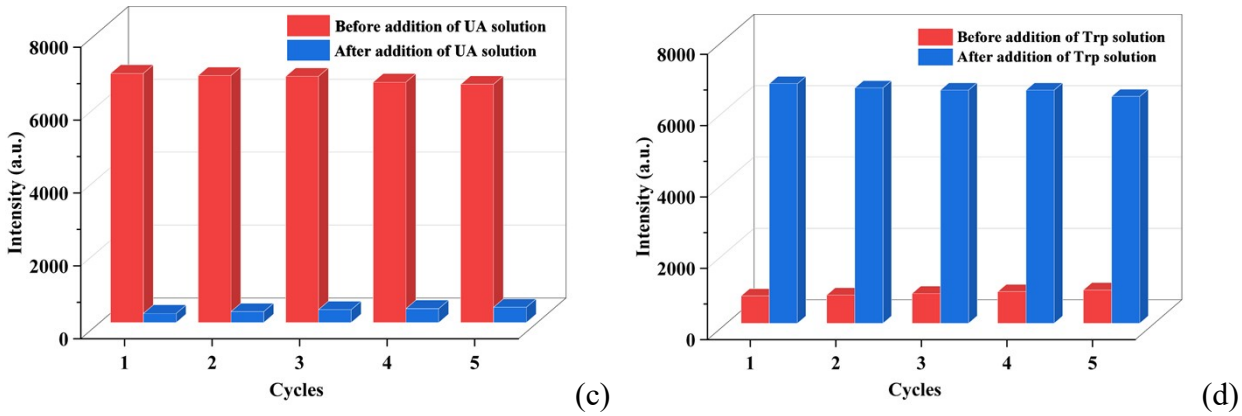


Fig. S21. The fluorescence intensities of **1** after five cycles toward UA in distilled water (a) and serum sample (c), Trp in distilled water (b) and milk sample (d).

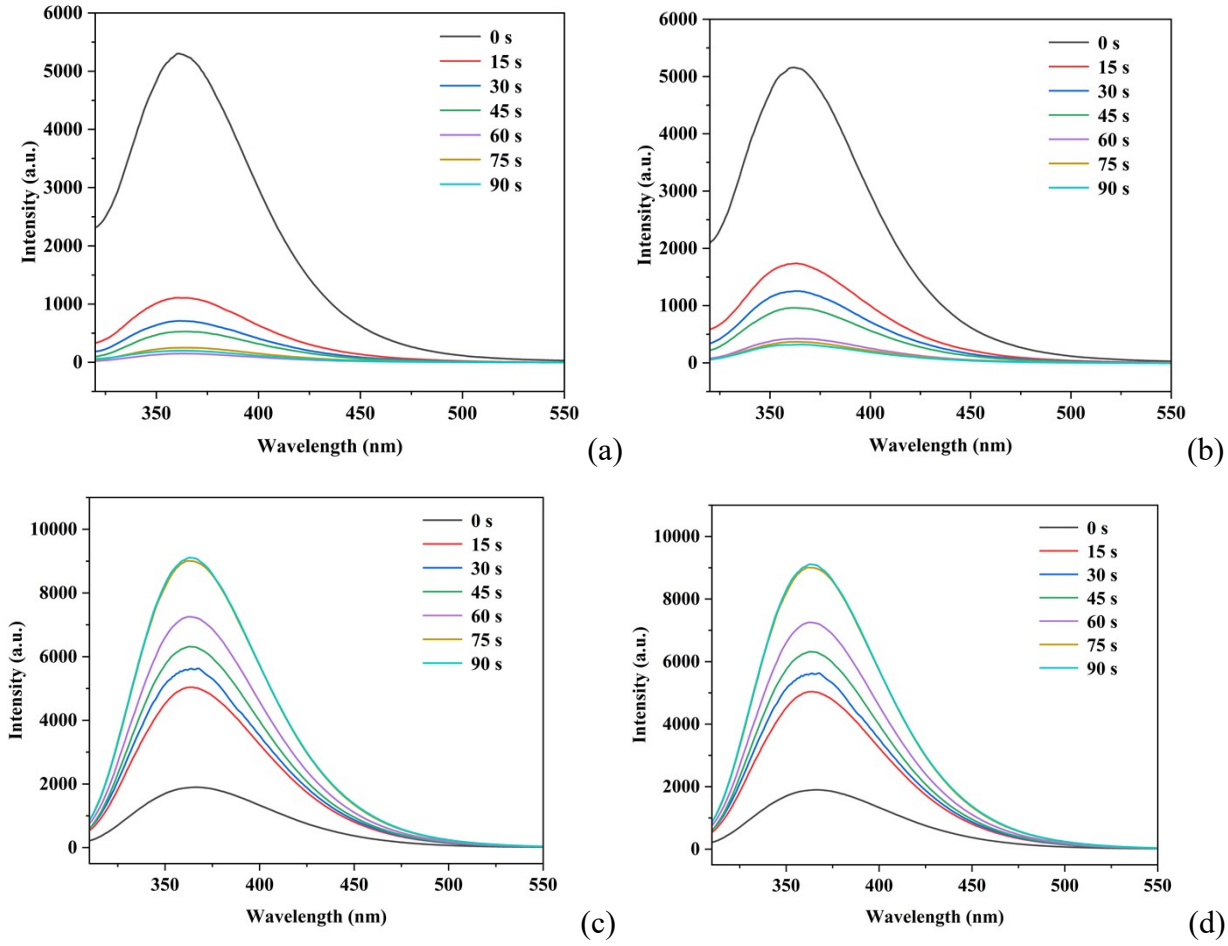


Fig. S22. The fluorescence response time of **1** toward toward UA in distilled water (a) and serum sample (b); and Trp in distilled water (c) and milk sample (d).

Table S3. Comparison between MOFs for the sensing of UA

Fluorescent MOFs	Solvent	Methods	K_{sv} / M^{-1}	LOD / μM	Ref.
$[Pr(TMOFB)(DMF)_3]_n$	Water	Turn-off	7.91×10^3	0.28	49
Cu^{2+}@Tb-MOFs	Water	Turn-on	3.10×10^5	0.65	50
$\{[Zn_3(BTC)_2(Bimb)_{3.5}][Zn(HCOO)(Bimb)_{1.5}]\cdot CH_3COO\cdot 2(CH_3)_2NH\cdot 2DMF\cdot 9H_2O\}_n$	Water	Turn-off	4.50×10^4	2.52	51
Tb-dtpa-bdap	Water	Turn-off	2.22×10^4	5.80	52
Cu^{2+}@MIL-91(Al:Eu)	Water	Turn-on	4.72×10^5	1.60	53
$\{[Zn_2(bptc)(1,2\text{-mbix})_2]_2\cdot EtOH\}_n$ (**1**)	Water	Turn-off	1.48×10^4	1.26	this work

Table S4. Comparison between MOFs for the sensing of Trp

Fluorescent MOFs	Solvent	Methods	K_{sv} / M^{-1}	LOD / μM	Ref.
$[Zn_4(pta)_3(H_2O)_{1.5}]$	Water	Turn-on	3.96×10^6	0.043	54
Tb^{3+}@$[Cd(3\text{-bpdb})(MeO\text{-ip})]_n$	Water	Turn-on	1.12×10^3	64.14	55
$[Cd(L)(TPA)_{0.5}(H_2O)]\cdot H_2O$	Water	Turn-on	2.00×10^3	0.065	56
$[Tb(ppda)(npdc)_{0.5}(H_2O)_2]_n$	Water	Turn-on	2.60×10^5	69.9	57
Cd-MOF	DMF	Turn-on	2.53×10^4	1.70	58
$\{[Zn_2(bptc)(1,2\text{-mbix})_2]_2\cdot EtOH\}_n$ (**1**)	Water	Turn-on	6.16×10^4	0.30	this work