A New Three-Dimensional Zinc(II) Metal-Organic Framework as a Fluorescent Sensor for Sensing Biomarker 3-Nitrotyrosine

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Section 1 Experimental

I. Materials and general methods

The ligand L was prepared according to the synthesis method of the literature.[1] The reagents and solvents used in the experiments were purchased from commercial sources and used without further purification. The single X-ray diffraction data for Zn-MOF was collected by using a Bruker SMART APEX II CCD diffractometer at 273 K with Mo Kα radiation (λ = 0.71073 Å). The infrared (IR) spectra data were gathered on a Varian640 FTIR spectrometer through KBr pellet from 500 cm^{-1} to 4000 cm^{-1} region, and the powder X-ray diffraction (PXRD) patterns were collected on a D/teX Ultra diffractometer. The thermal stabilities of Zn-MOF were analyzed with a thermogravimetric analyzer (NETZSCH STA 449C). The fluorescent spectra were recorded on a Hitachi F-4500 luminescence/phosphorescence spectrometer. Fluorescence lifetime and quantum yield data were obtained on the FLS1000 transient steady-state fluorescence spectrometer. UV−vis absorption spectra were carried out on SP-1900. The PHS-3C-meter with an E-201-C glass electrode was used to determine the pH of the solution.

II. X-ray crystallography.

Data collection was performed on a Bruker Smart APEX II diffractometer with Kα (λ = 0.71073 Å) by θ and ω scan mode at room temperature. The crystal structure was solved by direct method using the SHELXT program of the Olex 2 crystallographic software package and refined on F^2 by full-matrix least-squares methods.[2] Anisotropic thermal parameters were utilized in all non-hydrogen atoms. Crystal data and structural refinements were displayed in Table S1. CCDC number is 1992602. Selected bond

lengths and angles were shown in Table S2 for Zn-MOF.

Table S1. Crystallographic data for Zn-MOF.

Complex	Zn-MOF
Empirical formula	$C_{35}H_{24}N_4O_8Zn$
Formula weight	693.95
Temperature/K	273.15
Crystal system	Monoclinic
Space group	$P\,2_1/n$
a (Å)	10.643(4)
b (Å)	26.202(9)
c (Å)	10.933(4)
α (°)	90
β (°)	94.503(7)
γ (°)	90
V (Å ^{3})	3039.6(18)
Z	4
D_c (g cm^{-3})	1.516
μ (mm^{-1})	0.871
F (000)	1424.0
Reflections collected	17273
Data/restraints/parameters	5327/234/490
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0581, wR_2 = 0.1397
Final R indexes [all data]	R_1 = 0.1209, wR_2 = 0.1688

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table S2. Selected bond distances (Å) and angles (°) for Zn-MOF.

Zn-MOF			
Zn(1)-O(2)#1	1.955(4)	O(6)-Zn(1)-O(2)#1	121.7(3)
Zn(1)-O(6)	1.942(7)	O(6)-Zn(1)-N(2)	99.4(5)
Zn(1)-N(2)	2.034(4)	O(6)-Zn(1)-N(3)#2	102.9(5)
Zn(1)-N(3)#2	2.058(4)	N(2)-Zn(1)-N(3)#2	116.62(18)
Zn(1)-O(6)A	1.948(6)	O(6)A-Zn(1)-N(2)	108.1(5)
O(2)#1-Zn(1)-N(2)	110.56(16)	O(6)A-Zn(1)-N(3)#2	95.3(5)
O(2)#1-Zn(1)-N(3)#2	106.10(17)		
Symmetry code: #1 −1/2+X, 1/2−Y, −1/2+Z; #2 −1/2+X, 3/2−Y, 1/2+Z			

Section 2 Results Discussion Section

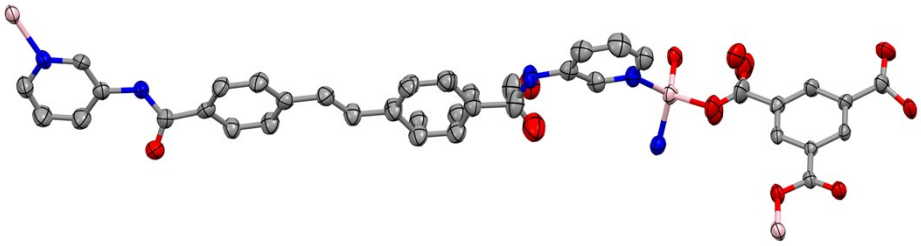

Fig. S1 ORTEP diagram of Zn-MOF at the 50% probability level.

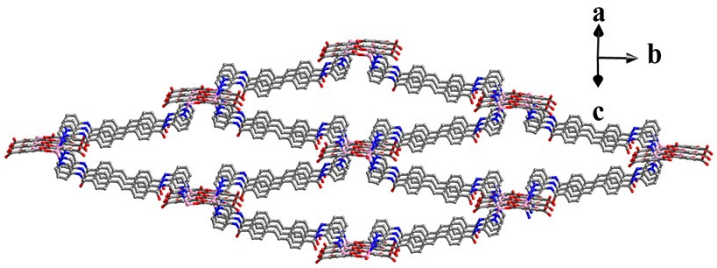

Fig. S2 View of the 3D framework of Zn-MOF.

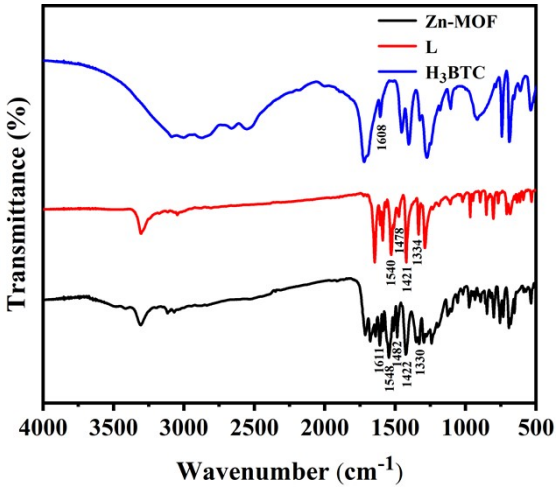

Fig. S3 FT-IR spectra of Zn-MOF and ligands.

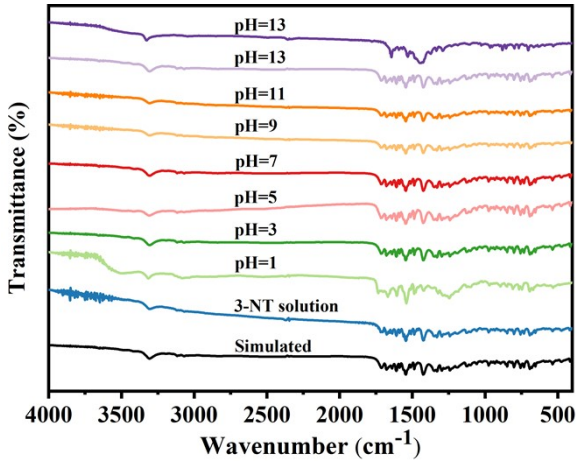

Fig. S4 FT-IR spectra of Zn-MOF in the diffident pH and after detecting 3-NT.

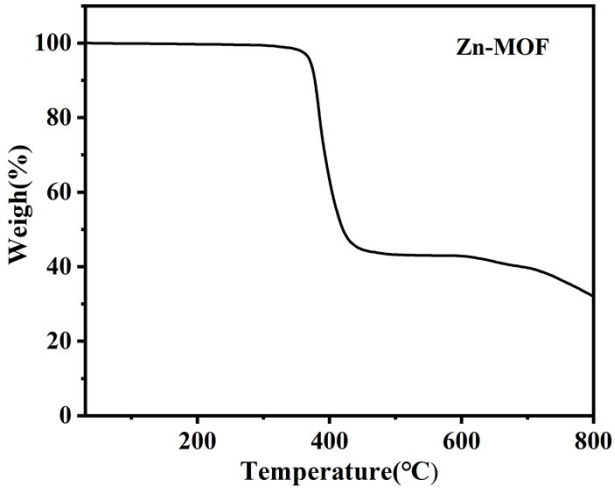

Fig. S5 The TG curve of Zn-MOF.

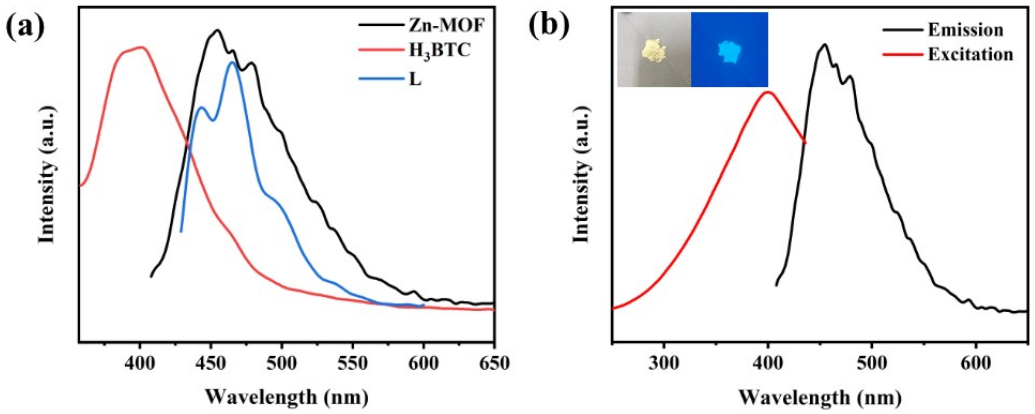

Fig. S6 (a) The emission spectra of solid-state Zn-MOF, L and H_3BTC; (b) The solid excitation and emission spectra of Zn-MOF.

Table S3 Comparison of various methods for 3-NT detection.

Methods	LOD (mol/L)	References
LC−MS/MS	1.70×10^{-11}	Göen et al. (2005)[3]
SPE[a] − HPLC	3.10×10^{-6}	Mergola et al. (2013)[4]
Real time-tandem mass spectrometry	8.80×10^{-7}	Song et al. (2015)[5]
HPLC	2.30×10^{-8}	Monica et al. (2017)[6]
Surface plasmon resonance	5.30×10^{-10}	He et al. (2019)[7]
Molecular Imprinting	2.23×10^{-8}	Martins et al. (2020)[8]
Electrochemiluminescence	8.40×10^{-9}	Zhu et al. (2021)[9]
Fluorescence	3.10×10^{-7}	Present work

[a] Solid-phase extraction.

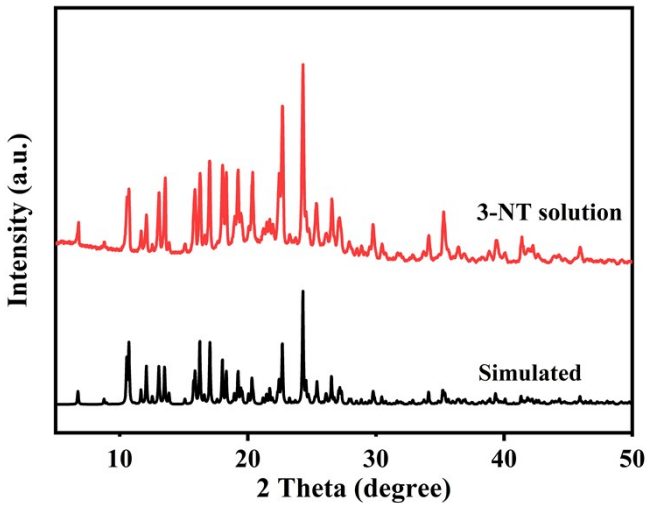

Fig S7. The PXRD pattern of Zn-MOF after detecting 3-NT.

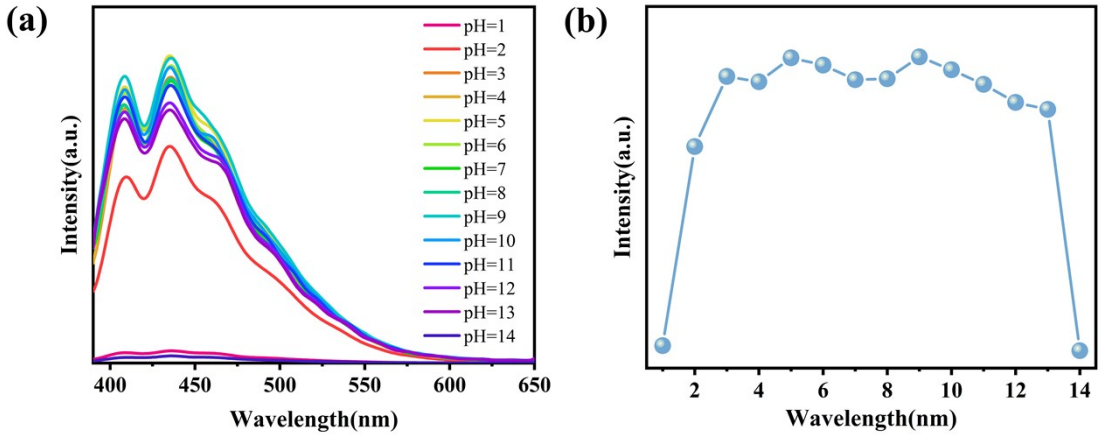

Fig. S8 (a) Emission spectra and intensities of Zn-MOF suspensions in different pH values; (b) Emission intensity line chart of Zn-MOF suspensions in different pH values.

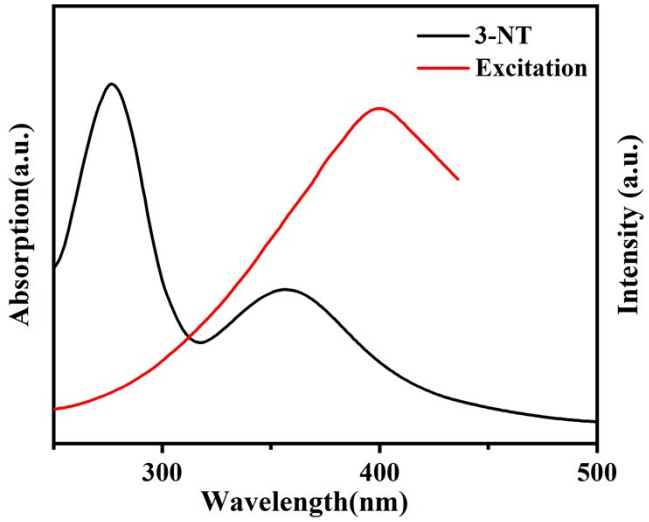

Fig. S9 The UV−vis absorption spectra of 3-NT and excitation spectra of Zn-MOF.

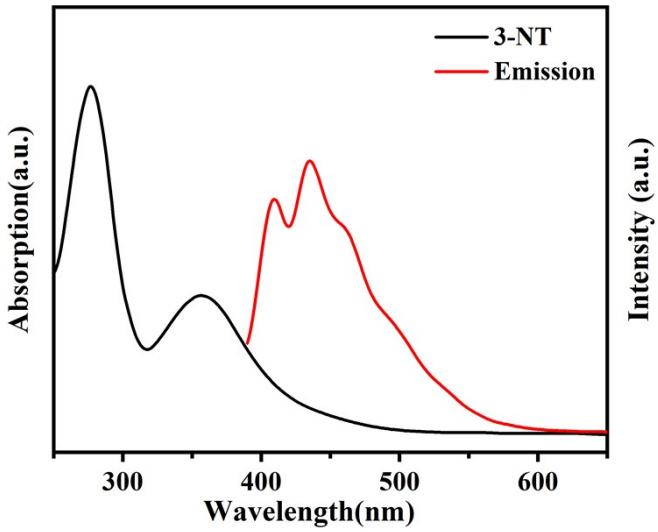

Fig. S10 The UV−vis absorption spectra of 3-NT and emission spectra of Zn-MOF.

Table S4. HOMO and LUMO energies calculated for ligand L and analyte at B3LYP/6-31G(d).

	HOMO (eV)	LUMO (eV)	Band Gap (eV)
L	−6.1293	−2.2503	3.8790
3-NT	−6.5713	−2.7987	3.7726

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