Three-fold Interpenetrated Metal–Organic Framework as a Multifunctional Fluorescent Probe for Detecting 2,4,6-Trinitrophenol, Levofloxacin and L-Cystine

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SQUEEZE results for **1** are as follows:

$\{[Zn_3(TLA)_2(H_2O)_2(4\text{-abpt})_2]\cdot 5CH_3OH\}_n$ (**1**)

```
loop_
   _platon_squeeze_void_nr
   _platon_squeeze_void_average_x
   _platon_squeeze_void_average_y
   _platon_squeeze_void_average_z
   _platon_squeeze_void_volume
   _platon_squeeze_void_count_electrons
   _platon_squeeze_void_content
    1 -0.009   0.107   0.750         336          90 ' '
    2 -0.044   0.393   0.250         336          90 ' '
    3  0.000   0.458   0.750           8           0 ' '
    4  0.000   0.542   0.250           8           0 ' '
    5 -0.045   0.607   0.750         336          90 ' '
    6 -0.010   0.893   0.250         336          90 ' '
    7  0.500   0.042   0.250           8           0 ' '
    8  0.500   0.958   0.750           8           0 ' '
```

That is, SQUEEZE gives 360 electrons/unit cell for the voids. If these electrons are all from CH_3OH (18 e^-), each unit cell has 360/18 =20 CH_3OH molecules, and each formula unit has 5 CH_3OH molecules (since Z = 4). So the suitable formula for this compound should be $\{[Zn_3(TLA)_2(H_2O)_2(4\text{-abpt})_2]\cdot 5CH_3OH\}_n$.

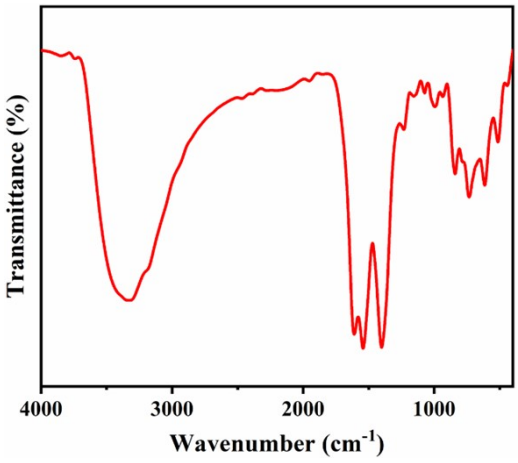


Figure S1. IR spectra of complex **1**.

Table S1. Crystal data and structure refinement for compound **1** (squeeze)

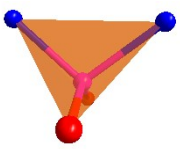
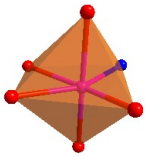
Identification code	**1**
Empirical formula	$C_{42}H_{30}N_{12}O_{14}Zn_3$
Formula weight	1122.89
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	10.086(2)
b/Å	30.644(6)
c/Å	17.347(4)
α/°	90
β/°	90.27(3)
γ/°	90
Volume/Å^3	5361.5(19)
Z	4
ρ_{calc}g/cm^3	1.391
μ/mm^{-1}	1.400
F(000)	2272.0
Reflections collected	15080
Independent reflections	4700 [R_{int} = 0.0692, R_{sigma} = 0.0687]
Data/restraints/parameters	4700/18/334
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0550, wR_2 = 0.1207
Final R indexes [all data]	R_1 = 0.0740, wR_2 = 0.1279

Table S2 Selected Bond Lengths (Å) and Angles (°) for **1**

Bond Lengths (Å)			
Zn1—O2A	2.170 (3)	Zn1—N6	2.128 (4)
Zn1—O3B	2.176 (3)	Zn2—O1A	2.008 (3)
Zn1—O4B	2.197 (3)	Zn2—O1	2.008 (3)
Zn1—O6	1.996 (3)	Zn2—N1C	2.066 (4)
Zn1—O7	2.163 (3)	Zn2—N1D	2.066 (4)
Bond Angles (°)			
O2A—Zn1—O3B	93.70 (12)	O1A—Zn2—O1	144.21 (17)
O2A—Zn1—O4B	93.00 (11)	O1—Zn2—N1D	97.88 (14)
O3B—Zn1—O4B	60.66 (11)	O1A—Zn2—N1C	97.88 (14)
O6—Zn1—O2A	86.96 (11)	O1A—Zn2—N1D	104.07 (14)
O6—Zn1—O3B	105.53 (12)	O1—Zn2—N1C	104.07 (14)
O6—Zn1—O4B	166.17 (12)	N1C—Zn2—N1D	103.5 (2)
O6—Zn1—O7	92.32 (12)	N6—Zn1—O2A	87.32 (13)
O6—Zn1—N6	97.98 (13)	N6—Zn1—O3B	156.49 (12)
O7—Zn1—O2A	178.67 (12)	N6—Zn1—O4B	95.83 (13)
O7—Zn1—O3B	85.40 (12)	N6—Zn1—O7	93.89 (14)
O7—Zn1—O4B	87.43 (12)		

Symmetry codes: (A) -*x*+1, *y*, -*z*+3/2; (B) *x*-1/2, -*y*+1/2, *z*-1/2; (C) *x*-1, -*y*+1, *z*+1/2; (D) -*x*+2, -*y*+1, -*z*+1; (E) *x*+1/2, -*y*+1/2, *z*+1/2.

Table S3. SHAPE analysis of Zn(II) ions in **1**.

	ZnO_2N_2	ZnO_5N
Coordination modes		
label	SS-4	OC-6
symmetry	C_{2v}	Oh
shape	SeeSaw	Octahedron
Calculation results	Distortion(τ_{min})	
	Zn1（2.609）	Zn2（2.285）

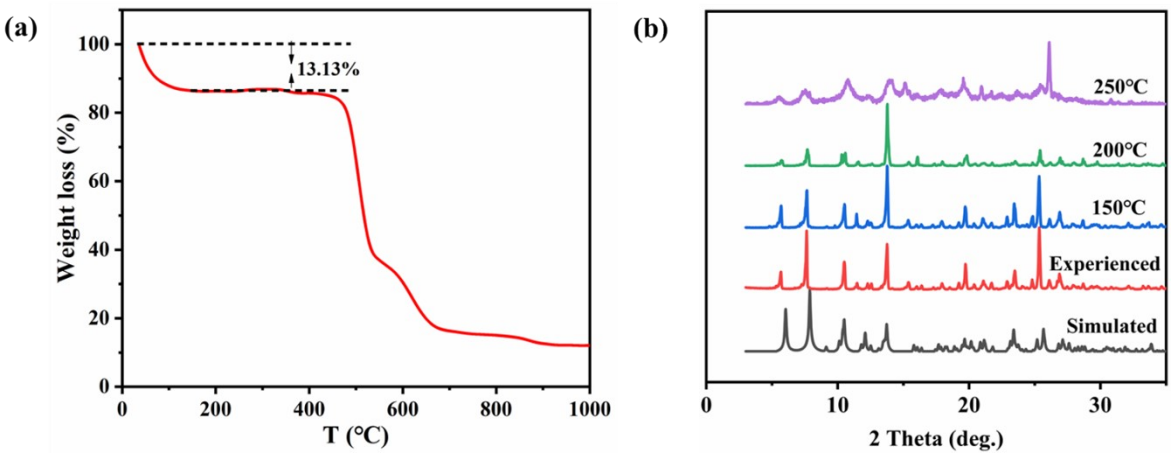


Figure S2. (a) TGA curve of **1**. (b) PXRD patterns of **1** at different temperatures and the simulated one calculated from the single crystal structure analysis.

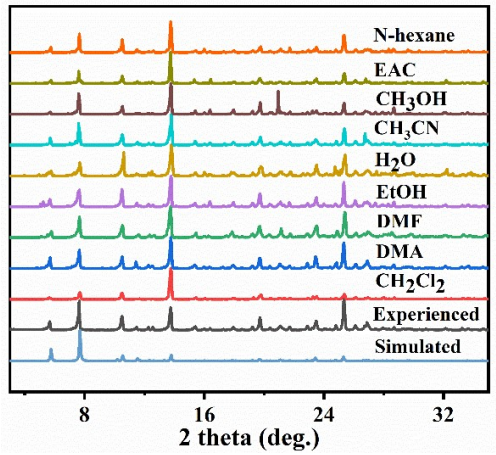


Figure S3. The PXRD patterns of **1** treated in different solvents.

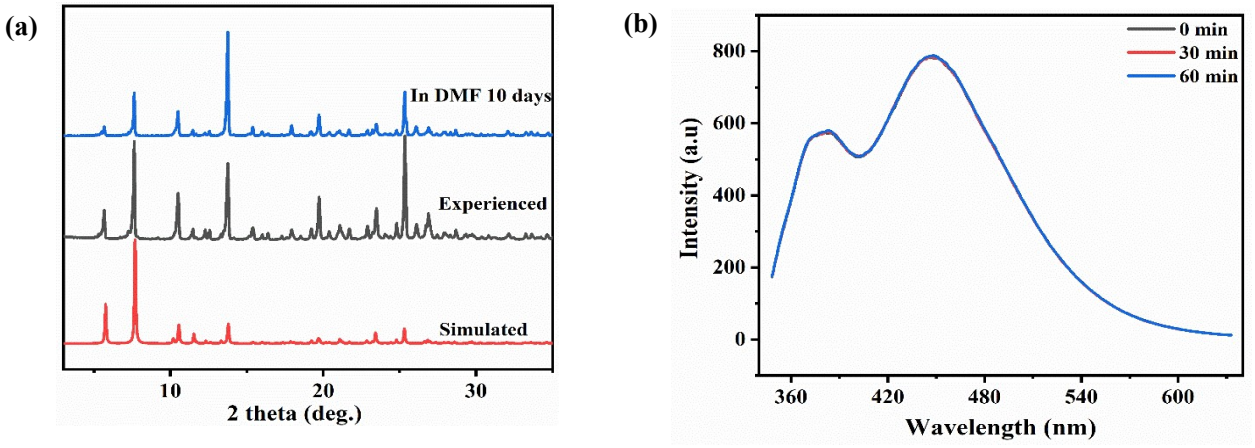


Figure S4. (a) PXRD of compound **1** in DMF for 10 days (b) Fluorescence measurements of **1** immersed into the DMF solvent as the suspensions for 0 min and after 60 min

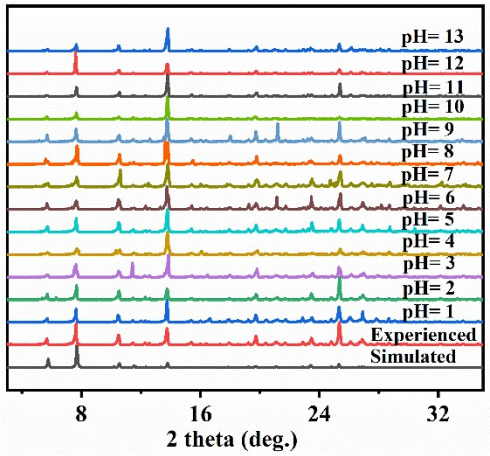


Figure S5. PXRD patterns of **1** in different pH values in the range of 1-13.

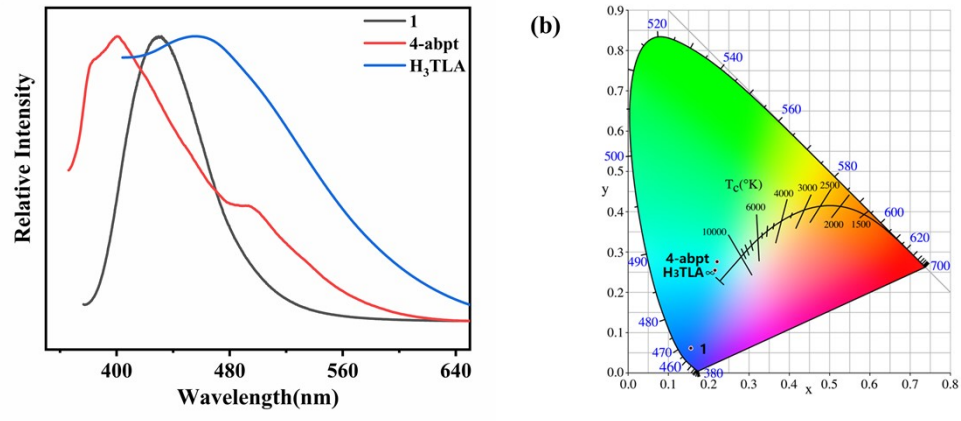


Figure S6. (a) (b)The solid luminescent emissions of ligand H_3TLA, 4-bpt and **1**.

Ksv and LOD calculation methods

The quantitative fluorescent quenching efficiency of **1** (for analyte) using the Stern−Völmer (S−V) equation.[1]

$$(I_0/I) = 1 + K_{SV}\,C \text{ ---------（1）},$$

Where I is the fluorescence intensity at TNP concentration of C, and I_0 signifies the initial fluorescence intensity of the MOF.

The quenching constant is indicated by K*sv* (M^{-1}). A linear curve is obtained at relatively low concentrations of analyte. The equation

$$LOD = 3\sigma/Ksv \text{ ---------（2）},$$

(where σ signifies the standard deviation of the initial fluorescence intensity of MOF) was used to calculate the detection limit of analyte.

Table S4. Ksv and LOD of MOF-based luminescent sensors for TNP, LVX and L-Cys

MOF-based fluorescent materials	Analyte	Quenching constant (M^{-1})	Detection limits	Recycle ability	Ref
$[Zn_3(TLA)_2(H_2O)_2(4\text{-abpt})_2]_n \cdot 5CH_3OH$	TNP	4.23×10^5	5.24 μM	Yes	**This work**
$[Cd_3(NTB)_2(DPP)(DMA)_2]\cdot 4DMA$	TNP	4.1×10^4	9.5 μM		2
$[Cd_3(NTB)_2(DPP)_2]\cdot 3DMA\cdot H_2O$	TNP	4.89×10^4	8.0 μM		2
$\{[Zn_4(\mu_3\text{-}OH)_2(BTC)_2(BBI4PY)_2]\cdot 10H_2O\}_n$	TNP	2.94×10^4	7.86 μM		3
$\{[Cd_4(HDDCP)_2(4,4'\text{-bibp})_2(H_2O)_2]\cdot 2.5(DOA)\cdot 1.5(H_2O)\}_n$	TNP	7.31×10^5	3.92 μM		4
$\{[Cd_2(HDDCP)(1,4\text{-bib})(H_2O)]\cdot H_2O\}_n$	TNP	3.71×10^5	7.84 μM		4
Zr-NDI MOF	TNP	4.057×10^4	35.36 μM		5
$\{(Me_2NH_2)_4[Eu_4(DDAC)_3(HCO_2)(OH_2)_2]\cdot 8DMF\cdot 9H_2O\}_n$	TNP	8.6×10^4	3.5 μM		6
$Zn_5(\mu_3\text{-}OH)_2(TDA)_4(4,4'\text{-bpt})_2$	TNP	1.856×10^5	1.59 μM	Yes	7
$[Cd(NDC)(H_2O)]_n$	TNP	2.385×10^4	4 μM	Yes	8
$[Zn_4(DMF)(Ur)_2(2,6\text{-NDC})_4]_n$	TNP	10.83×10^4	7.11 μM		9
$\{[Cd_4(L)_2(L_2)_3(H_2O)_2]\cdot 8DMF\cdot 8H_2O\}_n$	TNP	3.89×10^4	8.64 μM	Yes	10

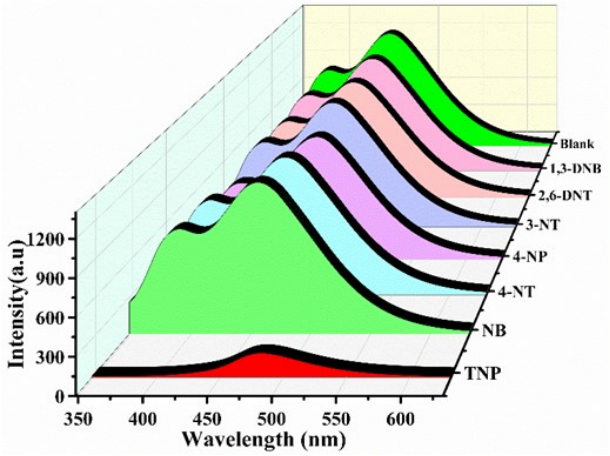


Figure S7. The luminescence intensity of **1**- nitroaromatic at 458 nm in 40 μM different nitroaromatics.

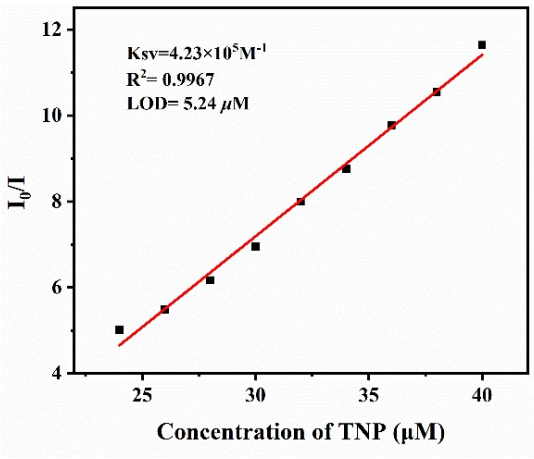


Figure S8 The Stern–Volmer plot of I_0/I versus TNP concentration.

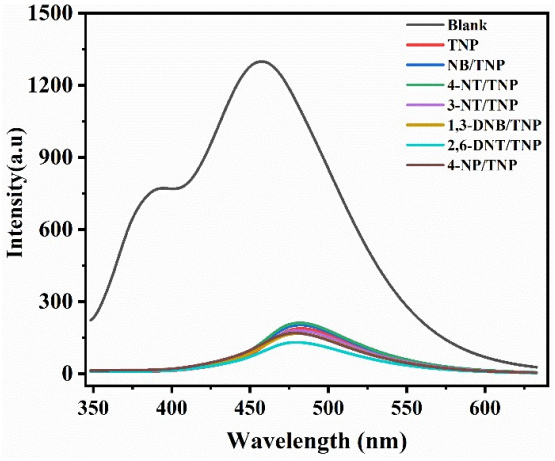


Figure S9. The luminescence intensity of **1**- TNP under other nitroaromatics.

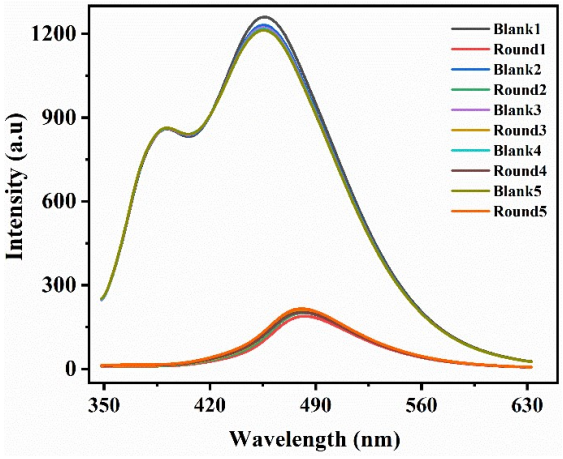


Figure S10. The quenching and recyclability test of **1**, the upper lines represent the initial fluorescence intensity and the lower lines represent the fluorescence intensity upon addition of 40 μM TNP solution.

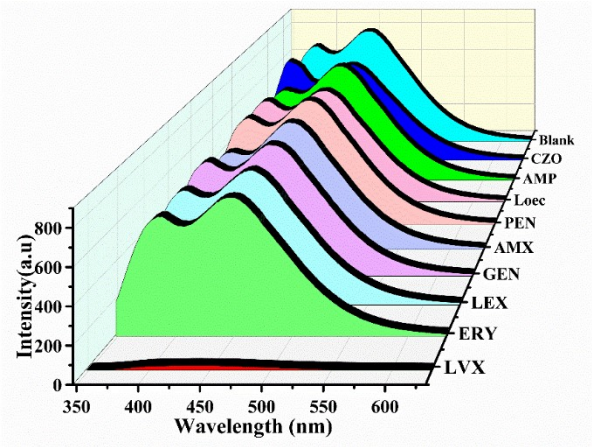


Figure S11. The luminescence intensity of **1**- antibiotics at 458 nm in 60 μM different antibiotics.

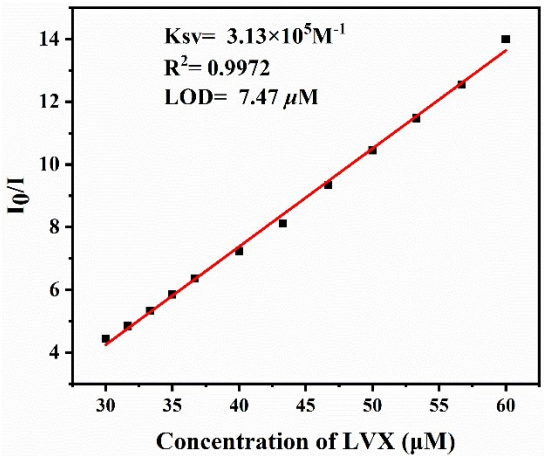


Figure S12 Stern–Volmer plot of I_0/I versus LVX concentration.

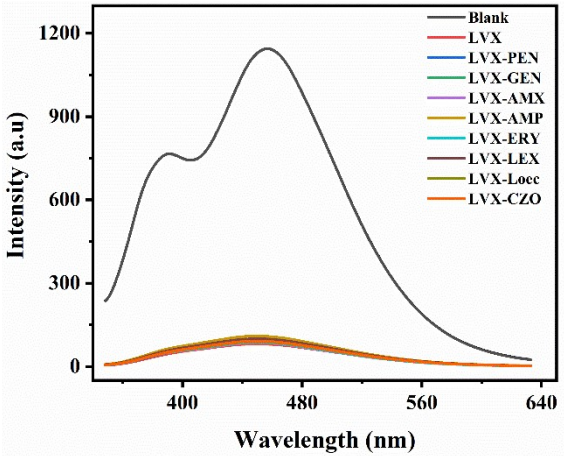


Figure S13. The luminescence intensity of **1**- LVX under mixed antibiotics.

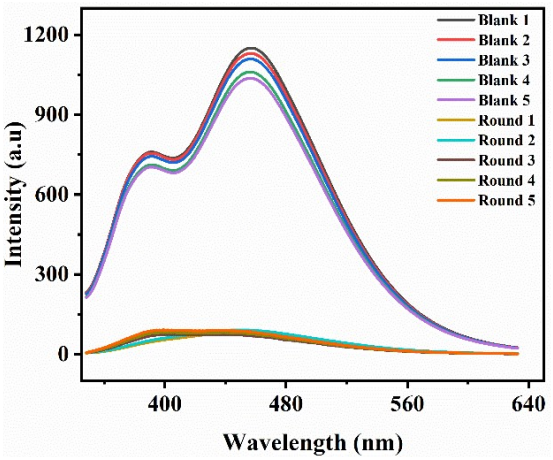


Figure S14. The quenching and recyclability of **1**, the upper lines represent the initial fluorescence intensity and the lower lines represent the fluorescence intensity upon addition of 60 μM LVX solution.

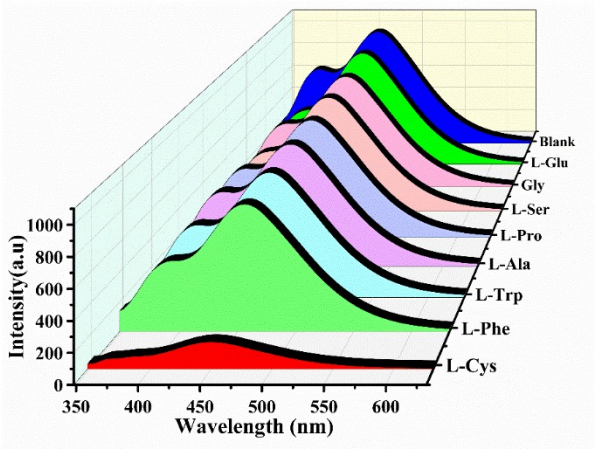


Figure S15. The luminescence intensity of **1**- amino acids at 458nm.

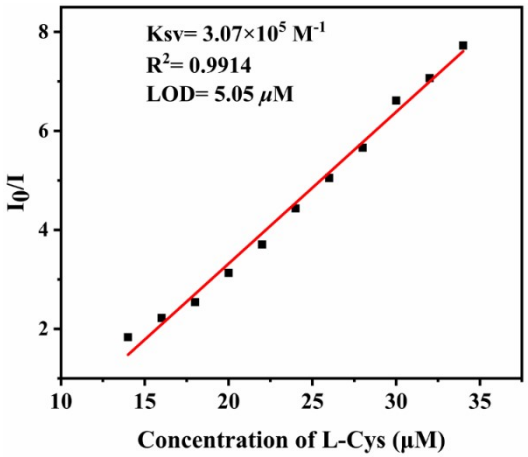


Figure S16 Stern–Volmer plot of I_0/I versus L-Cys concentration.

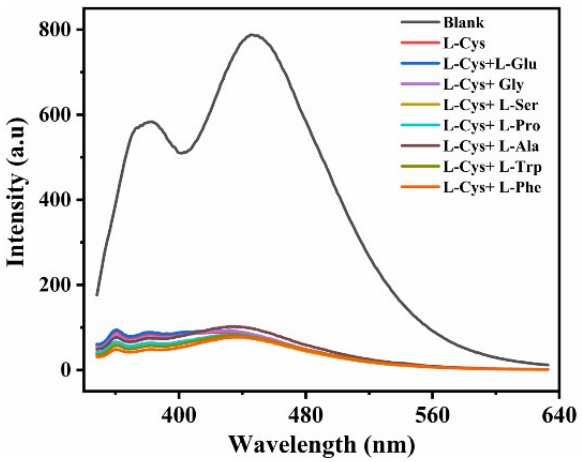


Figure S17. Luminescence intensity of **1** dispersed in a mixture of other amino acids with L-Cys.

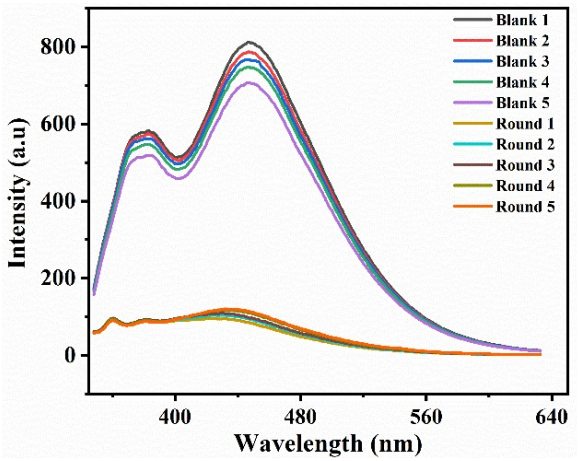


Figure S18. The quenching and recyclability of **1**, the upper lines represent the initial fluorescence intensity and the lower lines represent the fluorescence intensity upon addition of 40 μM L-Cys solution.

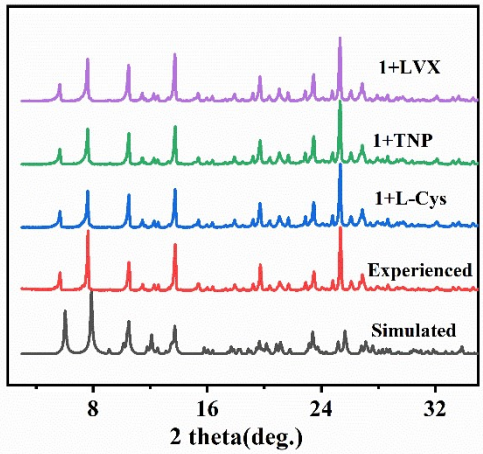


Figure S19. PXRD patterns of **1** after experiment.

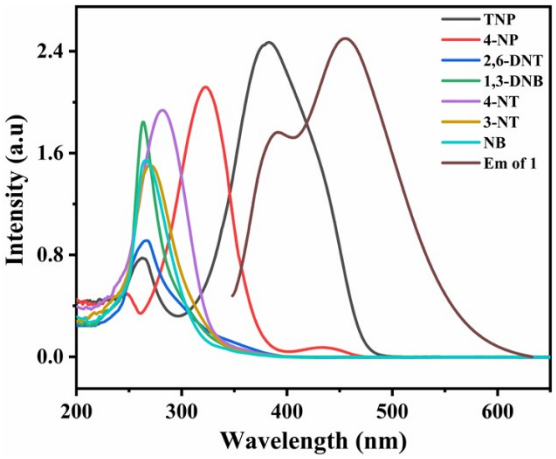


Figure S20. UV–vis spectral profiles of different nitroaromatics recorded in H_2O solution and E_m of **1** in DMF.

Table S5. HOMO and LUMO energy levels of different nitro-analytes

Analytes	3-NT[11]	TNP[12]	NB[13]	1,3-DNB	2,6-DNT[14]	4-NT[13]	4-NP[13]
LOMO	-2.83893	-3.92	-2.42	-2.83	-3.306	-2.79	-2.75
HOMO	-7.55031	-8.27	-7.56	-7.81	-8.391	-7.70	-7.34
Energy Gap（ev）	4.71138	4.35	5.14	4.98	5.085	4.91	4.59

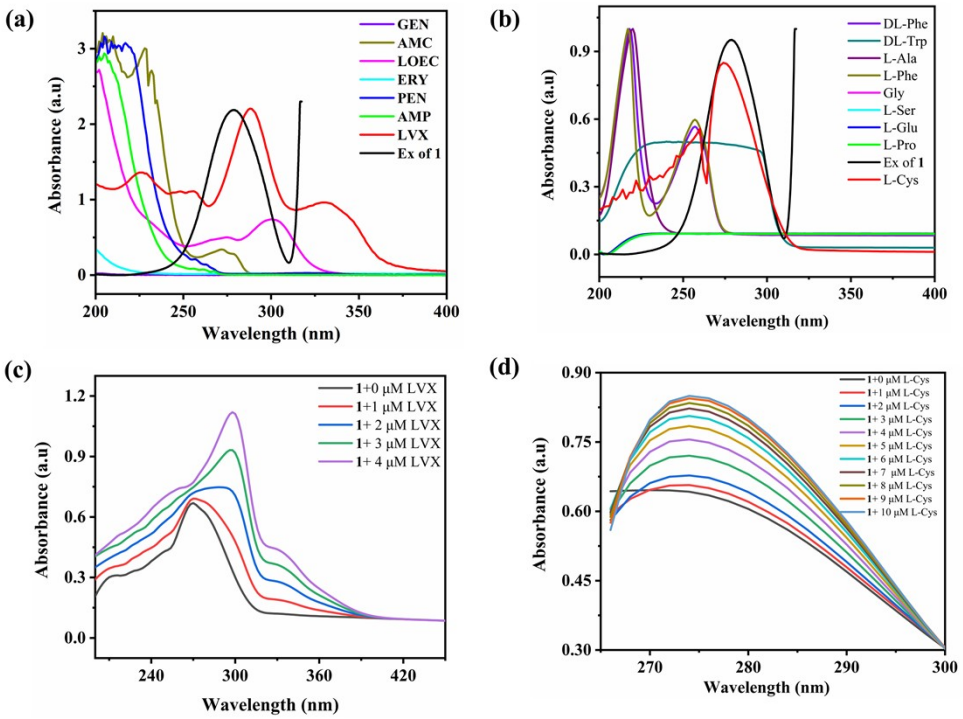


Figure S21. (a) UV-vis absorption spectra of various antibiotics (b) and various amino acids, (c) UV-vis absorption spectra of **1** upon addition of different concentrations of LVX and (d) L-Cys.

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