Supporting Information

Dual-mode detection of 2,6-pyridinedicarboxylic acid based on the enhanced peroxidase-like activity and fluorescence property of novel Eu-MOF

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1. Experimental section

1.1 Materials and reagents

Europium(III) chloride hexahydrate ($EuCl_3 \cdot 6H_2O$), 2-methylimidazole ($C_4H_6N_2$, 99%), 2, 6-pyridinedicarboxylic acid (DPA), 3, 3′, 5, 5′-tetramethylbenzidine (TMB), urea, 2, 4-dichlorophenoxyacetic acid (2, 4-D) were bought from Sigma-Aldrich. Albumin from bovine serum (BSA), hydrogen peroxide (H_2O_2, 30%), glutathione, L(+)-glutamic acid, D-(+)-glucose, horseradish peroxidase (HRP) and tertiary butanol (TBA) were purchased from Sangon Biological Engineering Technology & Services Company Ltd. (Shanghai, China). All other reagents were of analytical grade. Ultrapure water was obtained through a Millipore Milli-Q water purification system (Billerica), which had an electric resistance >18.25 MΩ.

1.2 Apparatus

The fluorescence spectra were measured on the FluoroMax-4 spectrofluorometer (HORIBA Jobin Yvon, Inc., NJ). The excitation and emission slits were set at 5.0 nm with a 900 V PMT voltage. The UV spectra were recorded using a UV-2700 UV-visible spectrophotometer (Shimadzu Instrument, Inc., Japan). The crystal phases of particles were obtained by the scanning electron microscope (Bruker, Germany). Transmission electron microscope (TEM) was performed on a field emission high resolution 2100F transmission electron microscope (JEoL, Japan). The Fourier transform infrared (FT-IR) spectroscopy were measured by spectrometer. The thermo gravimetric analysis (TGA) was measured from the TG 209 F1 Libra thermal gravimetric analyzer (Netzsch, Germany). The crystal phases of particles were

determined by D8-advance X-ray diffraction (Bruker, Germany). The zeta potential was measured on the Malvern Zetasizer Nano ZS90 at room temperature. The N_2 sorption isotherms were collected using ASAP-2460 surface area/pore size analyzer (Micromeritics, Shanghai).

1.3 The selectivity and specificity of Eu-MOF

The selectivity of Eu-MOF was evaluated by detecting the fluorescence intensity or the absorbance peaks at 652 nm in the presence of different interferents. The concentrations of interferents were 2.5 times higher than DPA in the reaction. Moreover, the specificity of Eu-MOF was evaluated by measuring the fluorescence intensity or the absorbance peaks at 652 nm in the presence of Eu-MOF and one of the interferents.

1.4 The practical detection of DPA by Eu-MOF

In a typical assay, three practical samples of tap water, orange juice and serum were respectively diluted twenty times. In a typical fluorescence assay, 10 μL of the diluted sample, 13 μL of Eu-MOF (12.5 mg/mL), 2 μL of DPA (5 mM), 175 μL of H_2O were reacted for 5 min at 37℃. The fluorescence intensity was measured under the excitation wavelength of 275 nm. In a typical colorimetric assay, 10 μL of the diluted sample, 7 μL of Eu-MOF (12.5 mg/mL), 3 μL of DPA (5 mM), 10 μL of TMB solution (5 mM), 10 μL of H_2O_2 (0.1 M), 37 μL of HAc-NaAc buffer (0.1 M, pH 4) and 73 μL of sterile water were incubated for 10 min at 25℃. Then the absorbance at 650 nm was detected.

2. Results and discussion

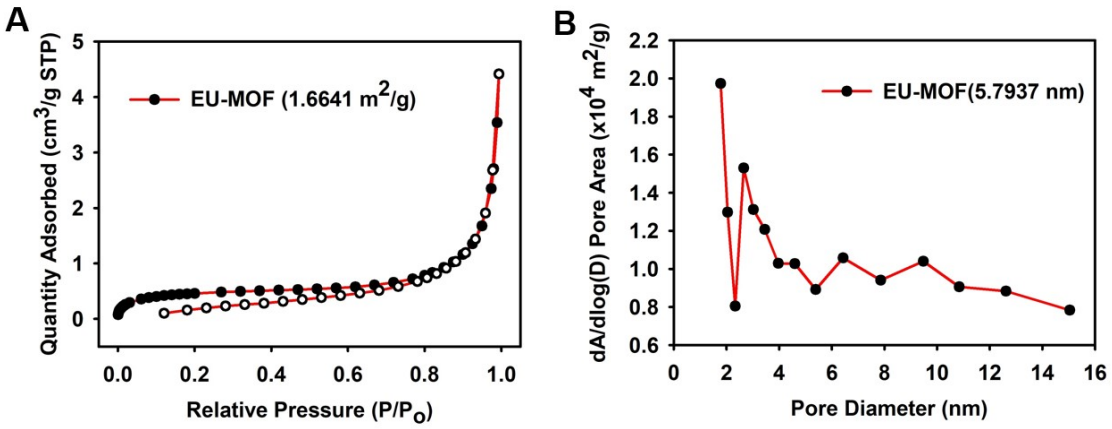

Fig. S1 Nitrogen adsorption analysis isotherms of Eu-MOF.

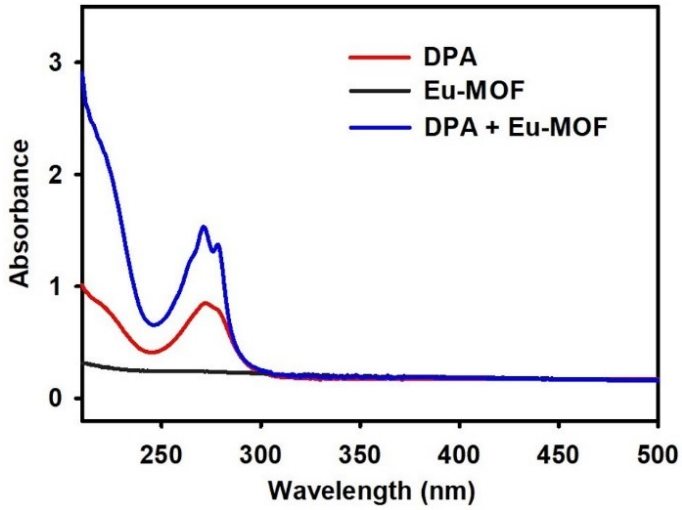

Fig. S2 The UV-vis absorption spectra of 0.63 mg/mL Eu-MOF, 200 μM DPA, 0.63 mg/mL Eu-MOF and 200 μM DPA.

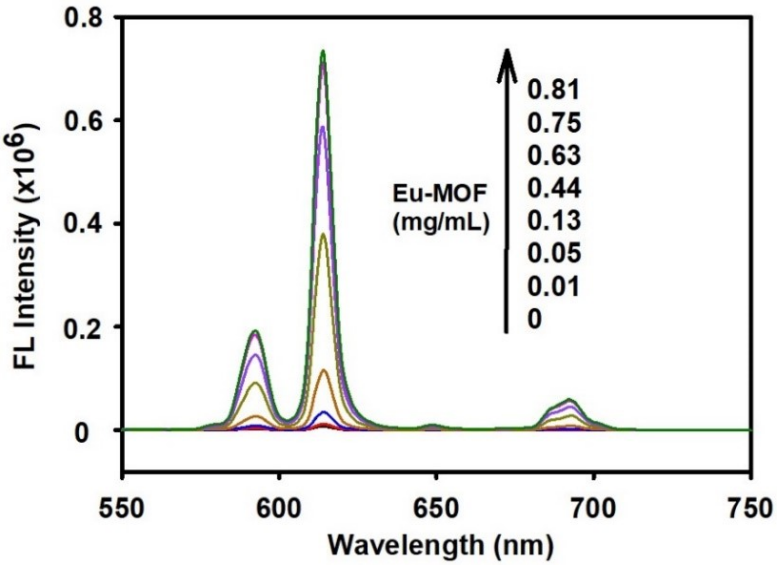

Fig. S3 The concentrations optimization of Eu-MOF for DPA fluorescence detection from 0 to 0.81 mg/mL, with the excitation wavelength at 275 nm.

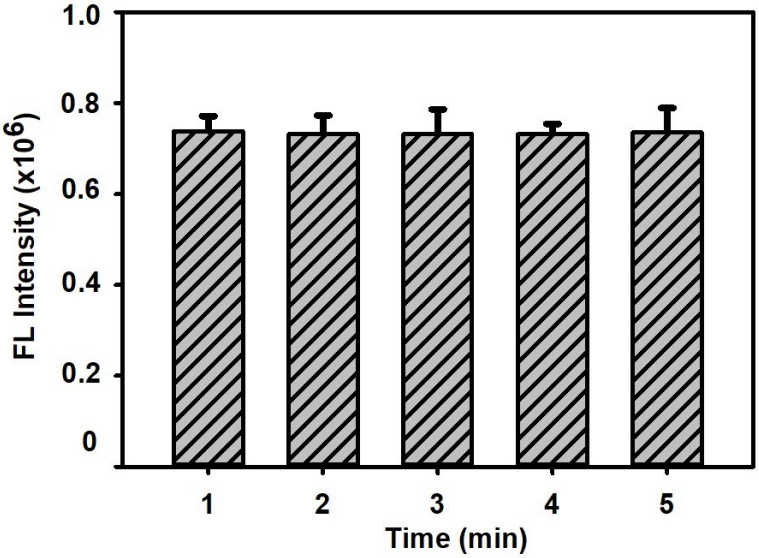

Fig. S4 The time optimization of DPA fluorescence detection, 200 μM DPA and 0.63 mg/mL Eu-MOF were incubated for different time, with the excitation wavelength at 275 nm. Error bars were obtained from three parallel experiments and represented the standard deviation, λ=614 nm.

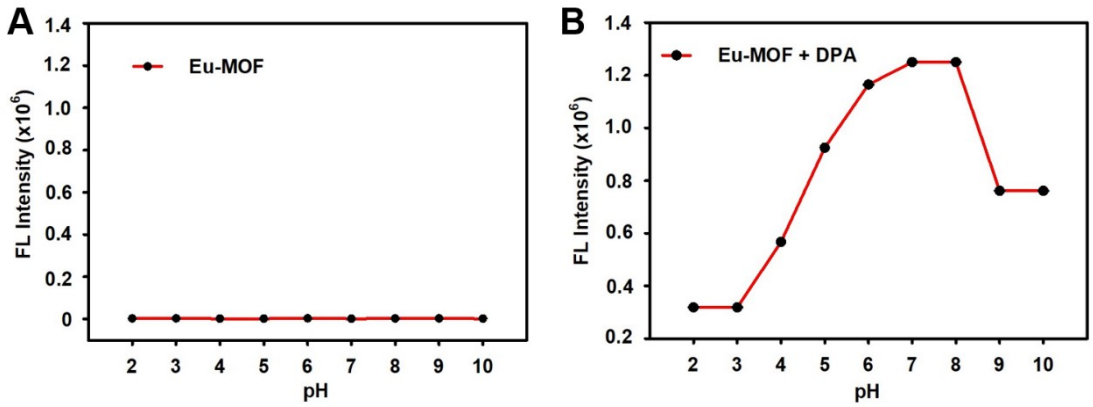

Fig. S5 The effect of pH (2, 3, 4, 5, 6, 7, 8, 9, 10) on the fluorescence intensity of (A) 0.63 mg/mL Eu-MOF, (B) 0.63 mg/mL Eu-MOF and 200 μM DPA. The error bars represented the standard deviation of three parallel measurements.

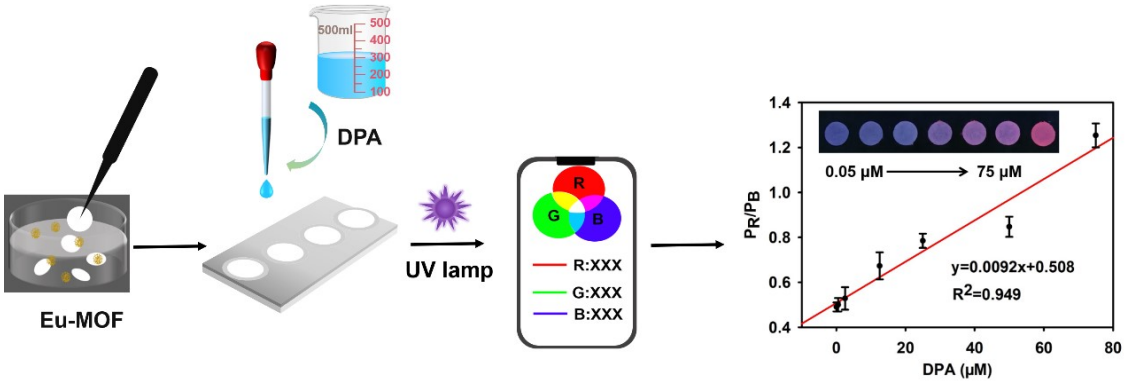

Fig. S6 The corresponding linear relationship of R/B intensity versus DPA concentration, insert: the fluorescence color image. Error bars represented the standard deviation of three parallel experiments.

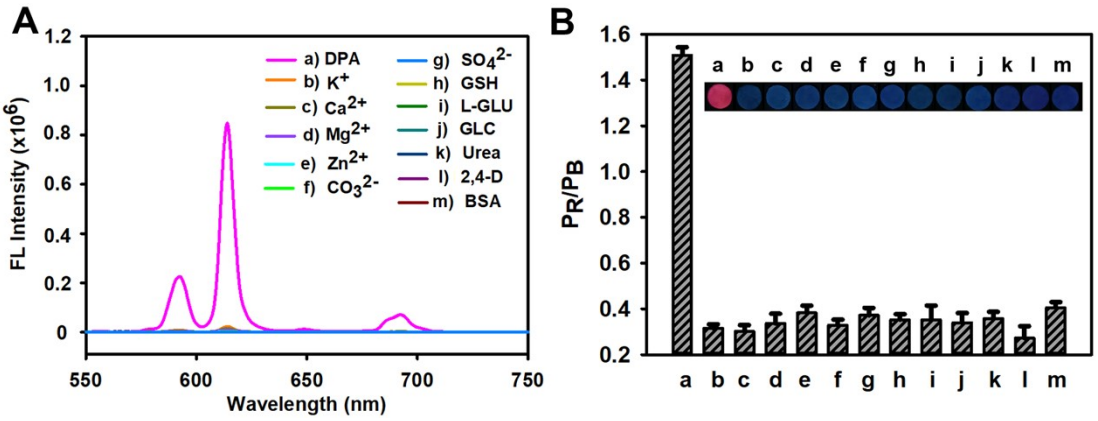

Fig. S7 The selectivity of DPA fluorescence detection, with the excitation wavelength at 275 nm, (A) the fluorescence spectrogram, (B) the corresponding R/B intensity, insert: the fluorescence image. The concentrations of interferents of K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, CO_3^{2-}, SO_4^{2-}, GSH, L-GLU, GLC, Urea, 2,4-D and BSA respectively were 500 μM and the DPA was 200 μM. Error bars represented the standard deviation of three parallel experiments.

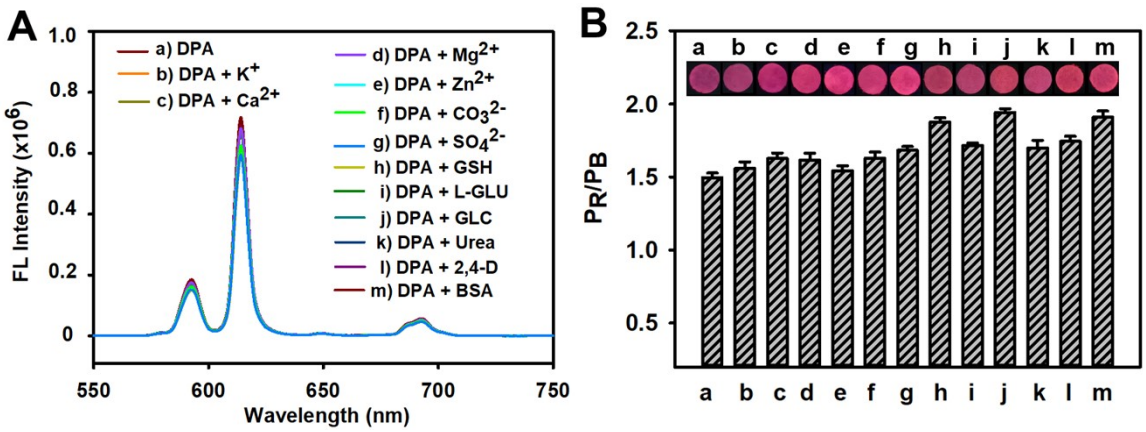

Fig. S8 The specificity of DPA fluorescence detection, with the excitation wavelength at 275 nm, (A) the fluorescence spectrogram, insert: the fluorescence image, (B) the corresponding R/B intensity. The concentrations of interferents of K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, CO_3^{2-}, SO_4^{2-}, GSH, L-GLU, GLC, Urea, 2,4-D and BSA respectively were 500 μM and the DPA was 200 μM. Error bars represented the standard deviation of three parallel experiments.

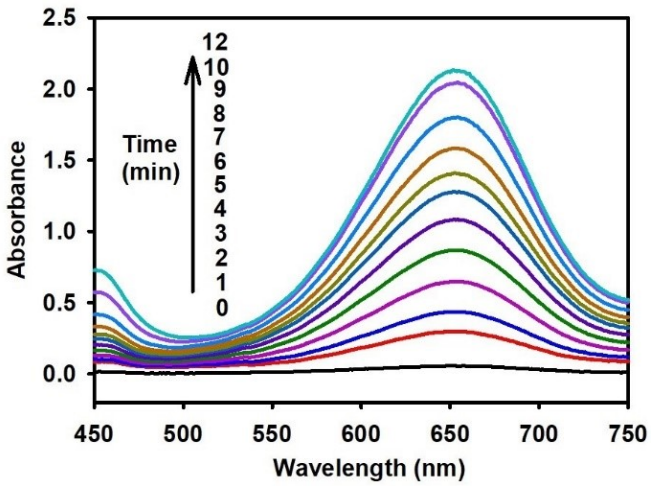

Fig. S9 The time optimization of DPA colorimetric detection, 0.58 mg/mL Eu-MOF, 500 μM DPA, 0.33 mM TMB and 6.67 mM H_2O_2 were incubated for different time at pH 4.

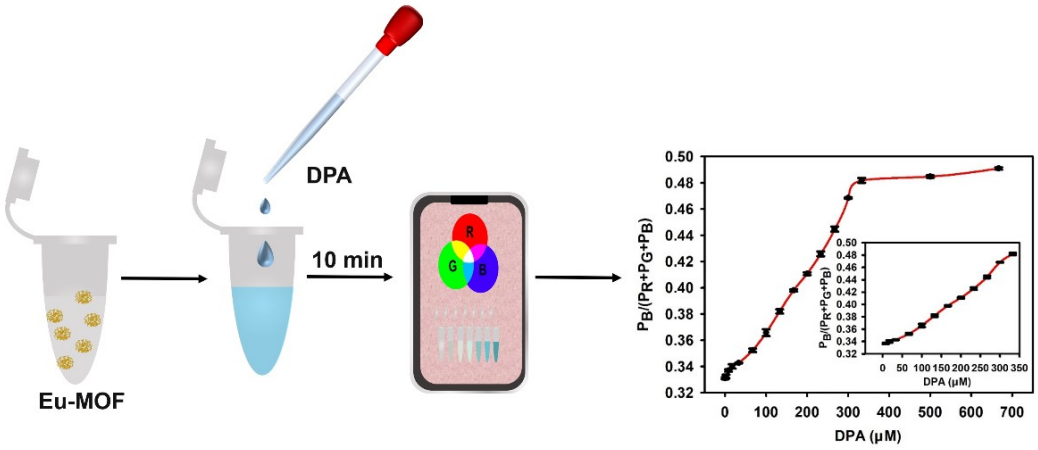

Fig. S10 The corresponding linear relationship of B/C intensity versus DPA concentration. Error bars represented the standard deviation of three parallel experiments.

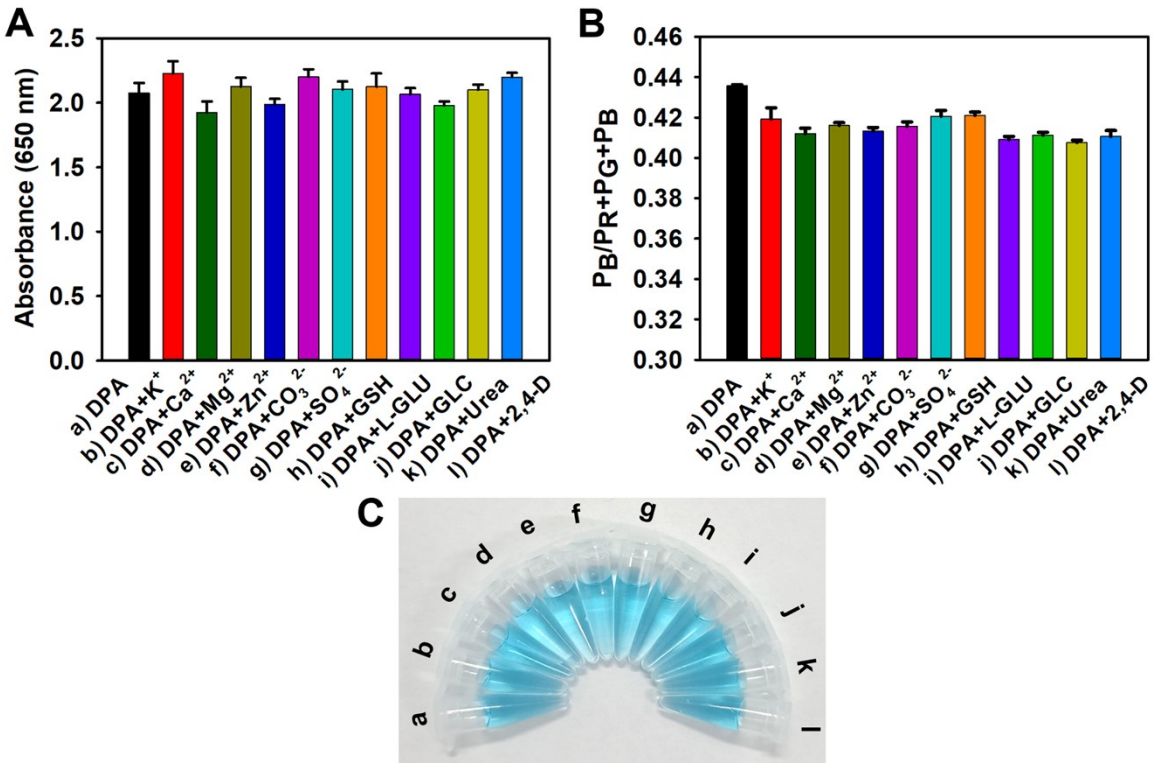

Fig. S11 The specificity of DPA colorimetric detection. (A) The UV-vis absorbance. (B) The corresponding RGB calculations. Error bars were obtained from three parallel experiments and represented the standard deviation. The concentrations of interferents of K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, CO_3^{2-}, SO_4^{2-}, GSH, L-GLU, GLC, Urea and 2,4-D respectively were 1.25 mM and the DPA was 500 μM. (C) The corresponding colorimetric images.