Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Dye-functionalized Metal-Organic Frameworks with the Uniform Dispersion of MnO_2 Nanosheets for Visualized Fluorescence Detection of Alanine Aminotransferase

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1. Experimental Section

Preparation of ZIF-8. ZIF-8 nanocrystals were synthesized according to reporting literature.[42] Briefly, a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.173 g) in 80 mL methanol was added into a solution of 2-methylimidazole (2.595 g) in 80 mL methanol under stirring with a magnetic bar. After keeping at room temperature for 1 h, ZIF-8 was formed, and then separated by centrifugation at 7000 rpm for 5 min and washed with methanol three times. The collected white powder was dried in the oven at 60 °C overnight.

Preparation of MnO_2 nanosheets**.** MnO_2 nanosheets were synthesized according to reporting literature with a little modification.[43] 2-Methylimidazole (0.03 g) and $KMnO_4$ (0.02 g) were dissolved in 30 ml deionized water in a flask (100 ml). With continuous magnetic stirring in an ice bath, the mixture was allowed to react for 1 h. The black product was collected by centrifugation (6 min at 5000 rpm) and washed thoroughly using deionized water. The obtained MnO_2 powders were dried at 80 °C for 12 h before further experiment.

2. Supporting Figures and Tables

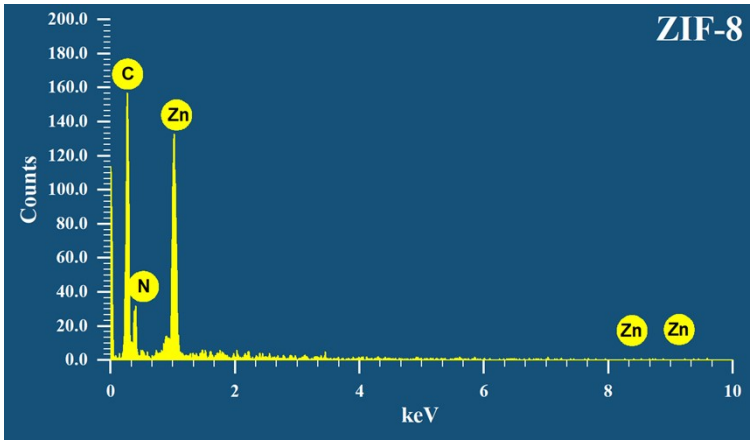

Fig. S1. EDX image of ZIF-8.

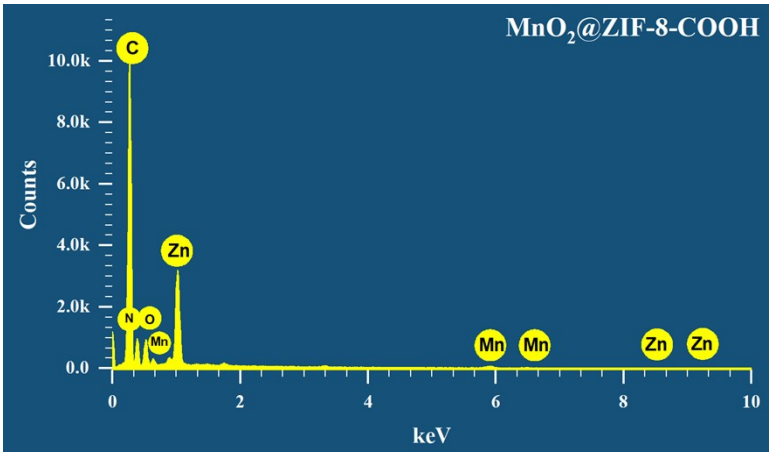

Fig. S2. EDX image of **MnO_2@ZIF-8-COOH**.

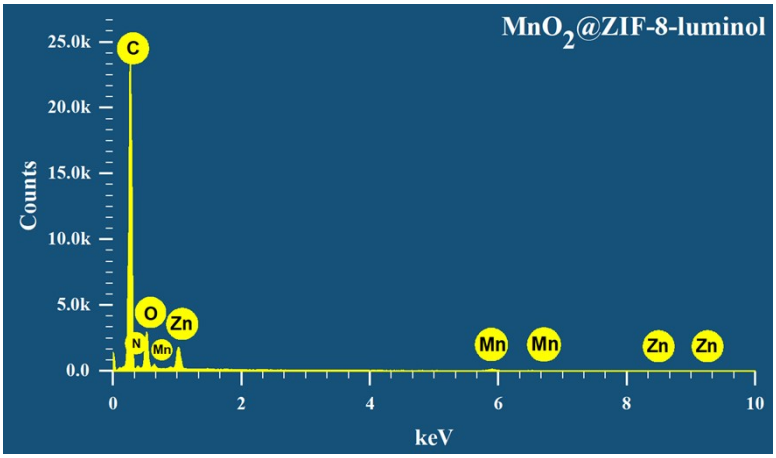

Fig. S3. EDX image of **MnO_2@ZIF-8-luminol**.

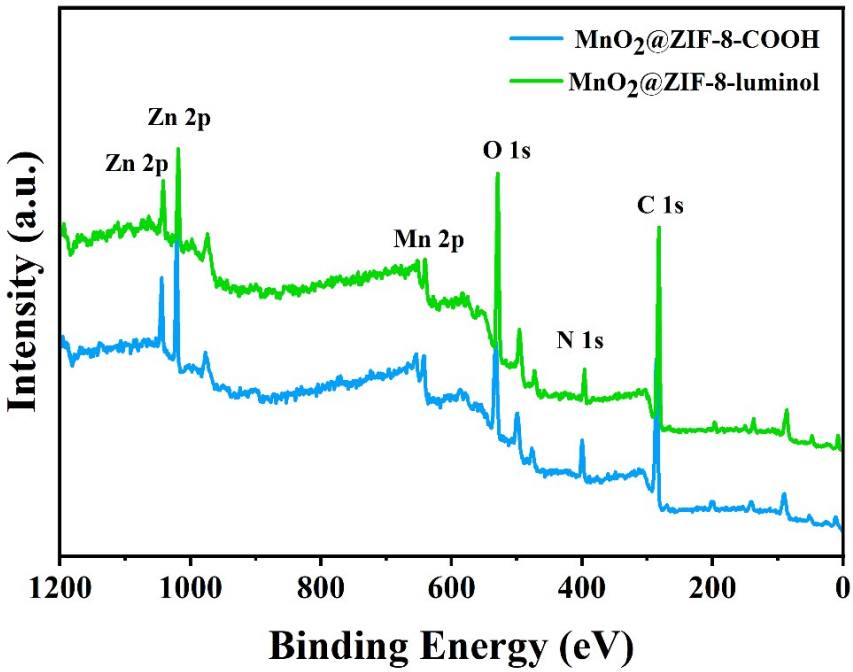

Fig. S4. XPS spectra of **MnO_2@ZIF-8-COOH** and **MnO_2@ZIF-8-luminol**.

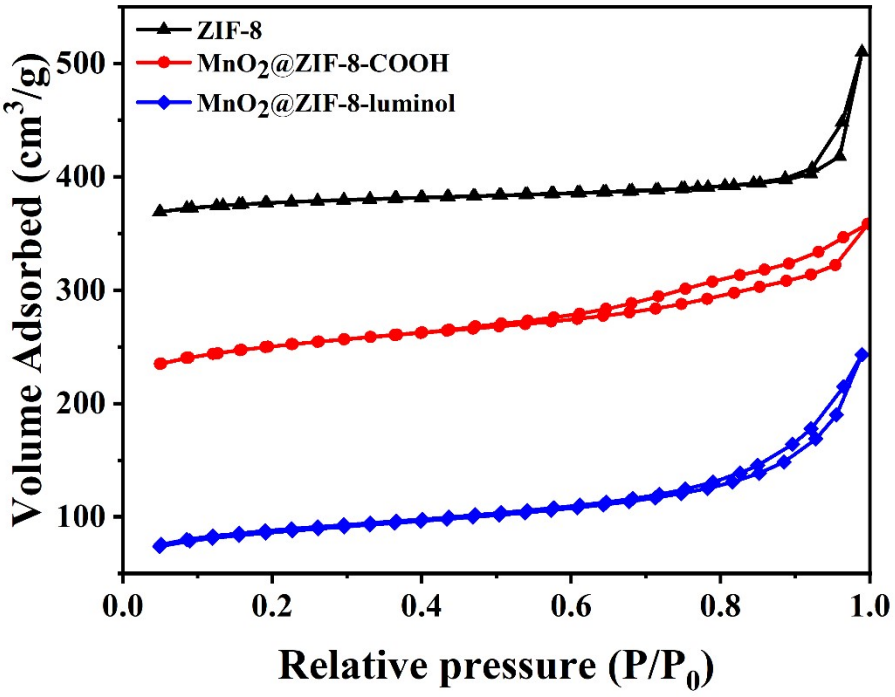

Fig. S5. N_2 adsorption/desorption isotherms of ZIF-8, **MnO_2@ZIF-8-COOH,** and **MnO_2@ZIF-8-luminol**.

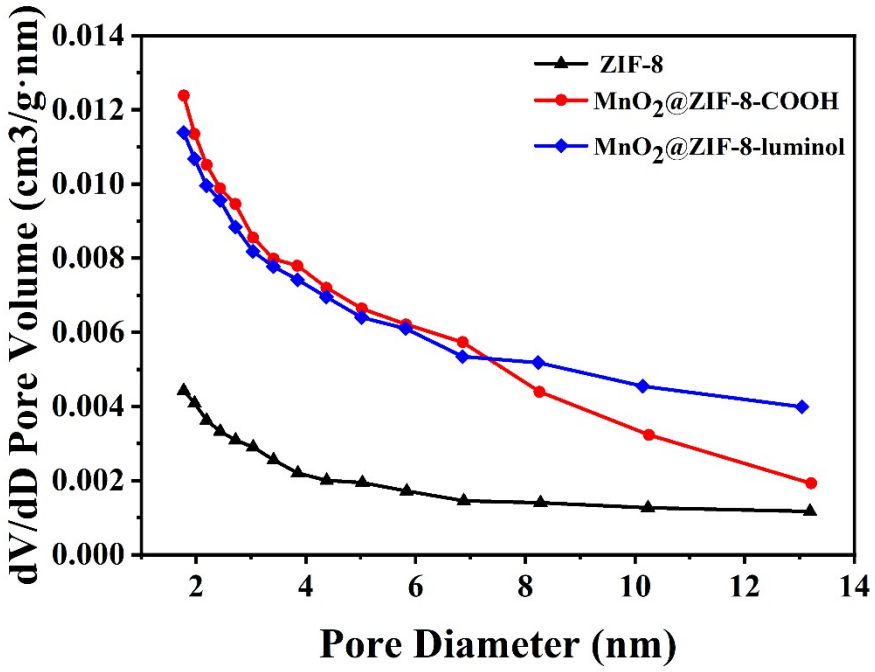

Fig. S6. Pore size distributions of ZIF-8, **MnO_2@ZIF-8-COOH,** and **MnO_2@ZIF-8-luminol**.

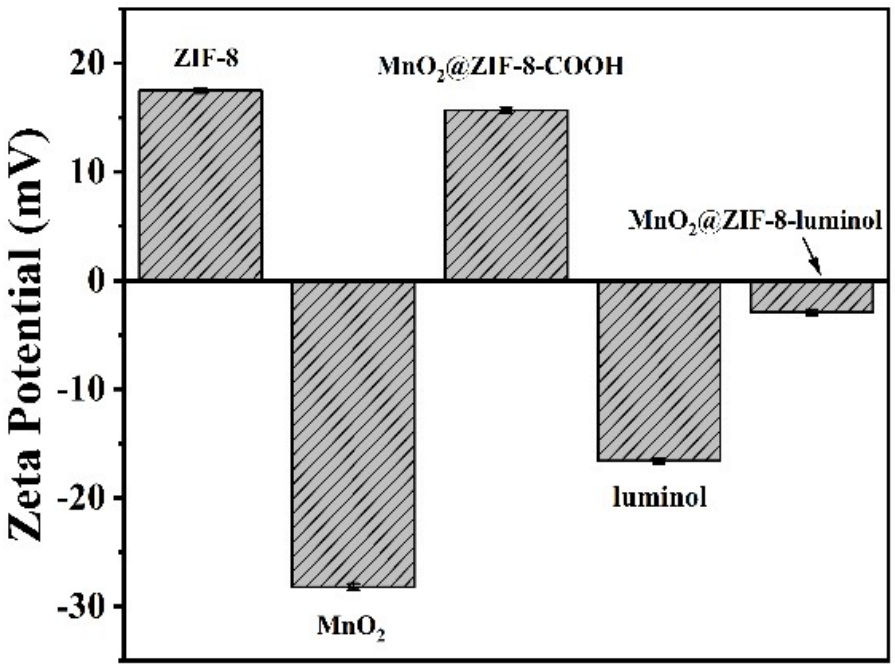

Fig. S7. Variation of ζ potentials of ZIF-8, MnO_2, luminol, **MnO_2@ZIF-8-COOH**, and **MnO_2@ZIF-8-luminol**.

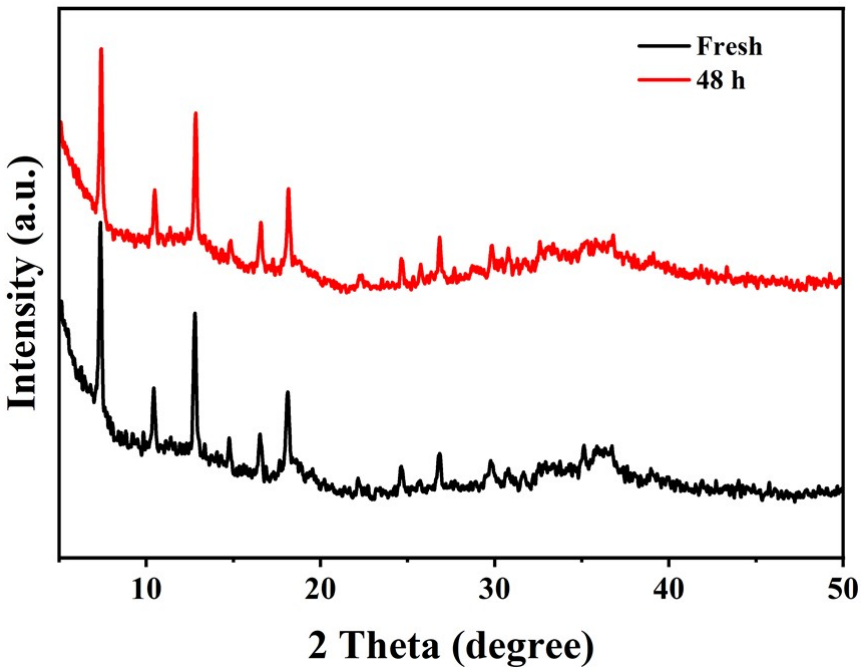

Fig. S8. PXRD patterns of **MnO_2@ZIF-8-luminol** before and after soaking in water for 48 h.

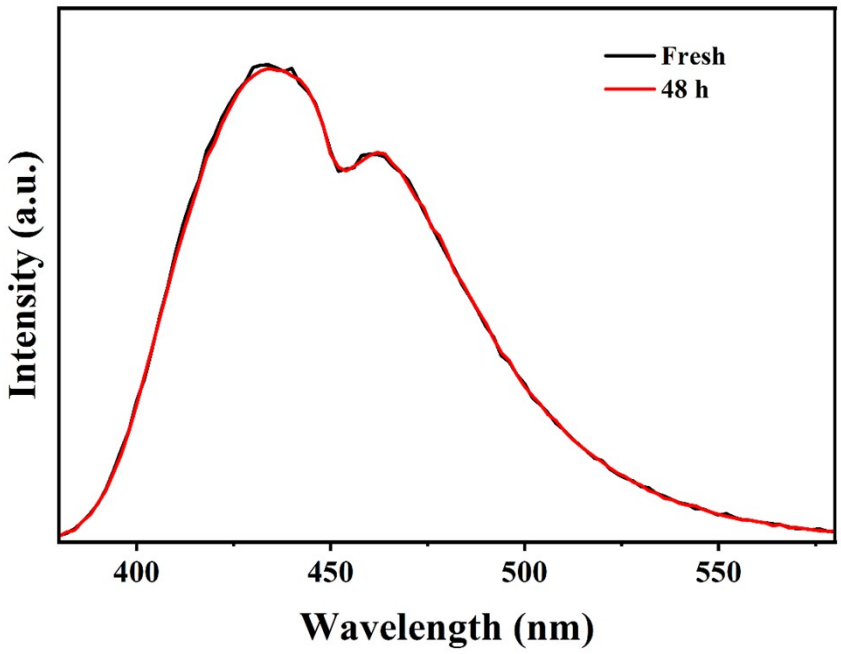

Fig. S9. Emission spectra of **MnO_2@ZIF-8-luminol** before and after soaking in water for 48 h (λex = 365 nm).

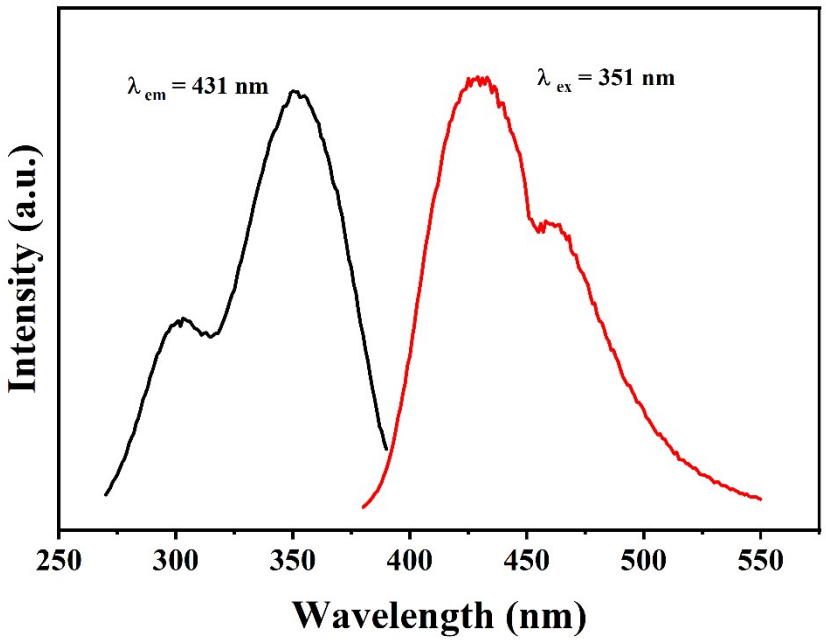

Fig. S10. Excitation and emission spectra of luminol.

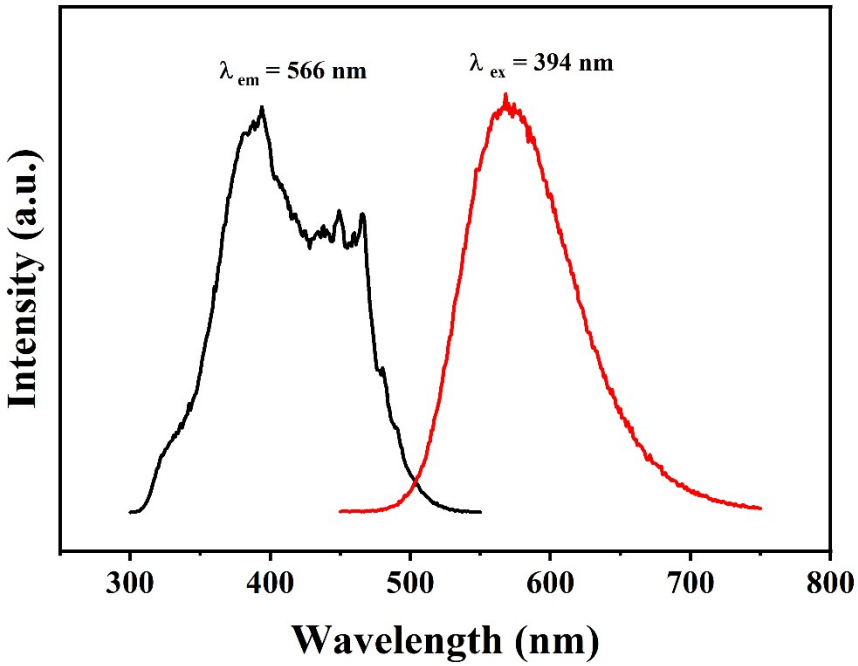

Fig. S11. Excitation and emission spectra of OPD in the presence of MnO_2.

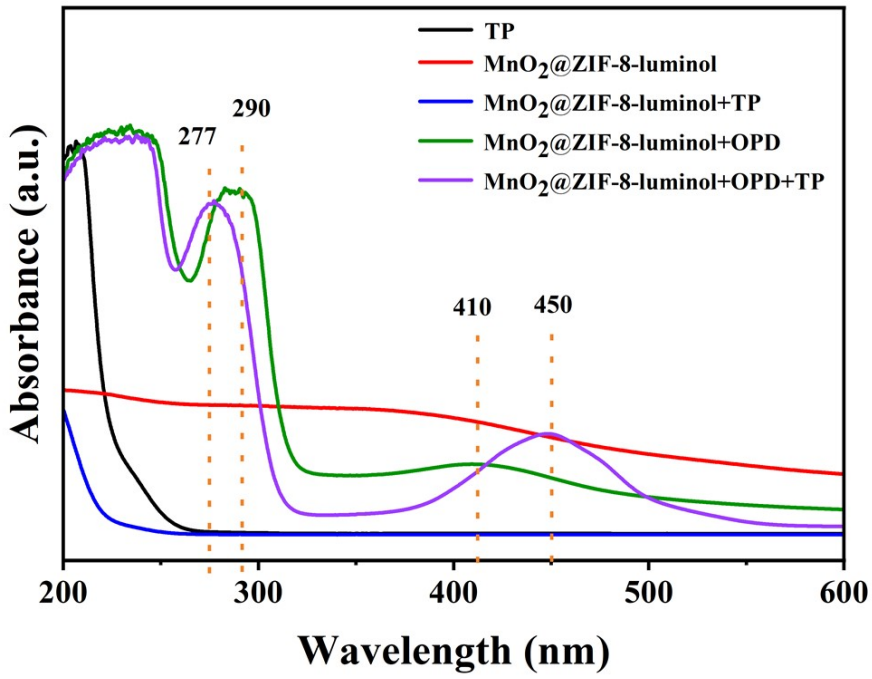

Fig. S12. The UV-vis absorption spectra of TP, **MnO_2@ZIF-8-luminol** without and with TP, and **MnO_2@ZIF-8-luminol** containing OPD in the absence and presence of TP.

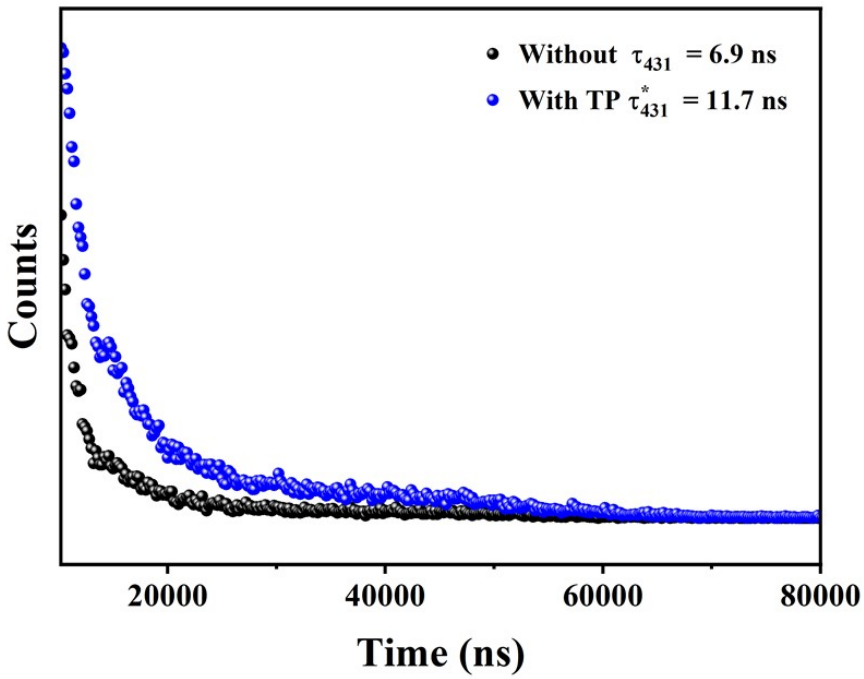

Fig. S13. Lifetime decay curve of **MnO_2@ZIF-8-luminol** containing OPD in the presence of 0.2 mg mL^{-1} TP (ex = 351 nm, em = 431 nm).

= 615 nm).

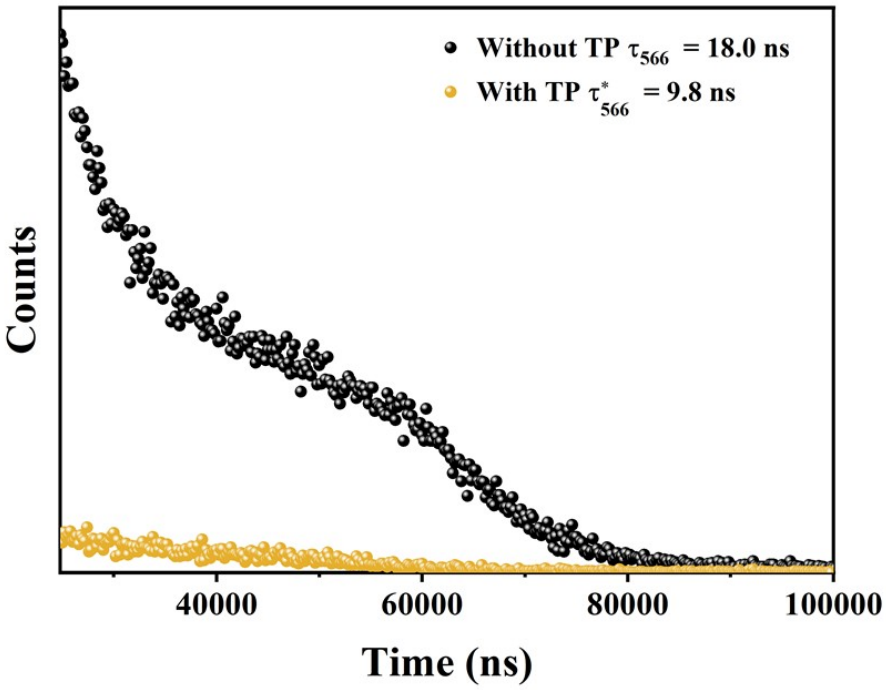

Fig. S14. Lifetime decay curve of **MnO_2@ZIF-8-luminol** containing OPD in the presence of 0.2 mg mL^{-1} TP (λ_{ex} = 394 nm, λ_{em} = 566 nm).

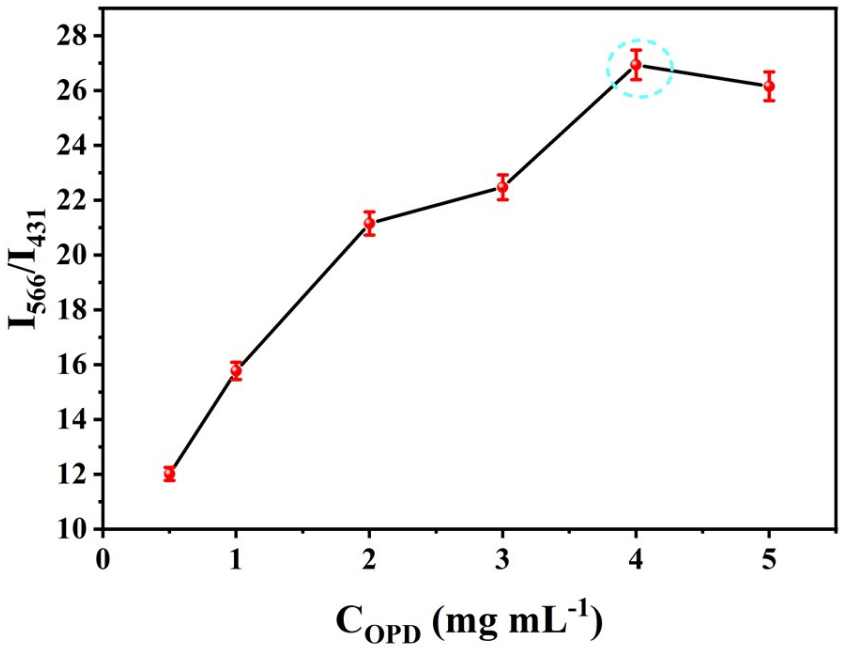

Fig. S15. Effect of various concentration of OPD on the values of I_{566}/I_{431} in aqueous solution of **MnO_2@ZIF-8-luminol** (λ_{ex} = 365 nm).

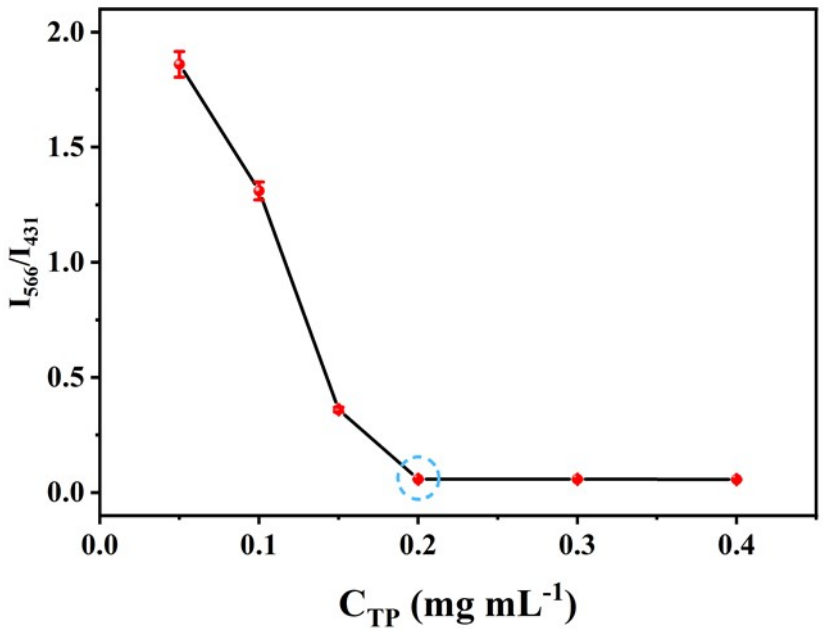

Fig. S16. Effect of various concentration of TP on the values of I_{566}/I_{431} of the sensor with 1500 U L^{-1} ALT (λ_{ex} = 365 nm).

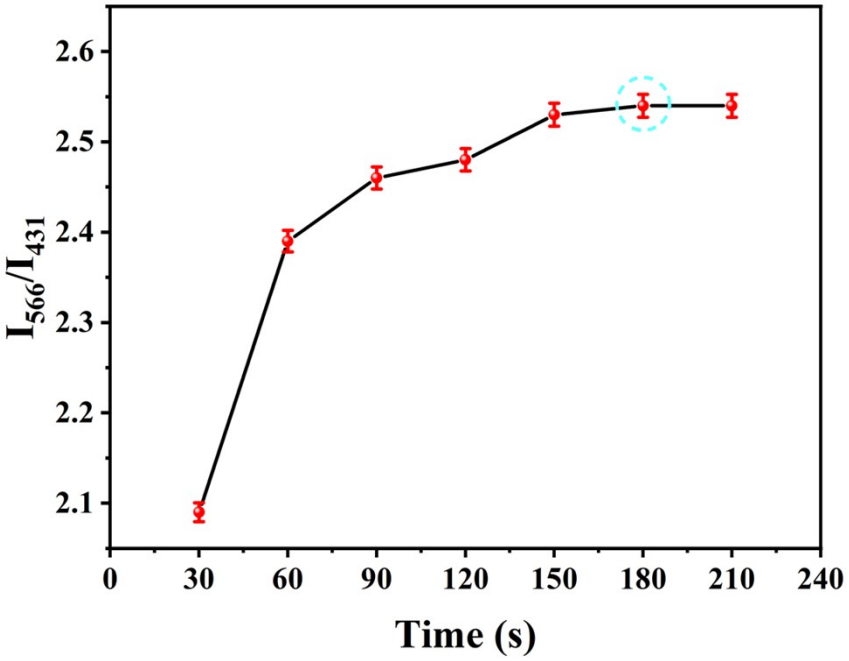

Fig. S17. Effect of reaction time between ALT (1500 U L^{-1}) and TP on the values of I_{566}/I_{431} of the sensor (λ_{ex} = 365 nm).

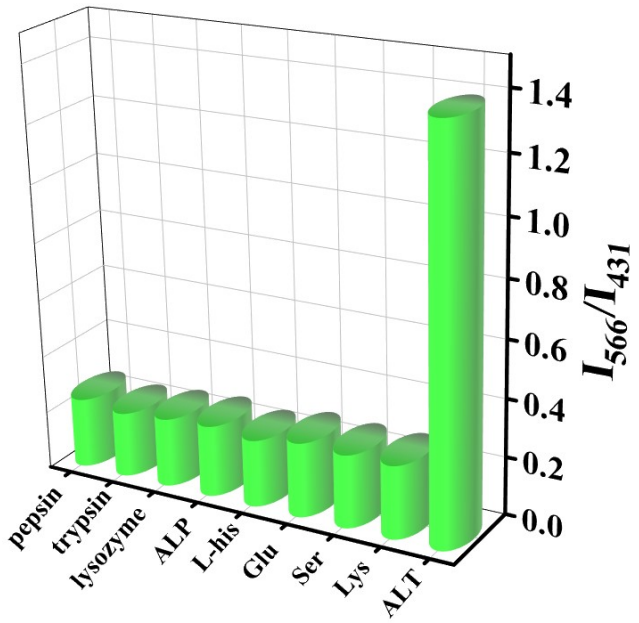

Fig. S18. Selectivity experiments of different substances, including pepsin, trypsin, lysozyme, ALP, L-his, Glu, Ser, Lys (1.0 mg mL^{-1}), and ALT (1000 U L^{-1}) (λ_{ex} = 365 nm).

Table S1. Analysis report of the energy dispersive X-ray analysis spectroscopy (EDS) of ZIF-8, **MnO_2@ZIF-8-COOH** and **MnO_2@ZIF-8-luminol**.

Material	Element	Weight %
ZIF-8	C	45.83
	N	22.95
	Zn	31.22
MnO_2@ZIF-8-COOH	C	54.02
	N	16.82
	O	6.42
	Mn	4.33
	Zn	18.41
MnO_2@ZIF-8-luminol	C	69.10
	N	4.21
	O	13.79
	Mn	5.61
	Zn	7.29

Table S2. Comparison of various detection method for ALT detection.

Detection method	Linear range ($U\ L^{-1}$)	Detection limit ($U\ L^{-1}$)	Refs
Electrochemistry	40−1990	20.6	[9]
Electrochemistry	0−80	2.18	[10]
Electrochemistry	10−1000	3.29	[11]
Paper-based analysis	5.38−86.1	/	[12]
Fluorescence	1−1500	0.5	This work

Table S3. The results of recovery experiments.

Samples	Spiked ($U\ L^{-1}$)	Measured ($U\ L^{-1}$)	Recovery (%)	RSD (%)
1	10	10.02	100.2	2.56
2	100	98.58	98.6	3.14
3	500	483.5	96.7	4.37
4	1000	1053	105.3	5.02