Supporting Information

Dimensional Regulation of Lanthanide Metal-Organic Frameworks and Their Applications in Bacteria Detection

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1. Reagents and Chemicals

Nitroreductase (NTR), nicotinamide adenine dinucleotide (NADH) and glucose oxidase (GOx) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Europium nitrate ($Eu(NO_3)_3·6H_2O$), europium chloride hexahydrate ($EuCl_3·6H_2O$), nitroterephthalic acid (BDC-NO_2), pyridine-2,6-dicarboxylic acid (DPA), glucose (Glu), glutathione (GSH), glycine (Gly), arginine (Arg), and bovine serum albumin (BSA) were obtained from Aladdin (Shanghai, China). Metal salts including NaCl, KCl, $CaCl_2$ and $MgCl_2$ were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Ethanol, ethylene glycol and dimethyl sulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). *S. aureus* (ATCC 6538) and *P. aeruginosa* (ATCC 27853) were purchased from American Type Culture Collection (ATCC), USA. The buffer system used in this work was 10 mM HEPES (pH 7.4). All chemical and solvent were used directly without further purification, and the aqueous solution used in this experiment was prepared with ultrapure water (resistance >18 MΩ·cm).

2. Instrumentation and Characterization

The morphology and size characterization images were recorded on JEM-2100PLUS transmission electron microscope (TEM, JEOL, Japan) operated at 200 kV. The elemental mapping images were recorded on scanning electron microscope (SEM, Carl Zeiss AG, Germany) operated at 10 kV. All UV-vis absorption spectra were measured on a UV-2600 spectrophotometer (Shimadzu, Suzhou). All the fluorescence spectra were recorded by using a F-7000 spectrometer (Hitachi, Japan) with excitation wavelength of 270 nm, excitation and emission slits width of 5 nm, and PMT voltage of 700 V. All the Fourier Transform Infrared (FT-IR) spectra were measured on a Nicolet iS5 Fourier transform infrared spectrometer (Thermo Fisher, USA), with the range of 400 cm^{-1} to 4000 cm^{-1}. The Powder X-ray diffraction (PXRD) spectra were carried out a MiniFlex600 X-ray powder diffractometer (Rigaku, Japan). Atomic force microscopy (AFM) dimension icon (Bruker, USA). X-ray photoelectron spectroscopy (XPS) was obtained using a Nexsa X-ray photoelectron spectrometer (Thermo Scientific, USA).

3. Experimental section

Preparation of single crystal of Eu-BDC-NO_2/DPA ($Eu_3(DPA)_3$(BDC-NO_2)$(H_2O)_7·Cl$)

Facile one-pot method was developed to prepare single crystal of Eu-BDC-NO_2/DPA. Briefly, europium chloride hexahydrate ($Eu(Cl_3)_3·6H_2O$) (0.5 mmol, 183.2 mg) was firstly dissolved into 1.0 mL of ultra-pure water. 2-nitroterephthalic acid (BDC-NO_2)

(0.3 mmol, 63.3 mg) and pyridine-2,6-dicarboxylic acid (DPA) (0.6 mmol, 100.3 mg) were dissolved into 5.0 mL ethanol with 27 μL of triethylamine. Then, the two solutions were mixed in a 15 mL PTFE reactor and heated to 200 ℃ for 24 h. The mixture was cooled to room temperature and filtered, then cube colorless crystals were obtained. The crystals were washed with ethanol and dried in air. Anal. Calc. for Eu-BDC-NO_2/DPA ($C_{29}H_{26}ClEu_3N_4O_{25}$): C, 26.35%; H, 1.98%; N, 4.23%. Found: C, 26.36%; H, 1.94%; N, 4.15%.

To further investigate the crystal structure of 1D Eu-BDC-NO_2/DPA nanofibers, the cube single crystal of Eu-BDC-NO_2/DPA was dispersed into ultra-pure water for 12 h to obtain 1D line single crystal of Eu-BDC-NO_2/DPA. Then resulted 1D Eu-BDC-NO_2/DPA performed next study.

Preparation of 2D Eu-BDC-NO_2/DPA nanosheet

The 2D Eu-BDC-NO_2/DPA nanosheet was prepared similar to the single crystal of Eu-BDC-NO_2/DPA with more convenient conditions. Briefly, europium nitrate solution (0.05 mol/L) was firstly prepared by dissolving 0.25 mmol $Eu(NO_3)_3 \cdot 6H_2O$ into 5 mL of ultra-pure water. The mixture solutions of BDC-NO_2 and DPA with different molar ratios (1:1, 1:1.5, 1:2 and 1:3) were prepared by dissolving both of them (0.5 mmol) into ethanol (15 mL) with 278 μL of triethylamine. After mixing the two solutions, the resulted mixture was stirred gently at 40 ℃ for 2 hours. Being cooled to room temperature, the product was obtained by centrifugation, and then washed three times with ethanol and ultra-pure water in turn. Finally, the product was dried overnight in an oven at 40 ℃.

Preparation of 1D Eu-BDC-NO_2/DPA nanofiber

5 mg of ground powder of 2D Eu-BDC-NO_2/DPA was dispersed into 10 mL ultra-pure water. After standing in room temperature for 10 min, 1D Eu-BDC-NO_2/DPA nanofibers were obtained.

Fluorescence detection of NTR

Briefly, the 1D Eu-BDC-NO_2/DPA solution (50 μL, 0.5 mg/mL), the NADH solution (100 μL, 500 μmol/L), the NTR sample solution (100 μL) with different concentration were mixed into a 1.0 mL tube. After being adjusted to 1.0 mL with HEPES buffer solution (pH 7.4), the mixture was incubated at 37 ℃ for 60 min, then being transferred into a quartz cell and performed the fluorescence measurement under λ_{Ex} 270 nm with slits of 5 nm.

Fluorescence detection of the activity of NTR in bacteria

S. aureus (ATCC 6538) and *P. aeruginosa* (ATCC 27853) were cultured for 12 h in Luria-Bertani (LB) medium at 37 ℃, then the bacterial strains were harvested and dispersed in LB medium with an OD_{600} of 0.5-0.7. The aliquot of the cell suspension

(1.0 mL) was treated with 50 μL 1D Eu-BDC-NO_2/DPA (5 mg/mL) with or without NTR inhibitor of dicoumarol (0.2 mmol/L) in microcentrifuge tube and incubated at 37 ℃ for 2 h, then performed the fluorescence spectra measurement.

Confocal imaging of bacteria

The bacteria of *S. aureus* and *P. aeruginosa*, were cultured with same conditions as the above section. After that, 4.5 mL individual aliquot was treated with 0.5 mL of 1D Eu-BDC-NO_2/DPA solution (0.5 mg/mL), and incubated at 37 ℃ for 2 h. Fluorescence images were performed on a ZEISS LSM 880 Confocal Microscope.

4. Single Crystal X-ray Crystallography

A suitable single crystal was carefully selected under an optical microscope glued to a thin glass fiber. The single-crystal X-ray diffraction data for Eu-BDC-NO_2/DPA was performed on SMART APEX CCD diffractometer with graphite-monochromated Mo *Kα* radiation at 298 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-2018/3 program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to C atoms were located at geometrically calculated positions. And we located the H-atoms from the difference-Fourier Maps for all the water molecules and refined their positions under the restraints of DFIX and DANG. CCDC 2291212 for Eu-BDC-NO_2/DPA contains the supplementary crystallographic data for the structure. Crystal data collection are summarized in Table S1.

5. Structure of single crystal of Eu-BDC-NO_2/DPA

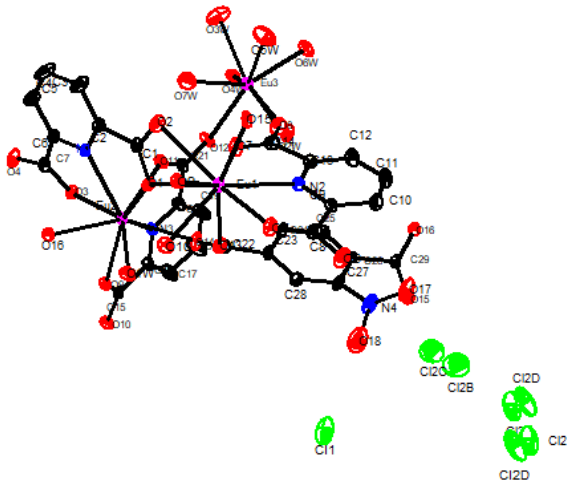

Figure S1 *ORTEP* plot showing the crystallographically asymmetric unit of Eu-BDC-NO_2/DPA. Thermal elliposoids are given at the 30% probability level. Hydrogen atoms are not shown.

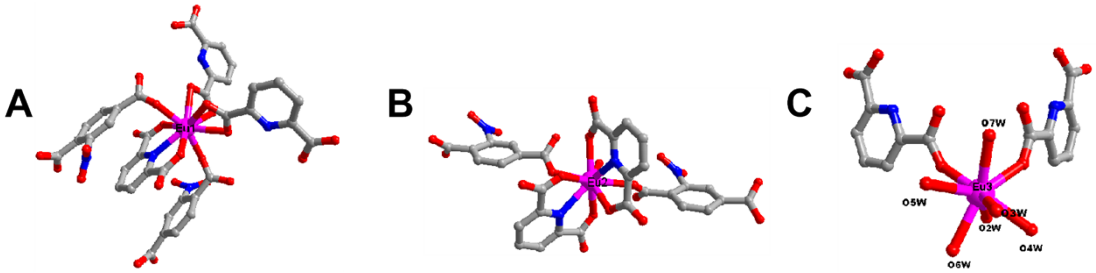

Figure S2 The coordination environments of Eu^{3+} ions in Eu-BDC-NO_2/DPA.

6. Characterization of Eu-BDC-NO_2/DPA

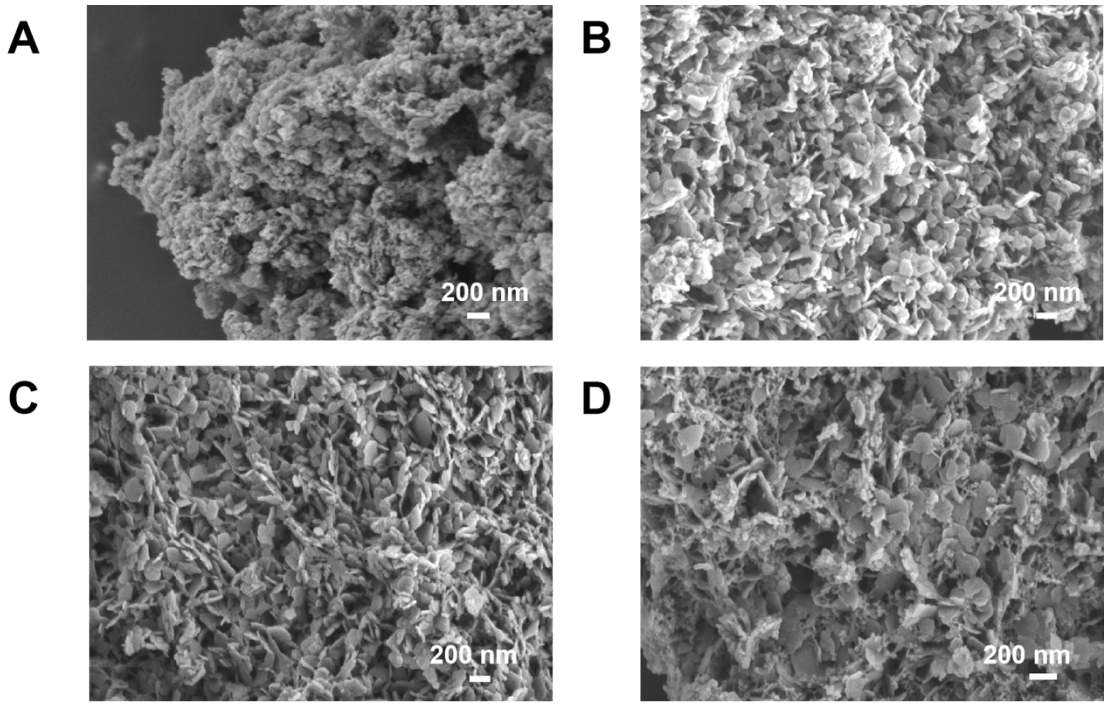

Figure S3 SEM images of Eu-BDC-NO_2/DPA with different ratios of BDC-NO_2:DPA: (A)1:1 (B)1:1.5 (C)1:2 (D)1:3.

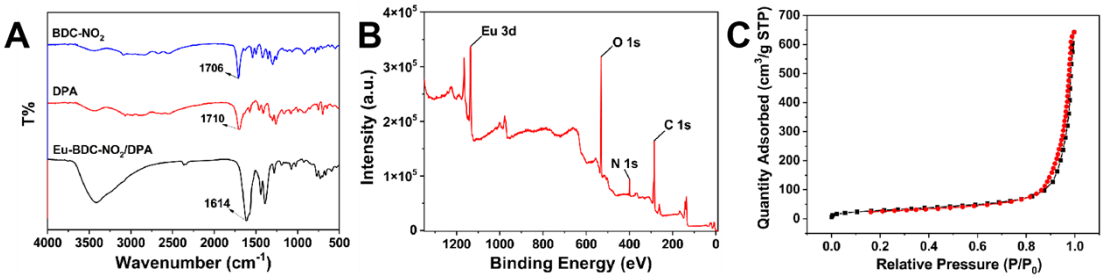

Figure S4 (A) FT-IR spectra of BDC-NO_2, DPA and Eu-BDC-NO_2/DPA (1:2). (B) XPS diagram and (C) N_2 adsorption (black line) and desorption (red line) isotherm of Eu-BDC-NO_2/DPA (1:2). Brunauer-Emmett-Teller (BET) surface area of Eu-BDC-NO_2/DPA was determined to be 94.58 m^2/g.

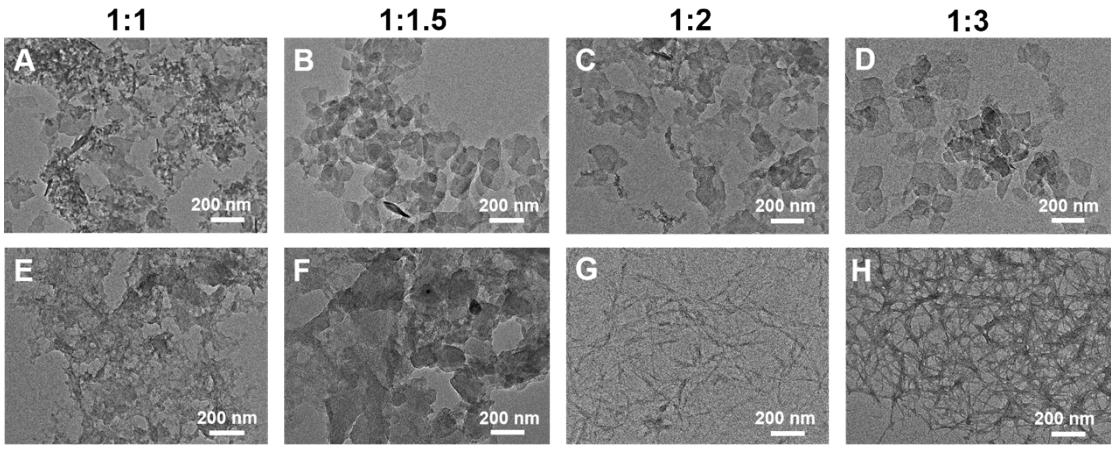

Figure S5 TEM images of Eu-BDC-NO_2/DPA with different BDC-NO_2/DPA ratios dispersed into (A-D) methanol and (E-H) water.

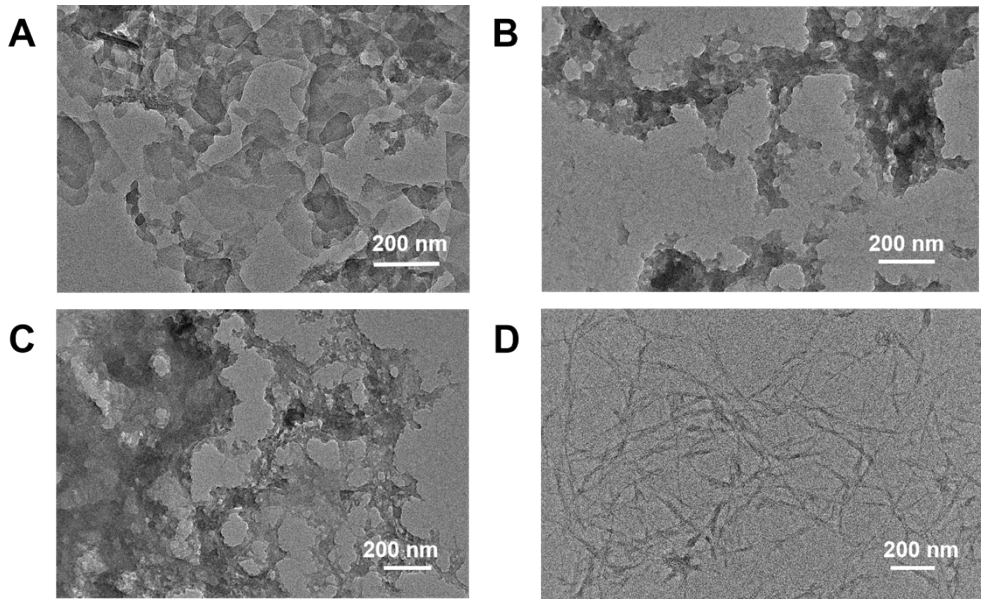

Figure S6 TEM images of Eu-BDC-NO_2/DPA (1:2) dispersed into (A) methanol, (B) ethylene glycol, (C) dimethyl sulfoxide and (D) aqueous solution.

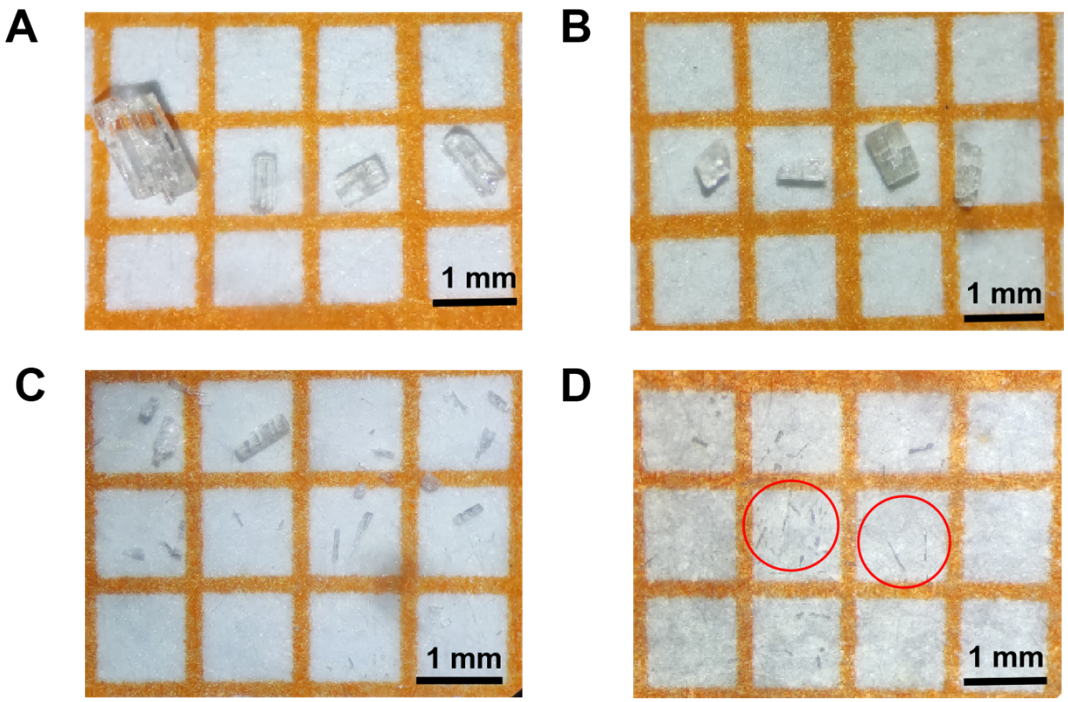

Figure S7 Photographs of the crystal of Eu-BDC-NO_2/DPA (1:2) soaked in water for (A) 0 h, (B) 2 h, (C) 6 h and (D) 12 h at room temperature.

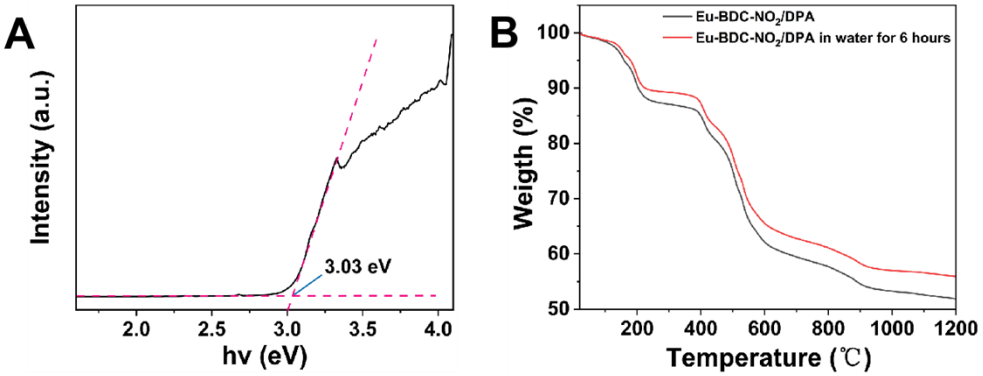

Figure S8 (A) The UV-Vis absorption spectra and (B) Thermogravimetric (TG) curves of Eu-BDC-NO_2/DPA (1:2) before dispersed into aqueous solution (black line) or dispersed into aqueous solution for 6 h (red line).

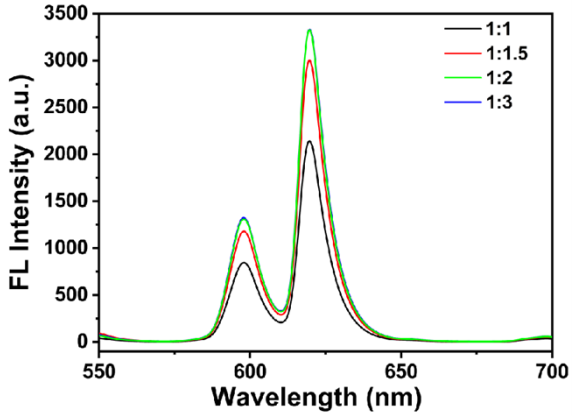

Figure S9 Emission spectra of Eu-BDC-NO_2/DPA with different ratios of BDC-NO_2/DPA.

7. Solution testing

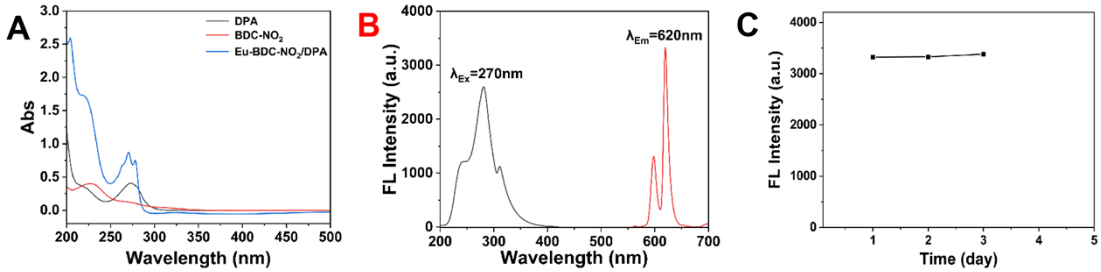

Figure S10 (A) UV-visible absorption spectra of BDC-NO_2, DPA and Eu-BDC-NO_2/DPA. (B) The excitation (Ex) spectra of Eu-BDC-NO_2/DPA with λ_{Em} = 620 nm (black) and the emission (Em) spectra of Eu-BDC-NO_2/DPA with λ_{Ex} = 270 nm (red). (C) Fluorescence intensity of 620 nm of 0.5 mg/mL Eu-BDC-NO_2/DPA aqueous solution stored in room temperature for three days under the excitation of 270nm.

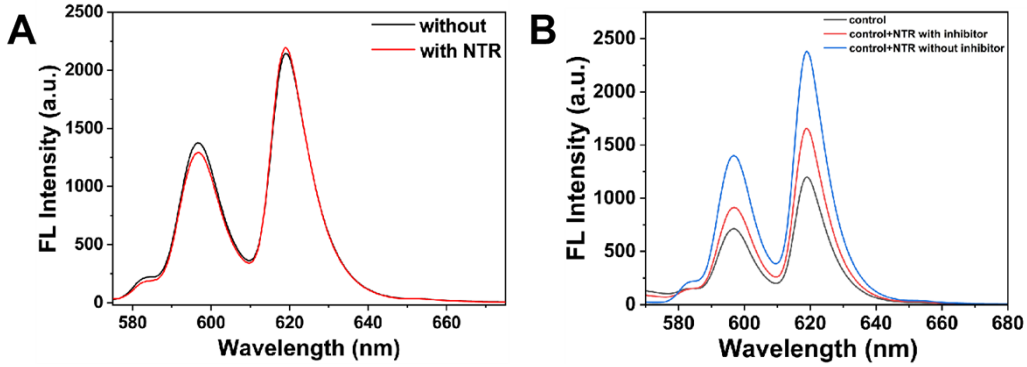

Figure S11 Fluorescence emission spectra (λ_{Ex} = 270 nm) of different reaction systems. (A) Eu-BDC-NO_2/DPA (0.5 mg/mL) with NTR (1.0 mg/mL) (red line) or without NTR (black line); (B) Eu-BDC-NO_2/DPA (0.5 mg/mL) with NADH (0.5 mmol/L) as a blank control (black line), control +NTR (1.0 mg/mL) with inhibitor (red line) or without inhibitor (blue line). All the reactions were performed in pH 7.4 HEPES buffer at 37 ℃ for 1 h.

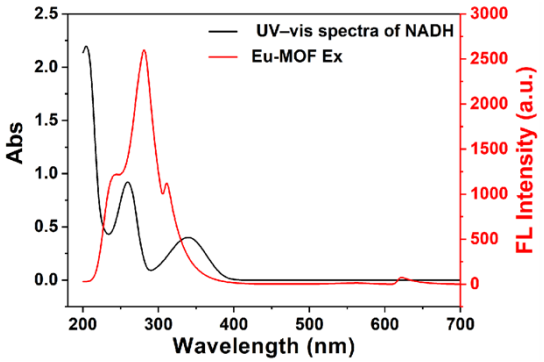

Figure S12 The UV-vis absorption spectrum of NADH and the fluorescence excitation spectrum of Eu-BDC-NO_2/DPA.

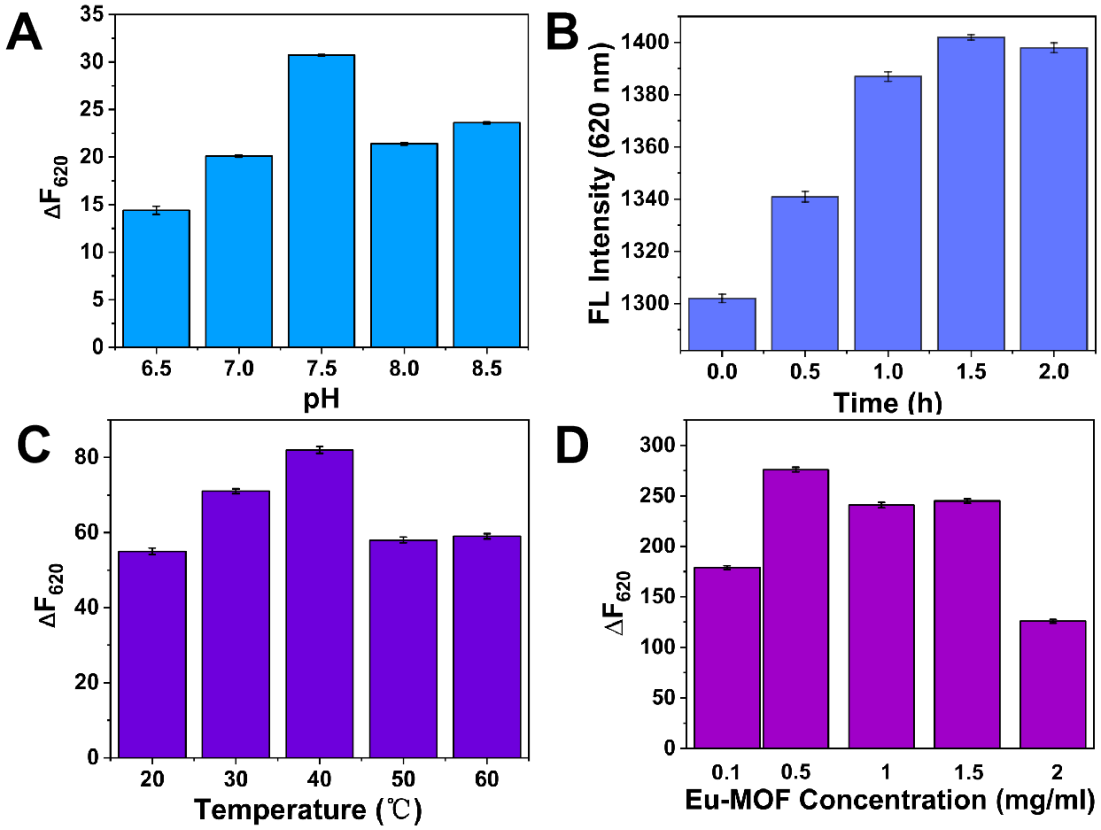

Figure S13 The condition optimizations of NTR detection experiment: (A) pH of buffer (B) reaction time (C) reaction temperature (D) Eu-BDC-NO_2/DPA concentration.

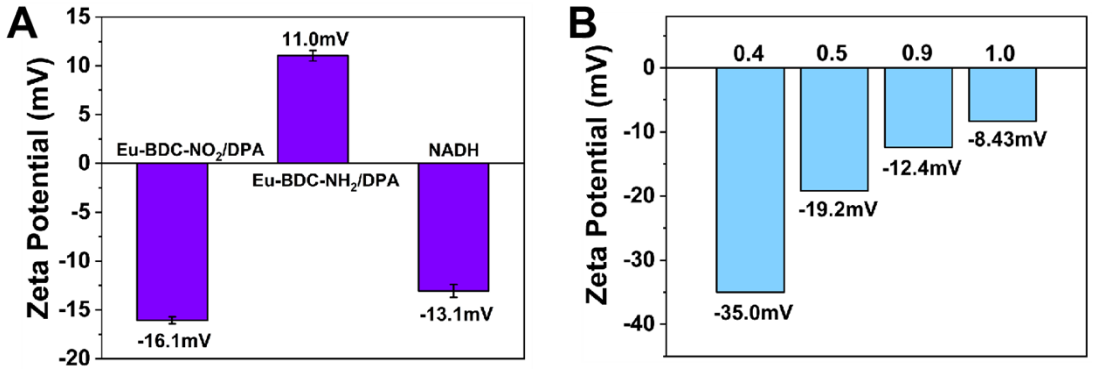

Figure S14 (A) Zeta potentials of Eu-BDC-NO_2/DPA, Eu-BDC-NH_2/DPA and NADH. (B) Zeta potentials of Eu-BDC-NO_2/DPA system in the presence of different concentrations of NTR sample solution (0.4, 0.5, 0.9, and 1.0 μg/mL).

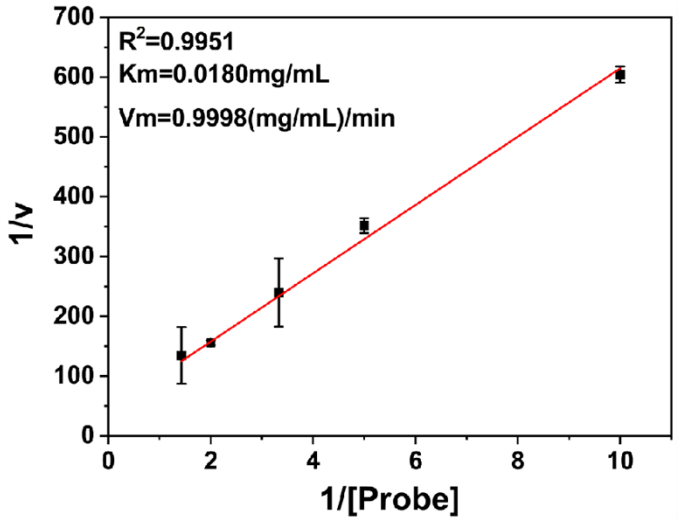

Figure S15 Enzyme-catalyzed reaction. The Michaelis-Menten equation was described as: $V=V_{max}S/(K_m+S)$, where V is reaction rate, S is the Eu-BDC-NO_2/DPA concentration (substrate), and K_m is the Michaelis constant. Conditions: 1.0 mg/mL NTR, 0.5 mmol/L NADH and different concentrations of Eu-BDC-NO_2/DPA. Reaction at each concentration was repeated three times, and the error bars represent standard deviations. Points were fitted using a linear regression model (correlation coefficient R^2=0.9951).

8. Cytotoxicity test of Eu-BDC-NO_2/DPA in live bacteria

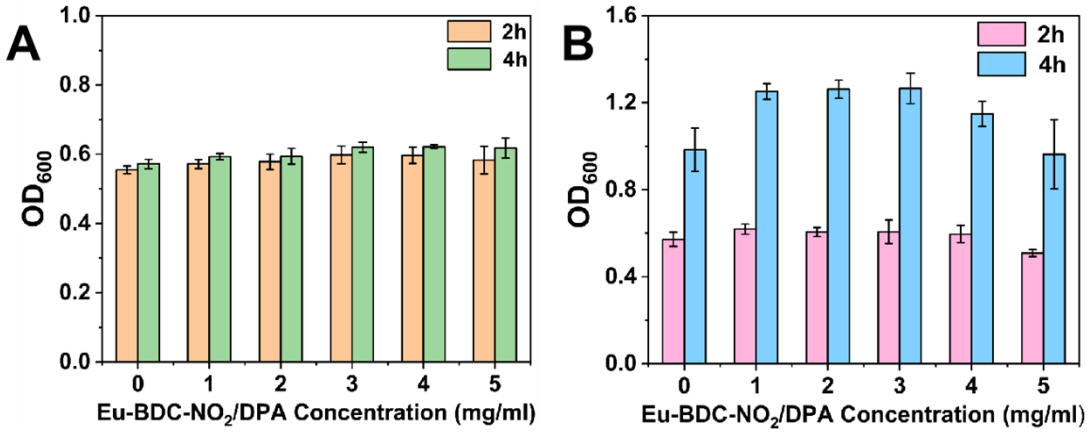

Figure S16 OD_{600} results showed that Eu-BDC-NO_2/DPA with different concentrations (from 1.0 to 5.0 mg/mL) had no inhibition of (A) *S. aureus* and (B) *P. aeruginosa* for 2-4 hours.

9. Supplementary tables

Table S1. Crystallographic data and refinement details for Eu-BDC-NO_2/DPA**.**

Compound	Eu-BDC-NO_2/DPA
Empirical formula	$C_{29}H_{26}ClEu_3N_4O_{25}$
Formula weight	1321.87
Crystal system	Monoclinic
Space group	$P2_1/c$
T/K	296(2)
λ/Å	0.71073
a/Å	11.8426 (9)
b/Å	14.2179 (11)
c/Å	24.756 (2)
α/°	90
β/°	98.899 (3)
γ/°	90
V/Å^3	4118.2 (6)
Z	4
D_c/ Mg·m^{-3}	2.132
μ/mm^{-1}	4.674
F(000)	2536
Measured refls.	63488
Independent refls.	10300
R_{int}	0.0689
No. of parameters	663
GOF	1.024
[a]R_1, [b]wR_2 [I >σ2(I)]	0.0342, 0.0629
R_1, wR_2 (all data)	0.0611, 0.0694
CCDC number	2291212

Table S2. Bond lengths of Eu-O for Eu-BDC-NO_2/DPA**.**

Eu(1)-O(15)#1	2.331 (3)
Eu(1)-O(13)	2.341(3)
Eu(1)-O(7)	2.406(3)
Eu(1)-O(5)	2.413(3)
Eu(1)-O(9)#2	2.521(3)
Eu(1)-O(1)	2.542(3)
Eu(1)-O(2)	2.554(3)
Eu(1)-O(10)#2	2.584(3)
Eu(2)-O(3)	2.433(3)
Eu(2)-O(16)#3	2.444(3)
Eu(2)-O(11)	2.452(3)
Eu(2)-O(14)	2.455(3)
Eu(2)-O(1W)	2.456(4)
Eu(2)-O(1)	2.458(3)
Eu(2)-O(9)	2.459(3)
Eu(3)-O(8)	2.347(3)
Eu(3)-O(4W)	2.366(3)
Eu(3)-O(12)	2.379(3)
Eu(3)-O(6W)	2.392(3)
Eu(3)-O(7W)	2.420(4)
Eu(3)-O(5W)	2.437(5)
Eu(3)-O(2W)	2.472(4)
Eu(3)-O(3W)	2.481(4)