Supporting Information

Synergistic Coordination-Driven Ratiometric Fluorescent Detection of Anthrax Biomarker Dipicolinic Acid

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1. Experimental

1.1 Materials and reagents

The reagents used for the reaction are all analytical pure, and the reagents used for the test are chromatographically pure, and no further purification is required. $Zn(NO_3)_2 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, 2-methylimidazole, 2,6-dipyridinic acid (DPA), nicotinic acid, lysine, alanine, aspartate, cysteine, ascorbic acid, benzoic acid, isophthalic acid, trimesic acid, phthalate, citric acid and glycine were purchased from China Aladdin Company. Bacillus subtilis was purchased from Wuhan Culture Center, China. The cationic salt solution used is the corresponding chlorine salt or nitrate, and the anionic salt solution is the corresponding potassium salt or sodium salt. The Tris-HCl buffer solution (10 mM, pH 6.5) was prepared by dissolving of Tris in ultrapure water and gradually adjusting it to 6.5 with HCl. Other Tris-HCl buffers of different pH values were prepared in the same way.

The fluorescence spectra were measured using the PerkinElmer FL8500 fluorescence spectrophotometer. The Zeta potential was measured using Omni nano particle size and zeta potential analyzer. The NMR spectra were measured on a Varian INOVA-400 MHz instrument. Tests for UV-visible absorption spectra were performed on a UV-1900i spectrophotometer. FT-IR spectra were recorded using the Thermo Fisher Nicolet-380 Fourier Transform Infrared spectrometer. Powder X-ray diffraction data were collected using the SmartLab SE diffractometer. Transmission electron microscopes and X-ray photoelectron spectrometers were both from Thermo Fisher Scientific. X-ray photoelectron spectroscopy data were collected using a VG Scientific

ESCALab220i-XL photoelectron spectrometer.

1.2 Synthesis of L1

9.00 g of 4-formylbenzoboronic acid ($C_7H_7BO_3$) was dissolved in 80 mL of ethanol within a 500 mL round-bottom flask. After weighing 15.90 g of 2-acetylpyridine on a balance and transferring it to the round-bottom flask, a sodium hydroxide-ethanol solution (13.50 g of sodium hydroxide, 200 mL of ethanol) was added to the flask. The mixture was stirred at 22-24°C for approximately 24 h. Once the reaction was completed, 25% ammonia water (100 mL) was added at 22-24°C, and the mixture was refluxed at 70°C for 15 h. The mixture was cooled to room temperature, and the solid was filtered out. The filter cake was washed with dilute hydrochloric acid to a weakly acidic pH, resulting in a large amount of solid precipitation. The filter cake was washed successively with ethanol and dichloromethane, and the solid was vacuum-dried to obtain a grayish-white solid of 11.24 g, with a yield of 52.31%. ^{1}H NMR (400 MHz, MeOH-d_4) δ 8.68 (ddd, *J*=4.9 Hz, 1.8 Hz, 0.9 Hz, 2H, Ar—H), 8.65(d, *J*=8.9 Hz, 4H, Ar —H), 8.00(td, *J*=7.8 Hz, 1.8 Hz, 2H, Ar—H), 7.91(t, *J*=7.1 Hz, 3H, Ph—H), 7.80(d， *J*=7.9 Hz, 1H, Ph—H), 7.48(ddd, *J*=7.5 Hz, 4.8 Hz, 1.2 Hz, 2H, Ar—H). ^{13}C NMR (100 MHz， DMSO-d_6) δ: 155.74, 154.97, 149.53, 149.41, 138.84, 137.54, 135.20, 125.87, 124.62, 120.99, 117.98. FT-IR (KBr，cm^{-1}) ν: 3396(w), 1600(s), 1490(s), 1378(s), 1073(s), 821(m), 791(s), 735(s).

2. Supplementary Figs S1-S23

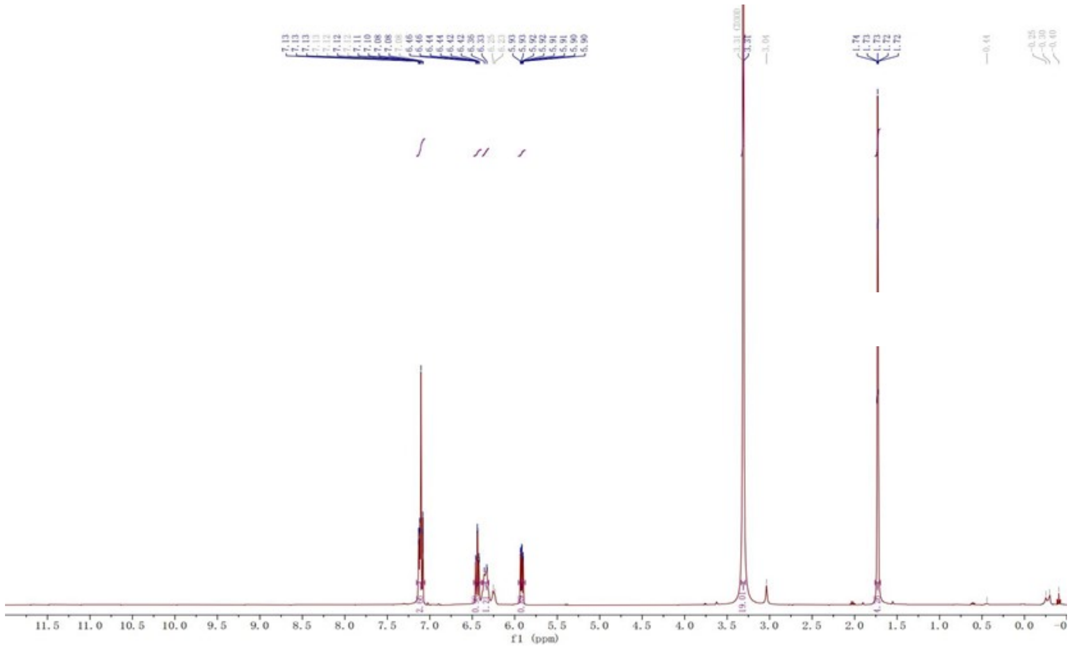

Fig. S1 ^{1}H NMR spectra of L1 in MeOH-d_4.

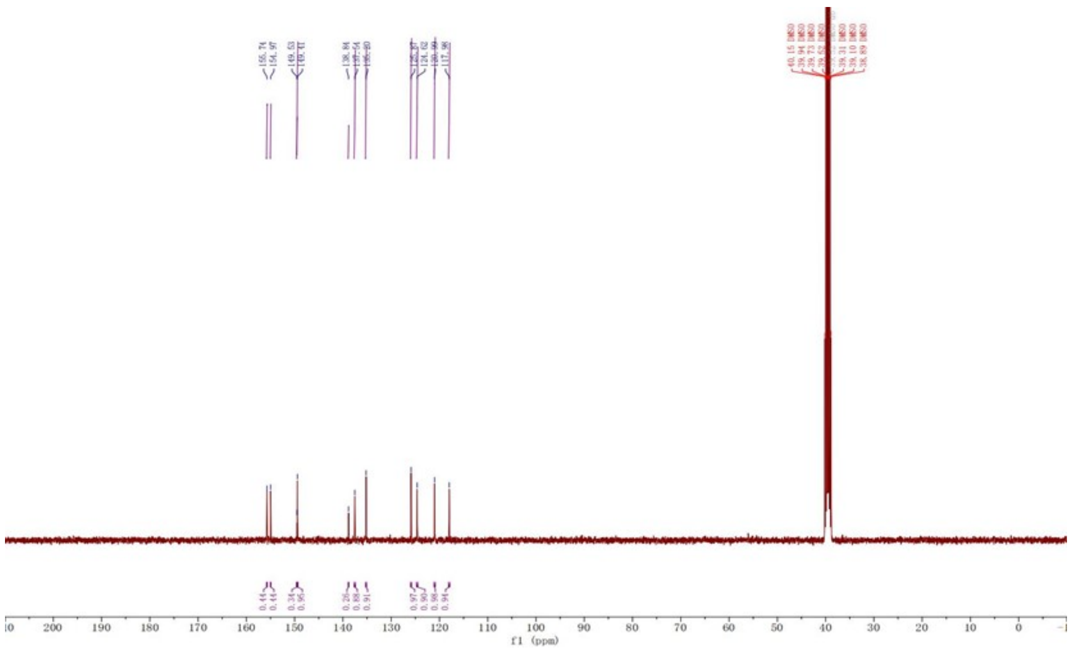

Fig. S2 ^{13}C NMR spectra of L1 in DMSO-d_6.

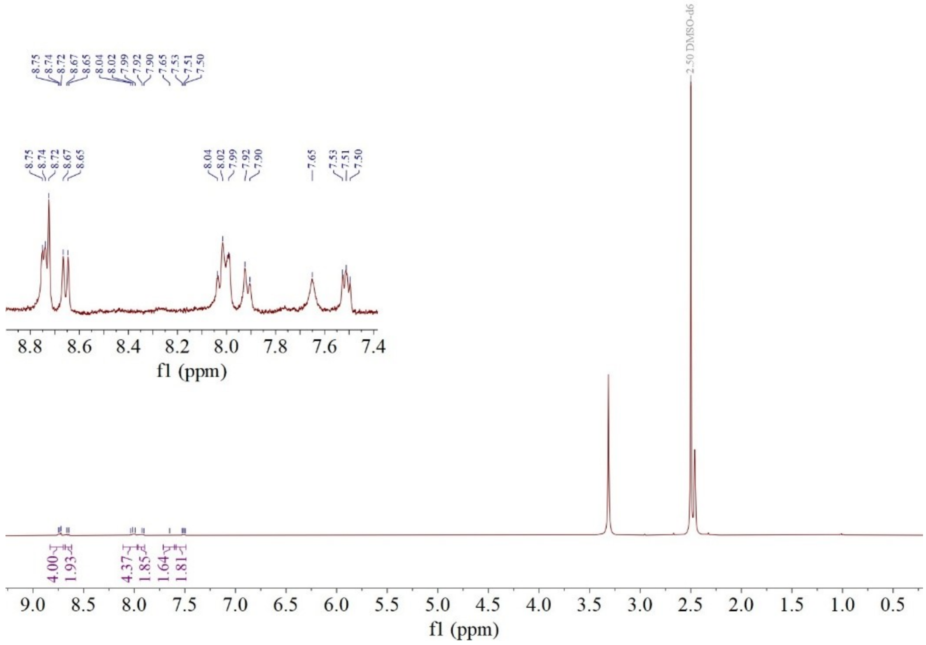

Fig. S3 ^{1}H NMR spectra of Tpy in DMSO-d_6.

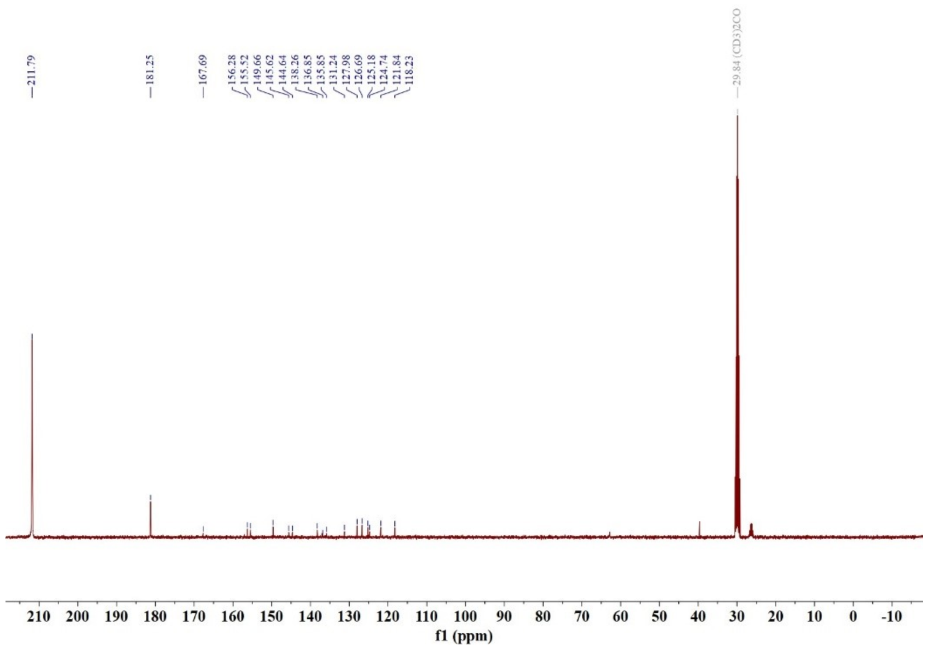

Fig. S4 ^{13}C NMR spectra of Tpy in CD_3COCD_3.

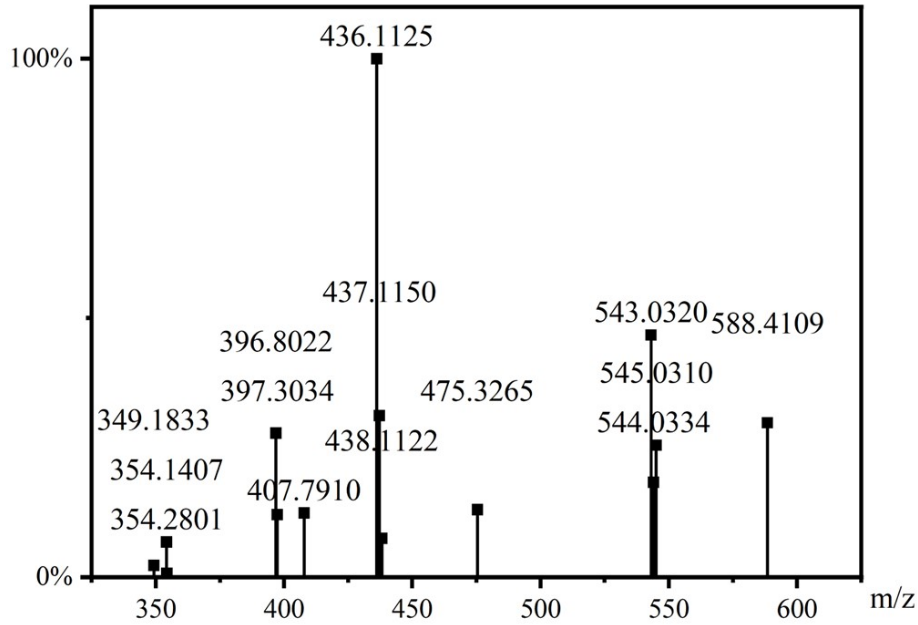

Fig. S5 ESI-MS of the Tpy.

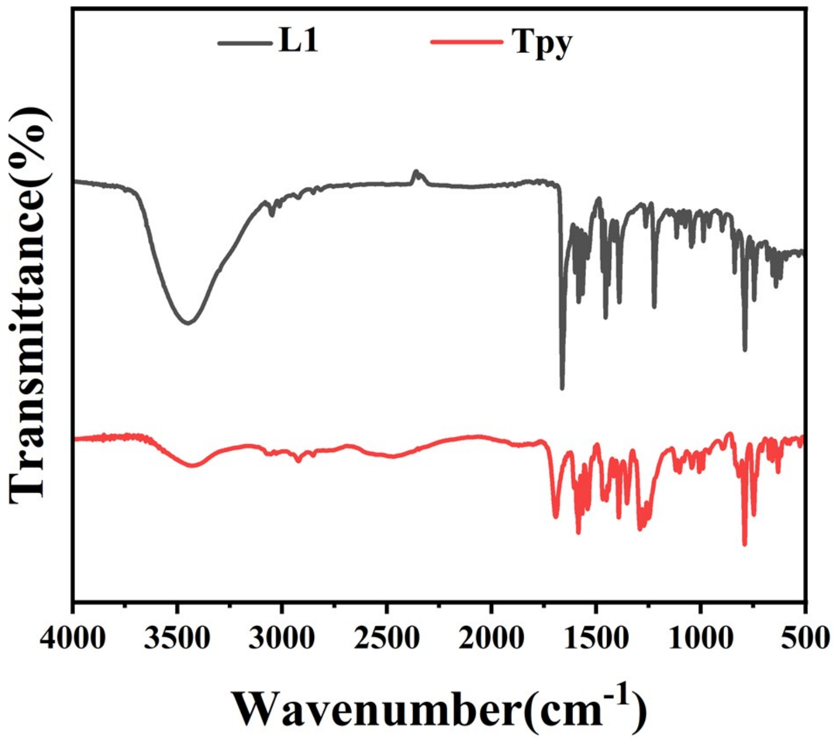

Fig. S6 FTIR spectra of L1 and Tpy.

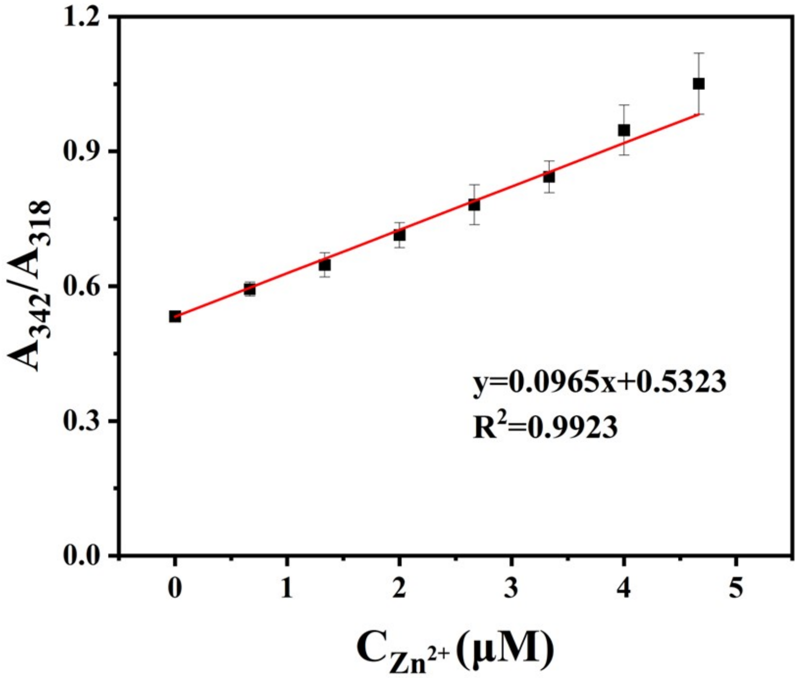

Fig. S7 Fitting curves of A_{342}/A_{318} of Tpy versus Zn^{2+} concentration.

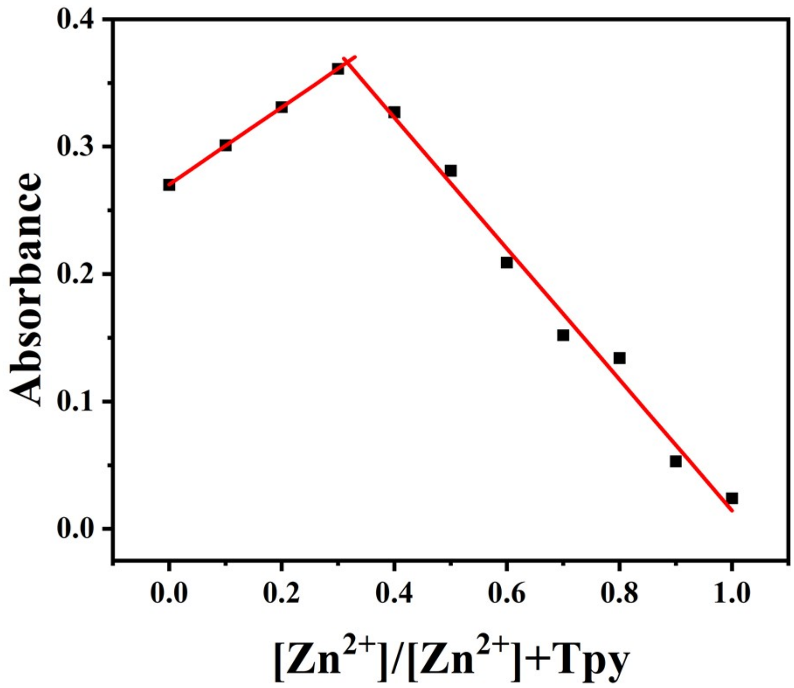

Fig. S8 Job's plots according to the method for continuous variations. The total concentration of Tpy and Zn^{2+} is 100 μM.

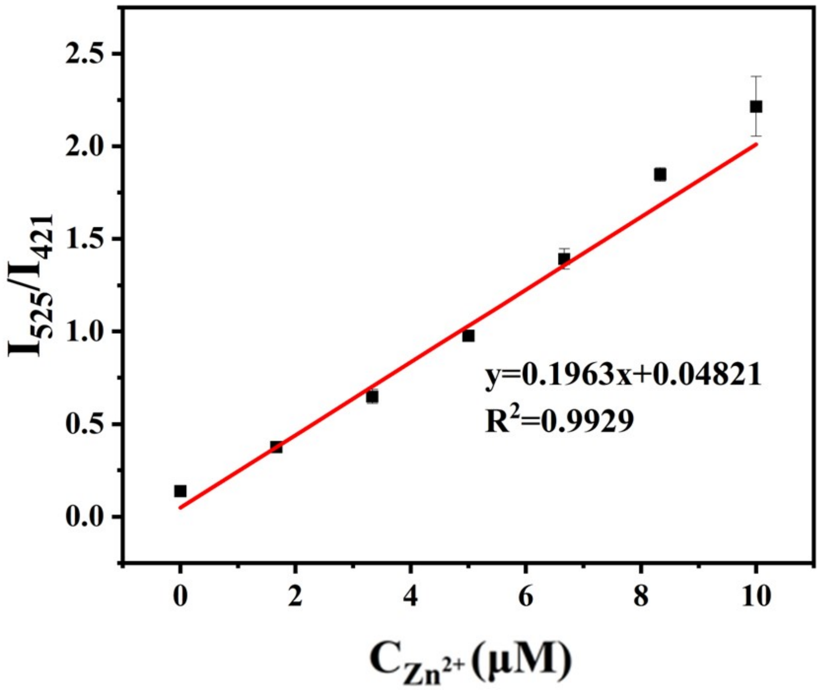

Fig. S9 Fitting curves of I_{525}/I_{421} of Tpy versus Zn^{2+} concentration.

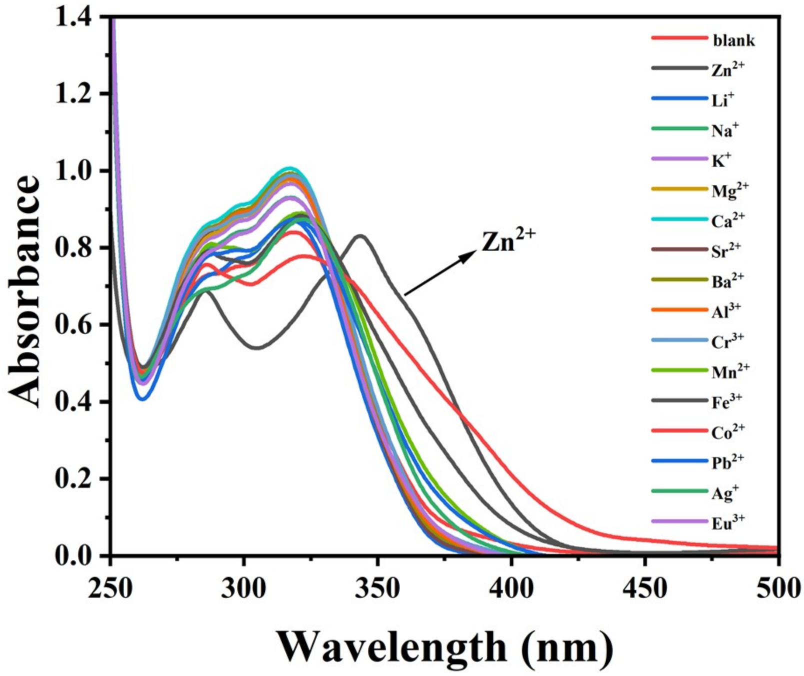

Fig. S10 UV-Vis Absorption spectra of Tpy response to diverse metal cations.

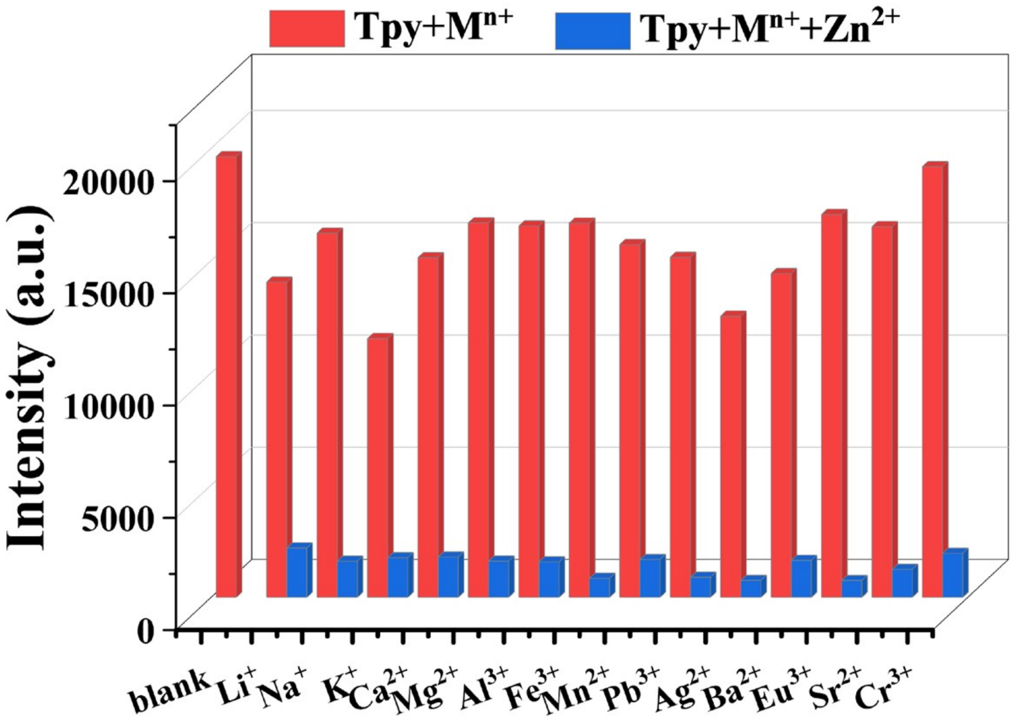

Fig. S11 Competitive tests for the fluorescence responses of Tpy in solution in the presence of Zn^{2+} ions.

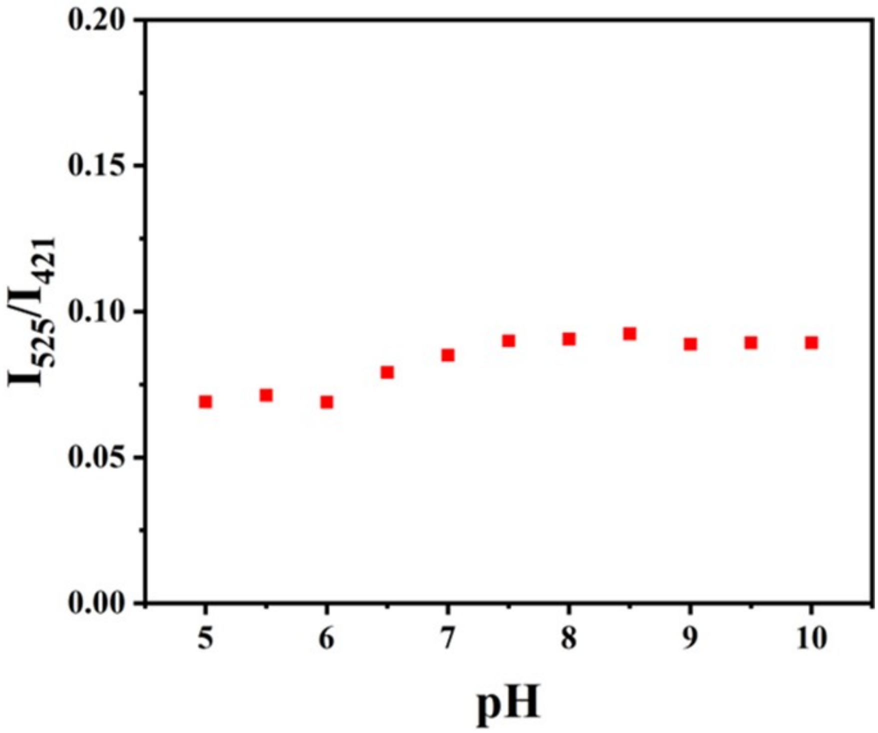

Fig. S12 The dependence of the Tpy with pH (pH = 5.0–10.0).

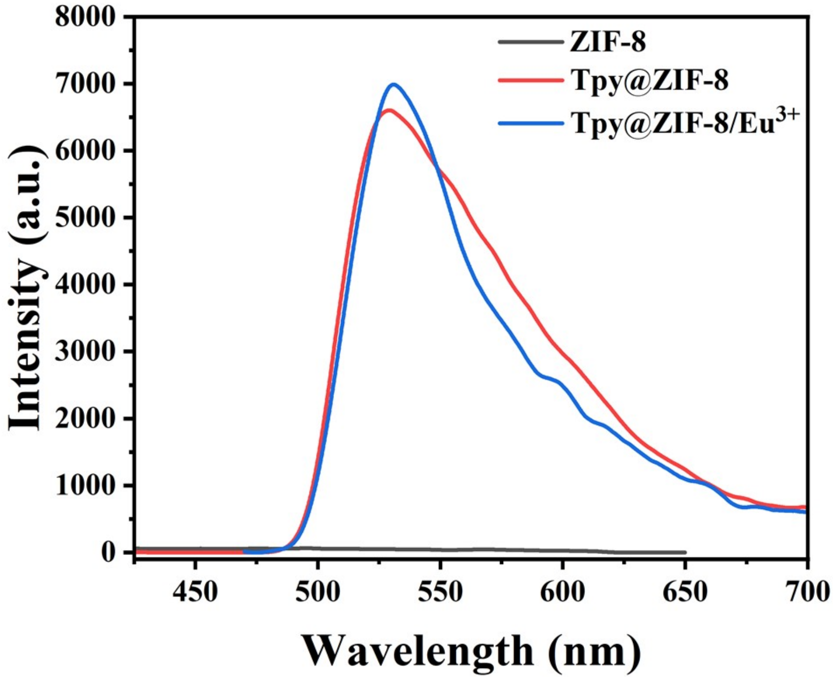

Fig. S13 Fluorescence spectra of ZIF-8 and Tpy@ZIF-8, Tpy@ZIF-8/Eu^{3+}.

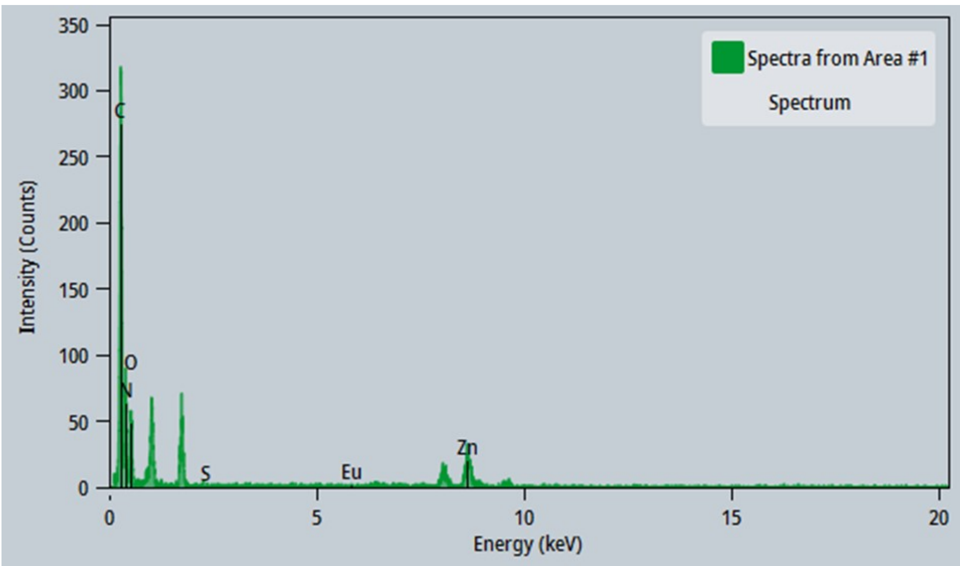

Fig. S14 EDX spectrum of scanning electron microscope for Tpy@ZIF-8/Eu^{3+}.

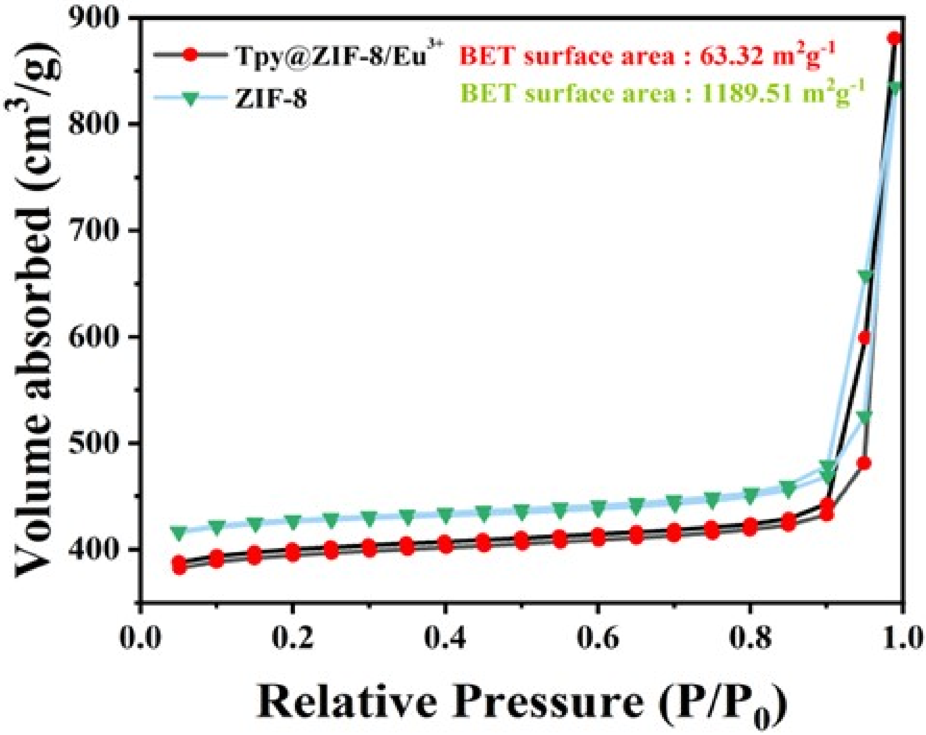

Fig. S15 Nitrogen sorption isotherms of ZIF-8 and Tpy@ZIF-8/Eu^{3+}.

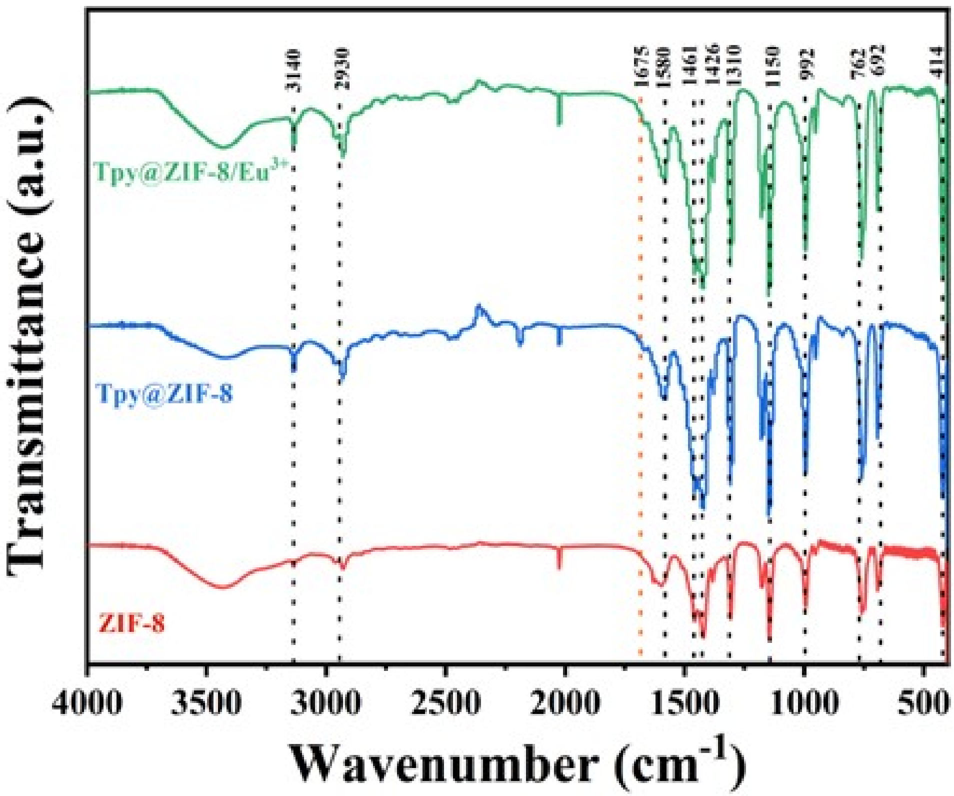

Fig. S16 FTIR spectra of ZIF-8, Tpy@ZIF-8 and Tpy@ZIF-8/Eu^{3+}.

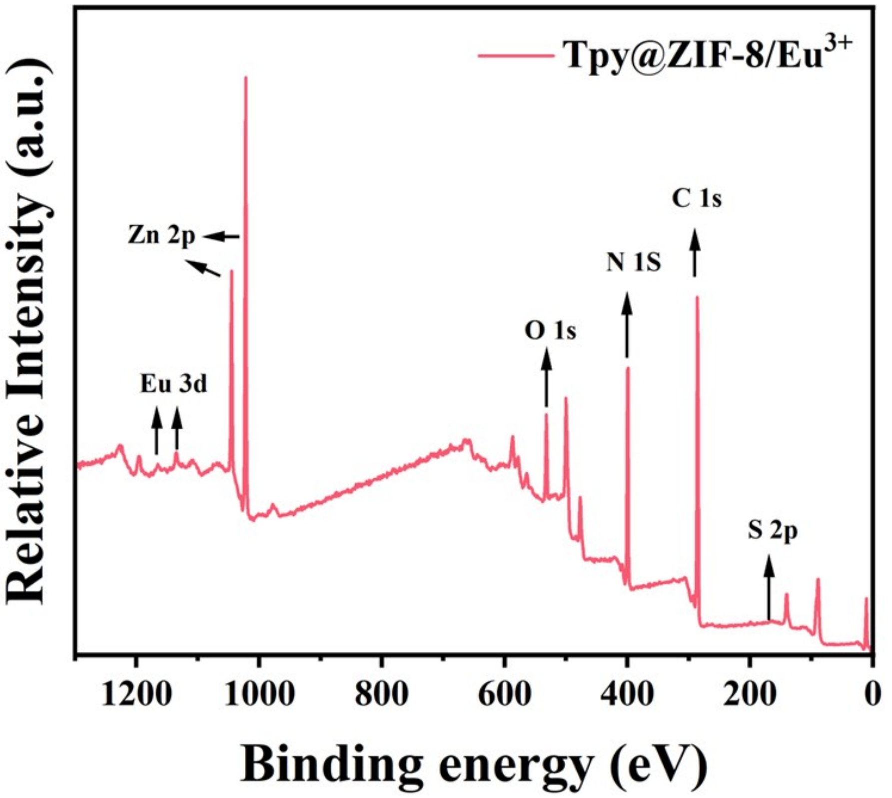

Fig. S17 The XPS full-scan spectrum of the Tpy@ZIF-8/Eu^{3+}.

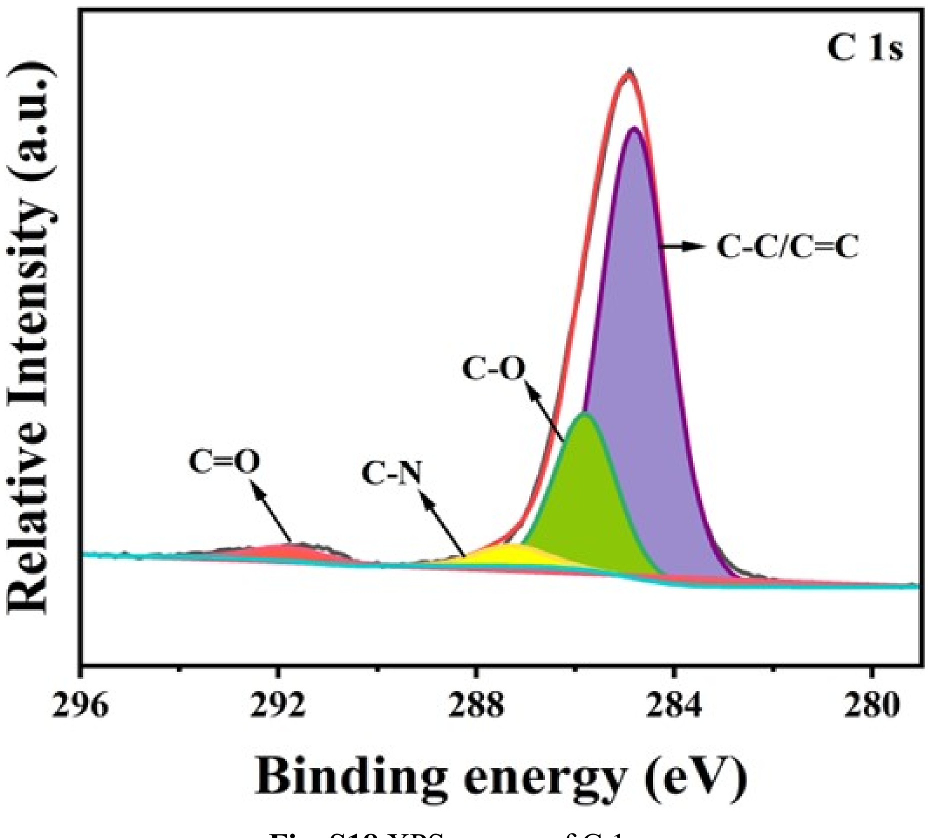

Fig. S18 XPS survey of C 1s.

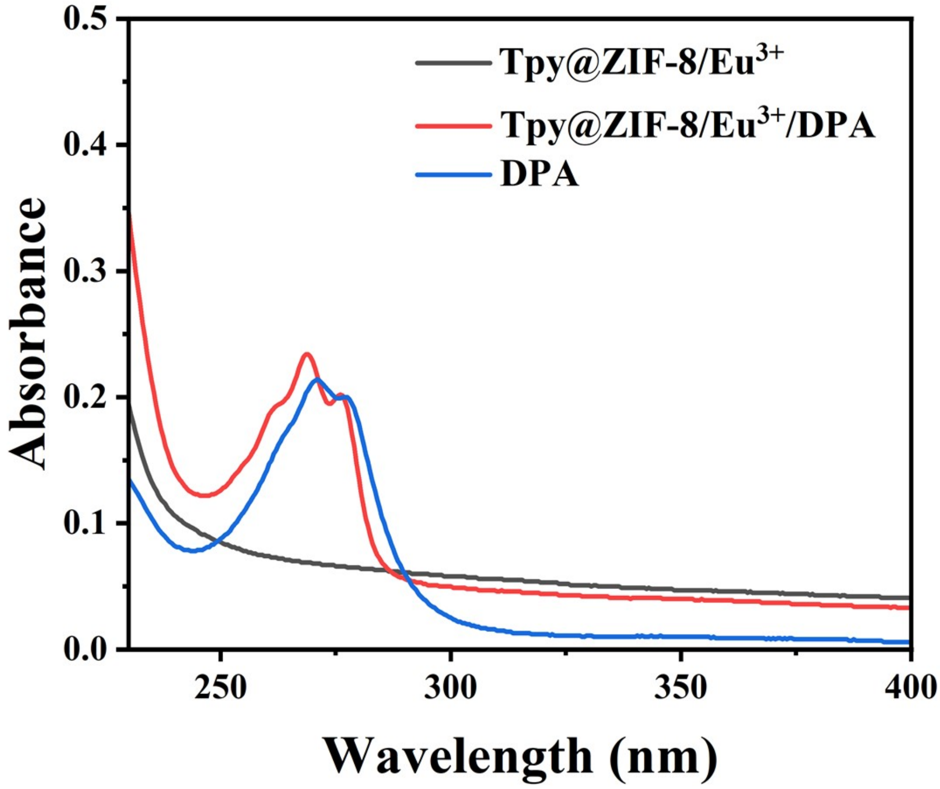

Fig. S19 UV–vis spectra of DPA, Tpy@ZIF-8/Eu^{3+} and Tpy@ZIF-8/Eu^{3+}/DPA.

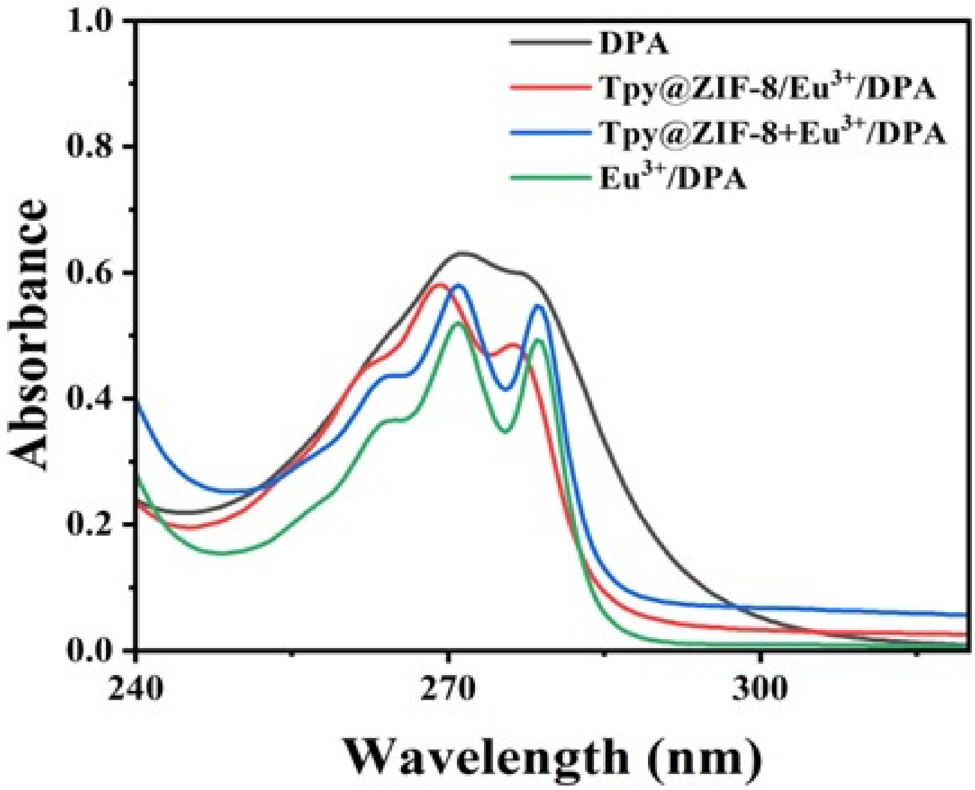

Fig. S20 UV–vis spectra of DPA, Tpy@ZIF-8/Eu^{3+}/DPA, Tpy@ZIF-8+Eu^{3+}/DPA and Eu^{3+}/DPA.

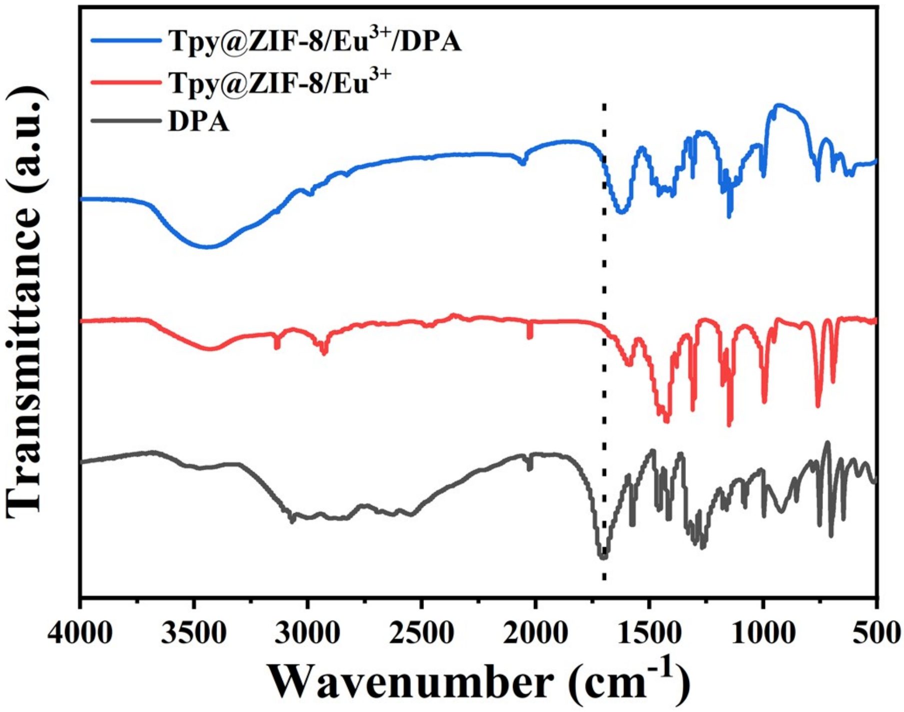

Fig. S21 FTIR spectra of DPA, Tpy@ZIF-8/$Eu^{3+}$and Tpy@ZIF-8/Eu^{3+}/DPA**.**

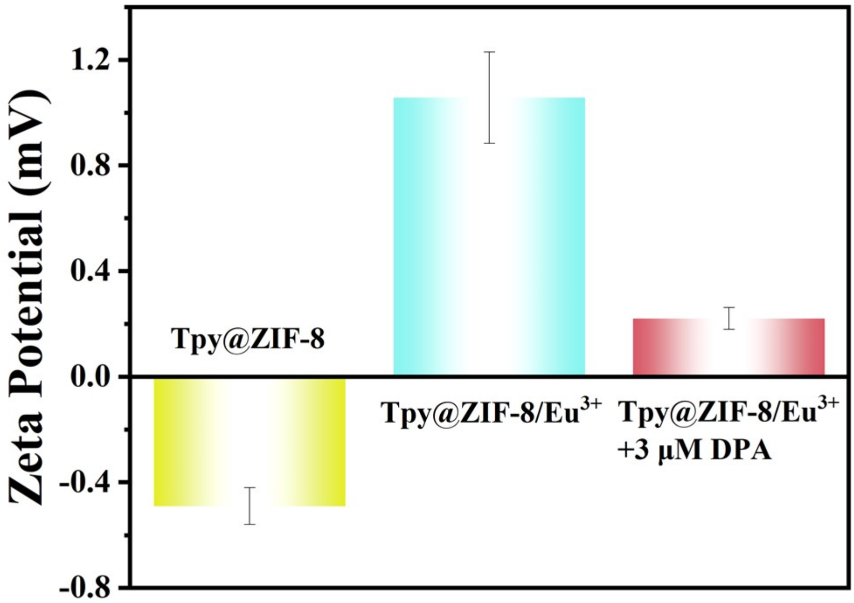

Fig. S22 The zeta potential of Tpy@ZIF-8, Tpy@ZIF-8/Eu^{3+} and Tpy@ZIF-8/Eu^{3+}/DPA.

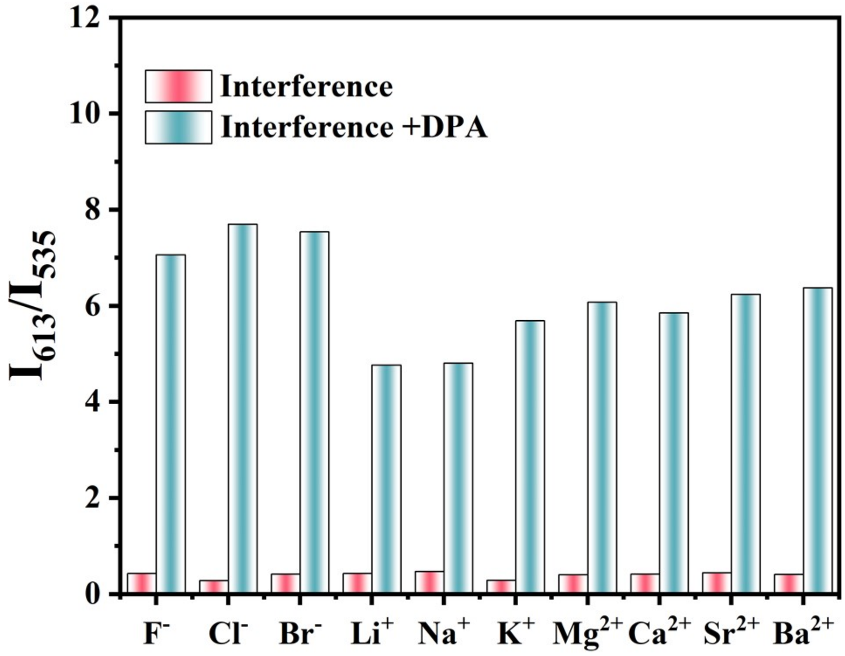

Fig. S23 Tpy@ZIF-8/Eu^{3+} probes to DPA and possible interfering substances.

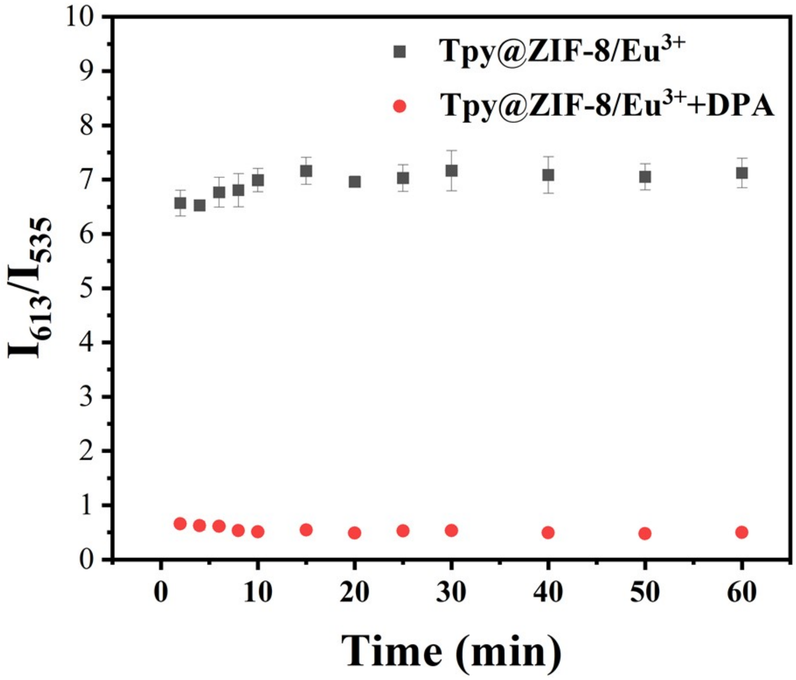

Fig. S24 Effect of reaction time on the fluorescence intensity of Tpy@ZIF-8/Eu^{3+} with DPA.

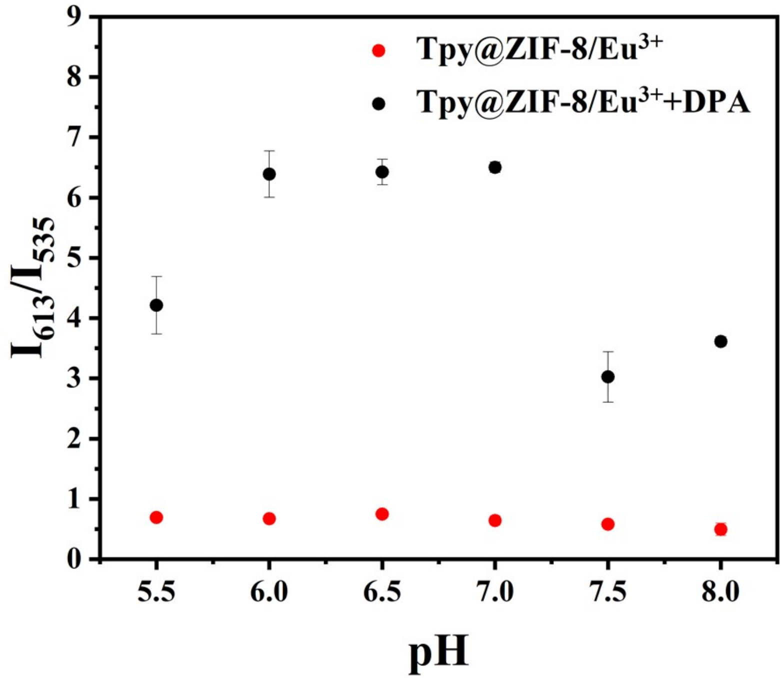

Fig. S25 The dependence of the Tpy@ZIF-8/Eu^{3+} with pH (pH = 5.5–8.0).

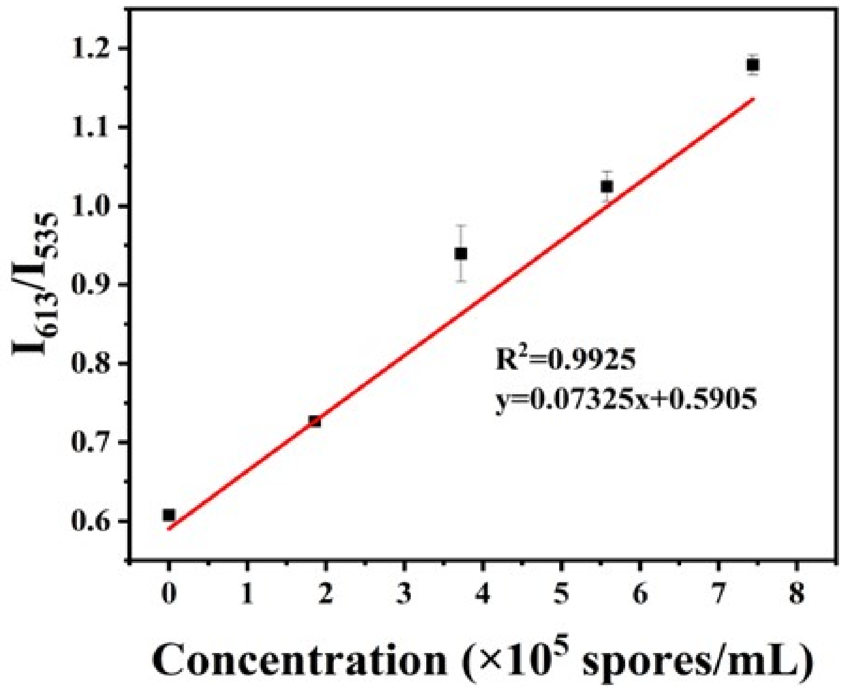

Fig. S26 The ratiometric calibration plot (I_{613}/I_{535}) of the Tpy@ZIF-8/Eu^{3+} sensor as a function of DPA concentration released by B. subtilis spores.

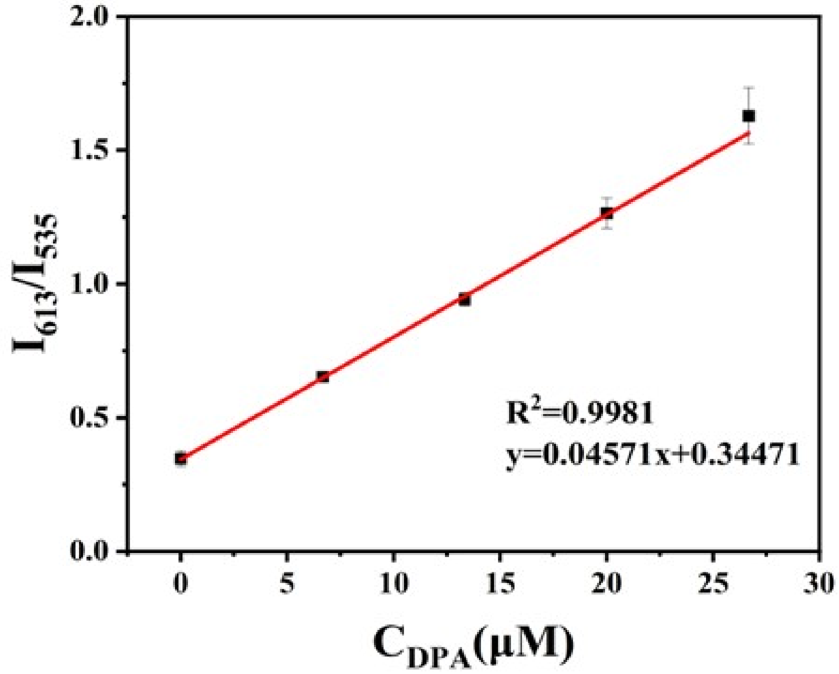

Fig. S27 The linear relationship between the ratio of fluorescence and the concentration of DPA added in seawater.

3. Supplementary Tables S1-S3

Table S1. Comparison of some reported probes on DPA detection.

Material probe	Linear range (μM)	LOD (nM)	References
His@ZIF-8/Tb^{3+}	0-10	20	[1]
Tb-MOF	0–100	2400	[2]
RSPh@EuBTC	0–140	2200	[3]
Ce@Eu@MOF-808	5–30	670	[4]
Eu-MOF@Tb	0.2–10	60	[5]
Eu-doped ZIF-8	0.1–150	31	[6]
$Tb_{0.875}Eu_{0.125}$-Hddb	0-100	849	[7]
Zn-CD@Eu	0-55	530	[8]
Tb^{3+}/JUC-505-COOH	0.5-120	600	[9]
UiO-66-(COOH)2-NH2	0-35	25	[10]
Tpy@ZIF-8/Eu^{3+}	0-60	37.55	This work

Table S2. Results of the analysis of Bacillus subtilis spores in real samples using Tpy@ZIF-8/Eu^{3+}

Method	Spores Added	Found	Recovery (n=3,%)	RSD (n=3,%)
Fluorescent	9.30×10^4	8.60×10^4	92.47	3.15
	1.86×10^5	1.74×10^5	93.55	1.44
	2.79×10^5	2.63×10^5	94.27	1.05

Table S3. RSD datas (n=3) for the relative intensities of Tpy@ZIF-8/Eu^{3+} in seawater

Method	Added (μM)	Found (μM)	Recovery (n=3,%)	RSD (n=3,%)
Fluorescent	10.00	9.32	93.20	2.72
	20.00	19.34	96.70	1.67
	30.00	28.09	93.63	4.98

Reference

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