Electronic Supplementary Material (ESI) for RSC Advances.

Aqueous-phase detection of antibiotics and nitroaromatic explosives by an alkali-resistant Zn-MOF directed by an ionic liquid

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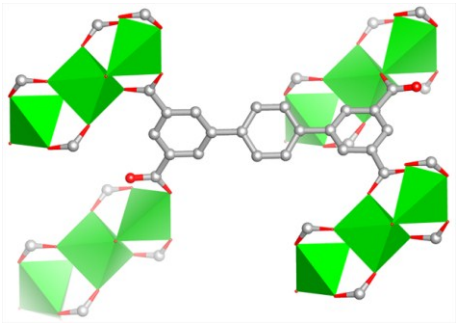
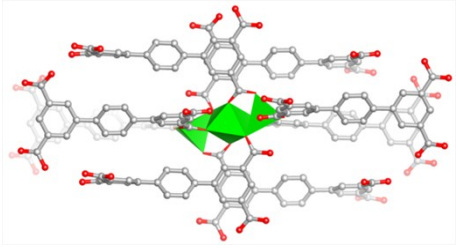
Supporting Information





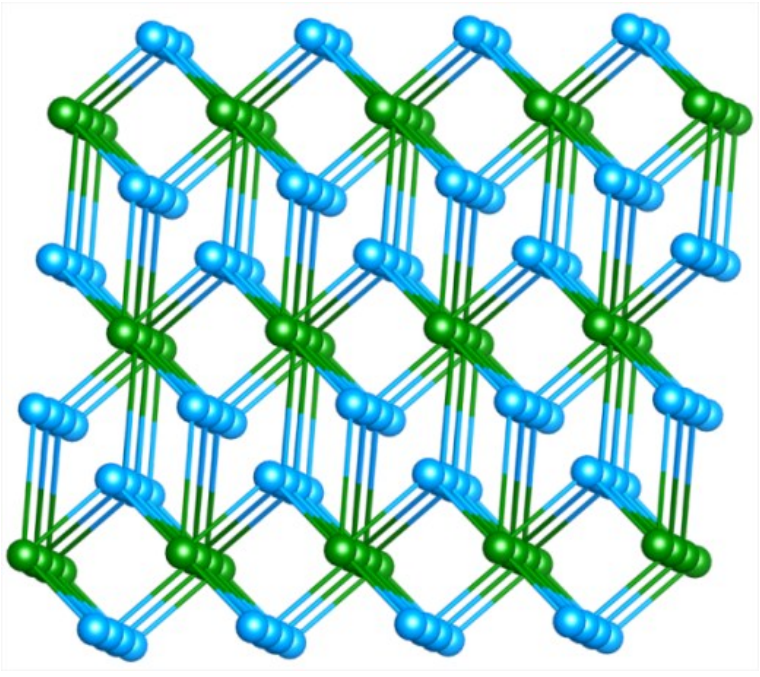


Fig. S1 Schematic representation of the 4,8-connected topology (CaF_2) (blue nodes for ptptc ligands and green nodes for $[Zn_3(CO_2)_8]$ clusters).

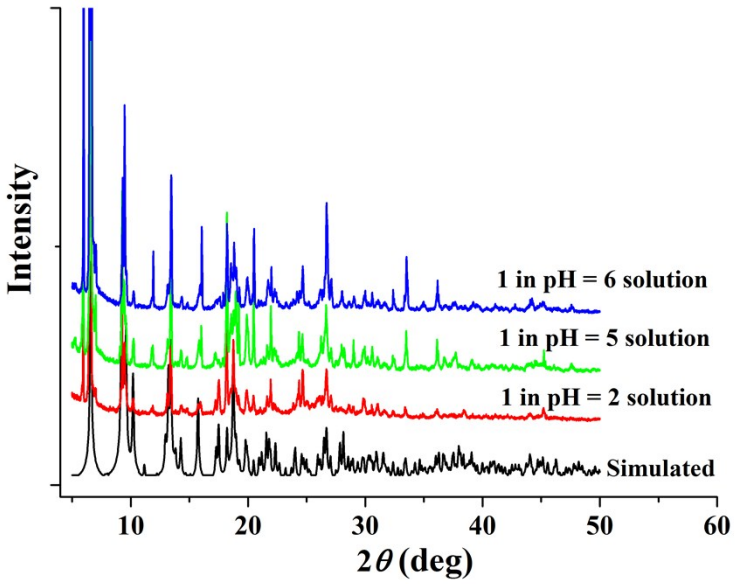


Fig. S2 PXRD patterns for simulated and experimental **1** sample soaked in aqueous solutions over the pH range from 2 to 6.

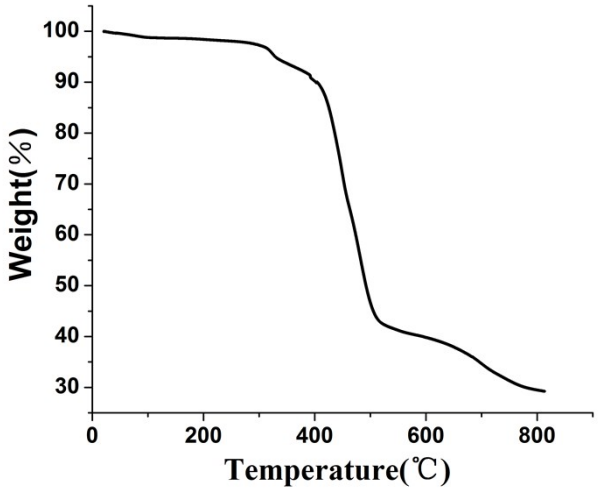


Fig. S3 Thermogravimetric curve of **1**.

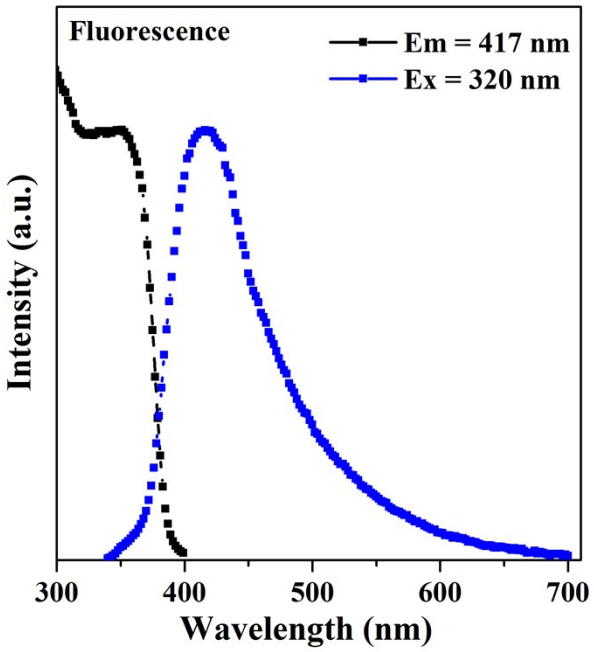
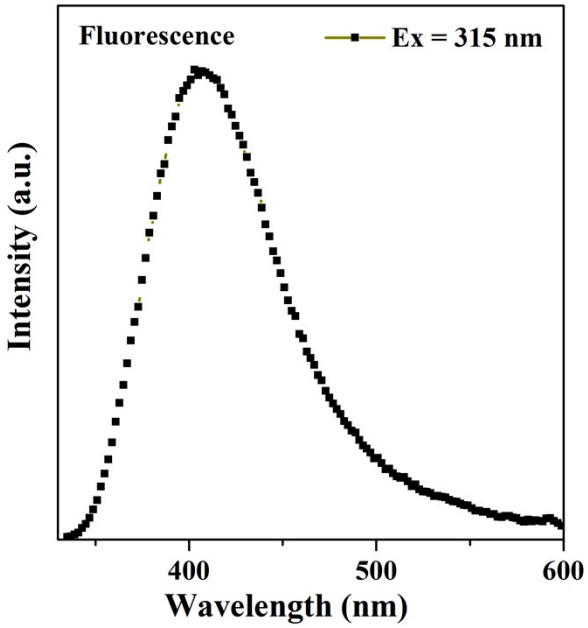
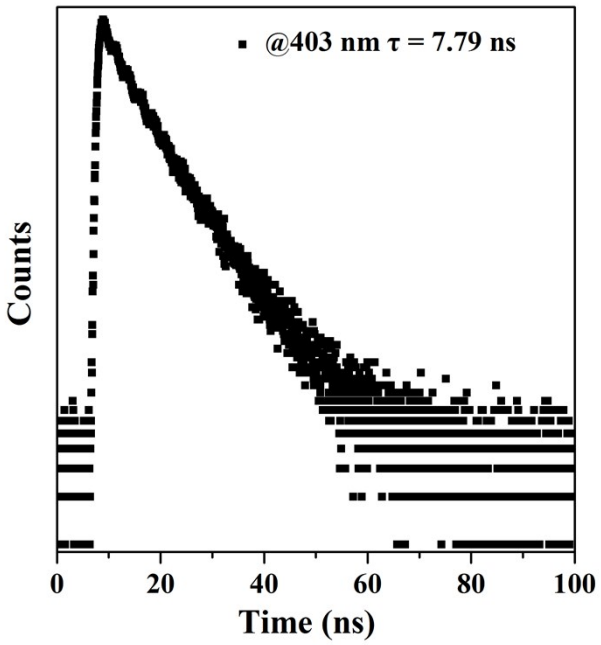


Fig. S4 Normalized excitation and emission spectra of H_4ptptc in solid state at room temperature.

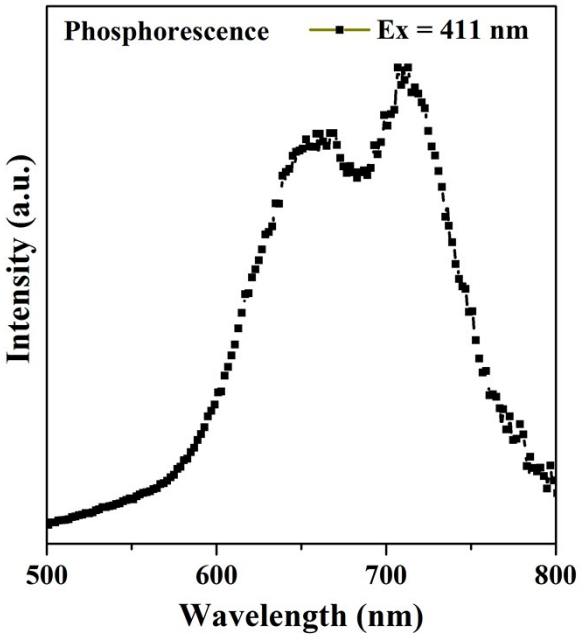


(a)

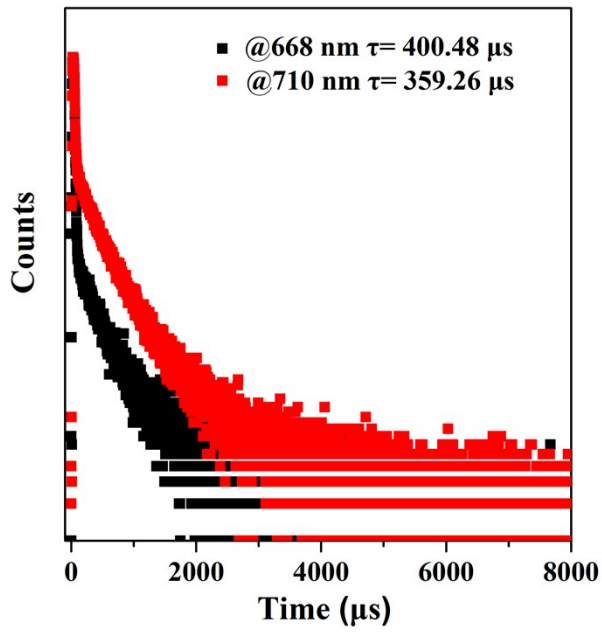


(b)

Fig. S5 Fluorescence spectra (a) and decay curve (b) of **1**.



(a)



(b)

Fig. S6 Phosphorescence spectra (a) and decay curve (b) of **1**.

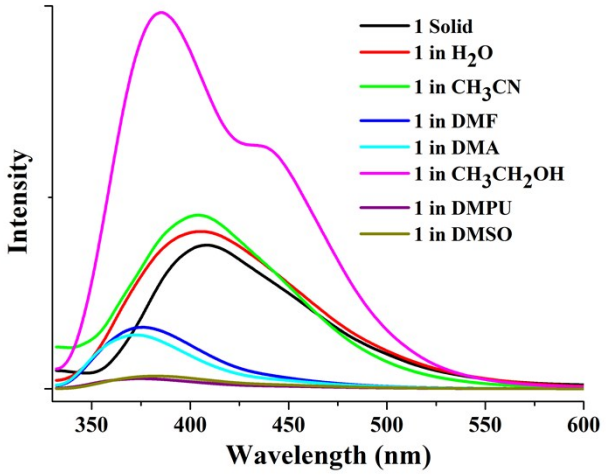


Fig. S7 The emission spectra for **1** dispersed in different solvents at room temperature.

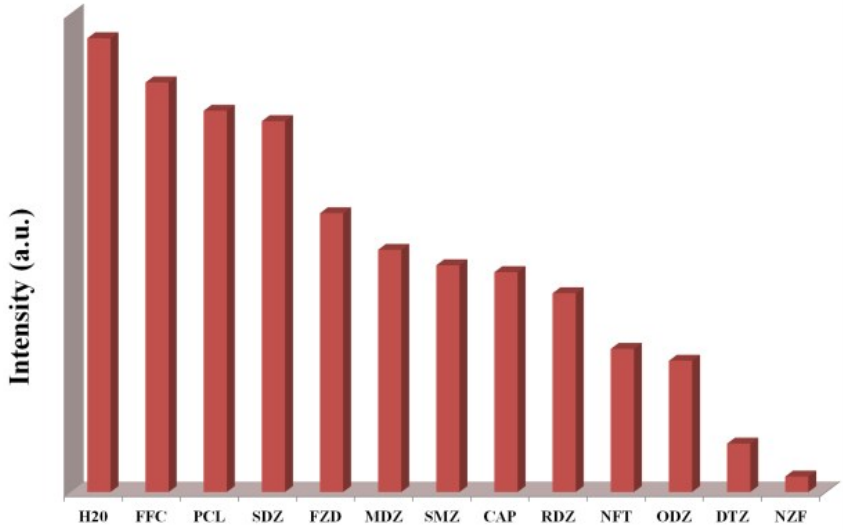


Fig. S8 The fluorescent intensity for **1** dispersed in 0.1 mM aqueous solutions of the selected antibiotics at room temperature.

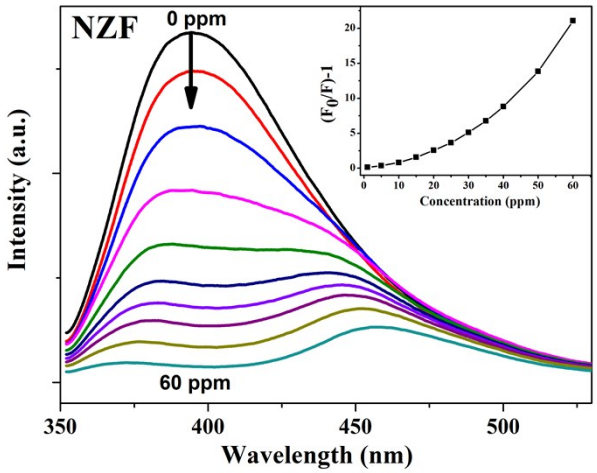


Fig. S9 Effect on the emission spectra of **1** dispersed in water upon incremental addition of NZF (inset: SV plots of NZF).

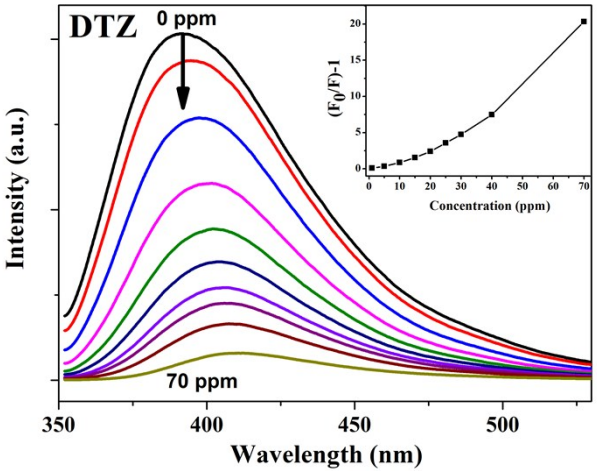


Fig. S10 Effect on the emission spectra of **1** dispersed in water upon incremental addition of DTZ (inset: SV plots of DTZ).

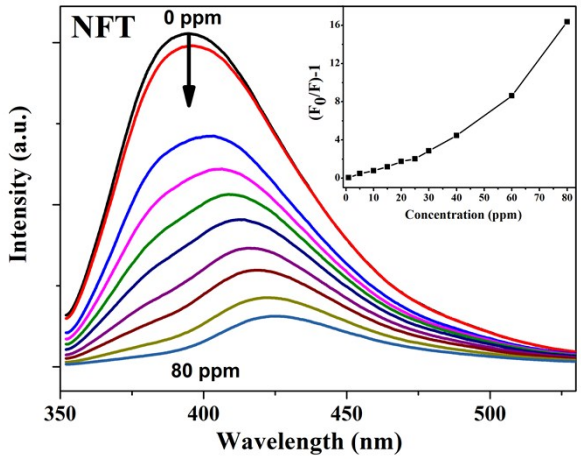


Fig. S11 Effect on the emission spectra of **1** dispersed in water upon incremental addition of NFT (inset: SV plots of NFT).

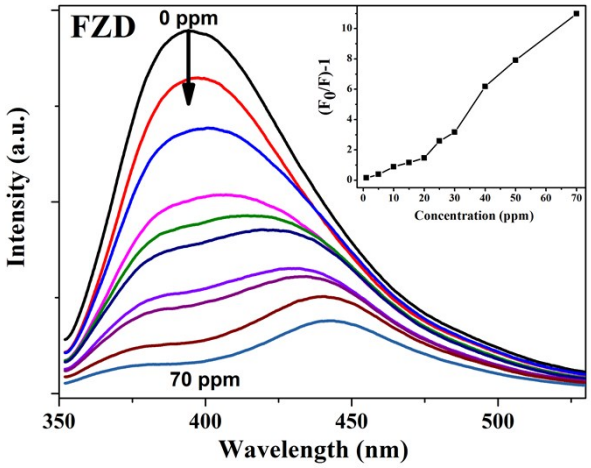


Fig. S12 Effect on the emission spectra of **1** dispersed in water upon incremental addition of FZD (inset: SV plots of FZD).

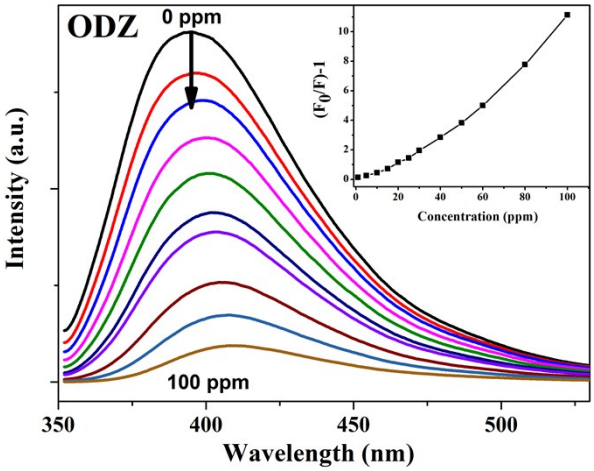


Fig. S13 Effect on the emission spectra of **1** dispersed in water upon incremental addition of ODZ (inset: SV plots of ODZ).

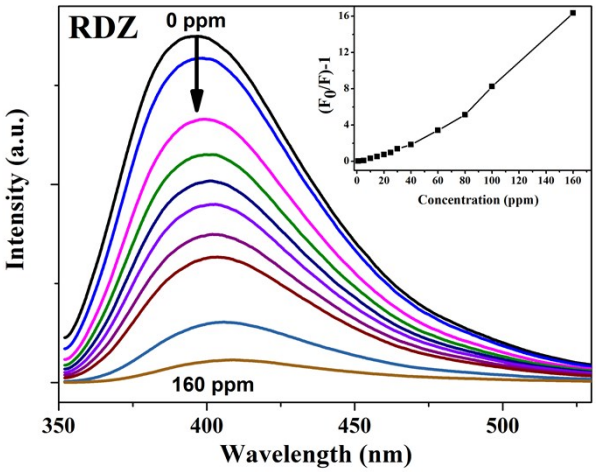


Fig. S14 Effect on the emission spectra of **1** dispersed in water upon incremental addition of RDZ (inset: SV plots of RDZ).

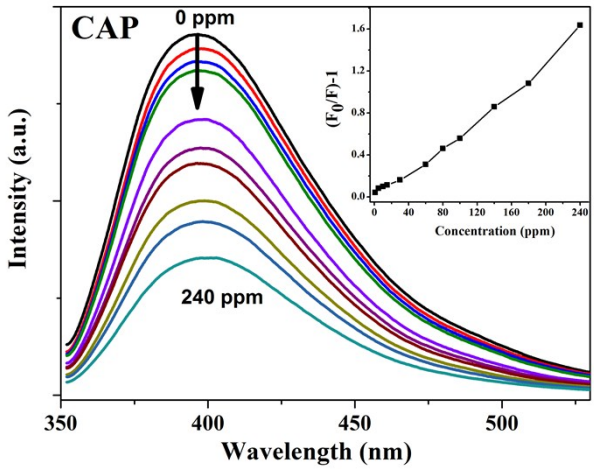


Fig. S15 Effect on the emission spectra of **1** dispersed in water upon incremental addition of CAP (inset: SV plots of CAP).

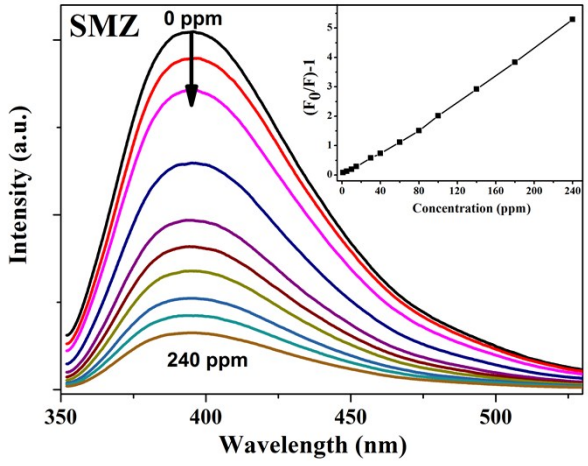


Fig. S16 Effect on the emission spectra of **1** dispersed in water upon incremental addition of SMZ (inset: SV plots of SMZ).

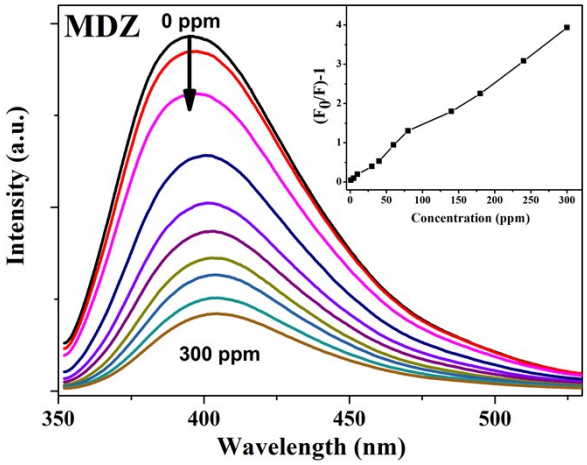


Fig. S17 Effect on the emission spectra of **1** dispersed in water upon incremental addition of MDZ (inset: SV plots of MDZ).

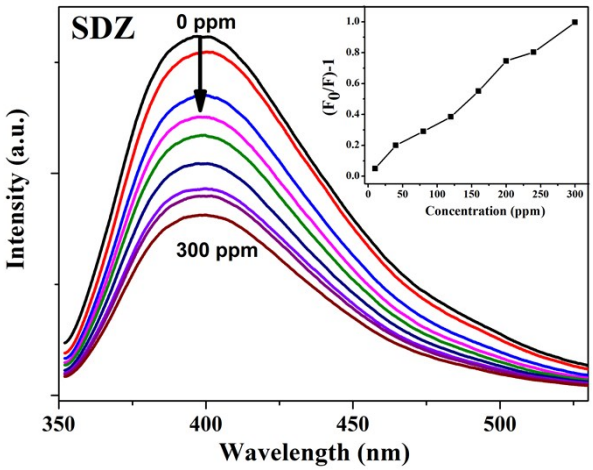


Fig. S18 Effect on the emission spectra of **1** dispersed in water upon incremental addition of SDZ (inset: SV plots of SDZ).

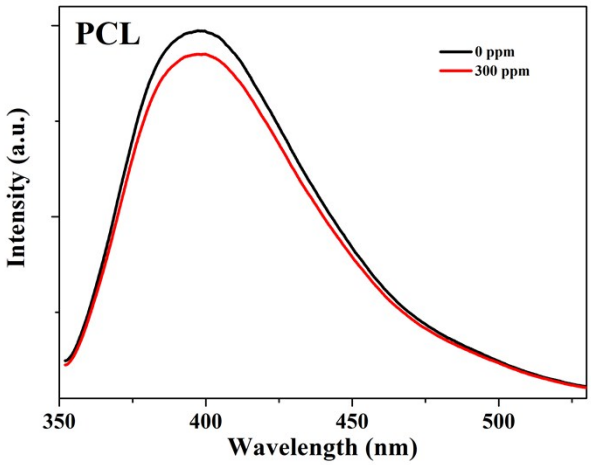


Fig. S19 Effect on the emission spectra of **1** dispersed in water upon incremental addition of PCL.

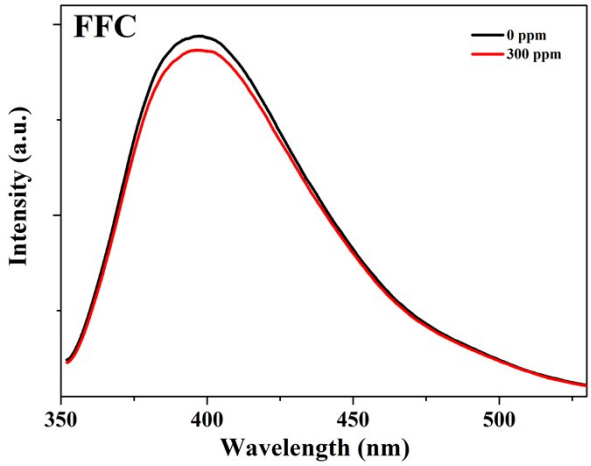


Fig. S20 Effect on the emission spectra of **1** dispersed in water upon incremental addition of FFC.

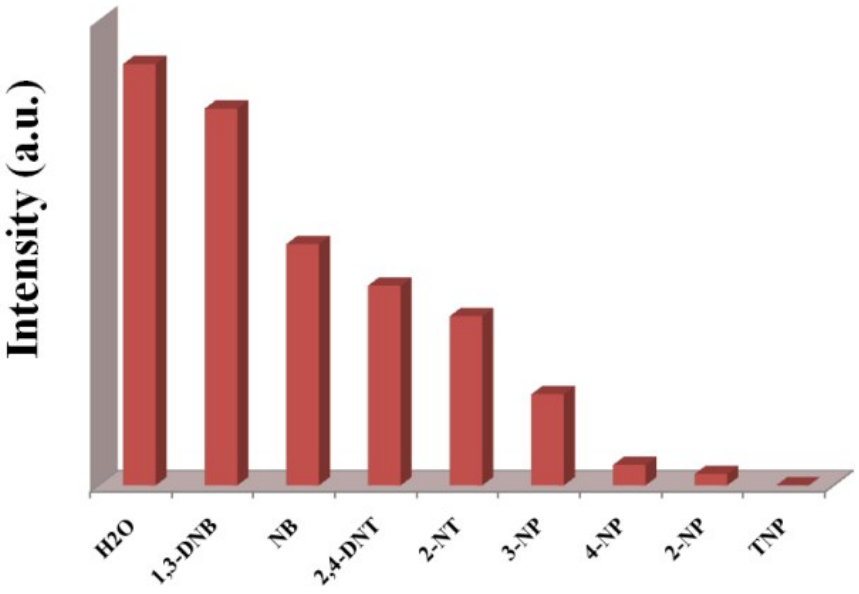


Fig. S21 The fluorescent intensity for **1** dispersed in 1 mM aqueous solutions of the selected nitroaromatics explosives at room temperature.

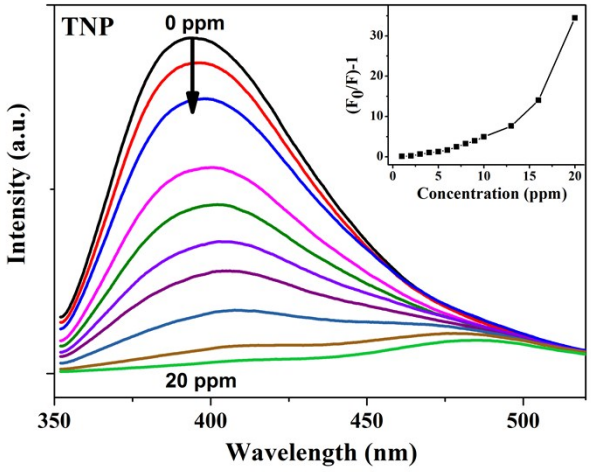


Fig. S22 Effect on the emission spectra of **1** dispersed in water upon incremental addition of TNP (inset: SV plots of TNP).

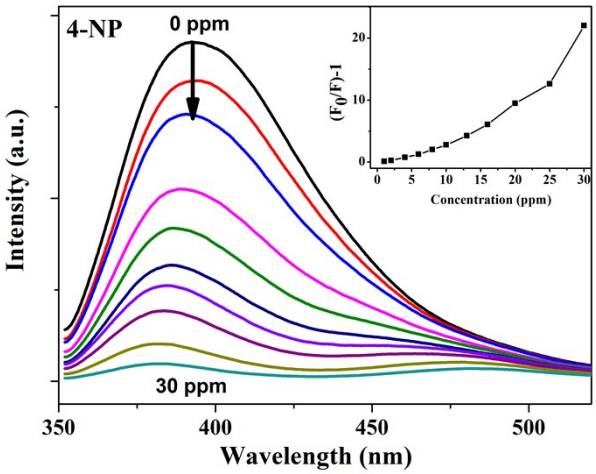


Fig. S23 Effect on the emission spectra of **1** dispersed in water upon incremental addition of 4-NP (inset: SV plots of 4-NP).

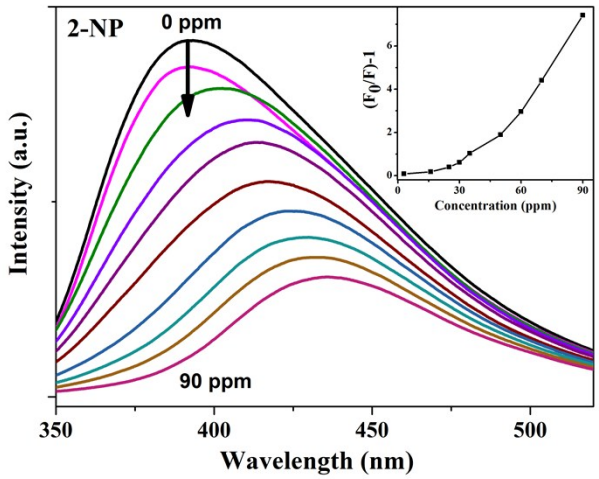


Fig. S24 Effect on the emission spectra of **1** dispersed in water upon incremental addition of 2-NP (inset: SV plots of 2-NP).

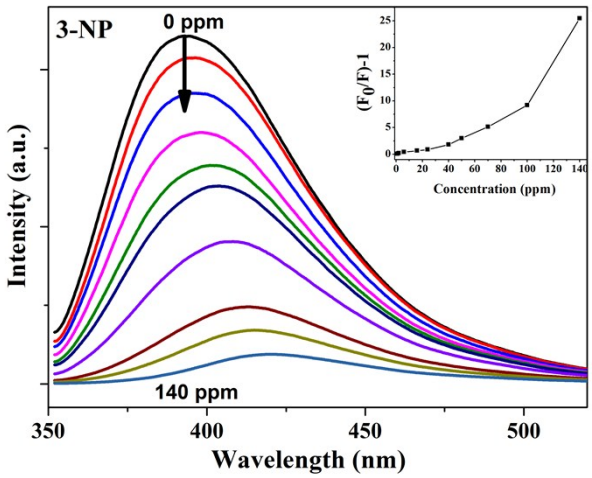


Fig. S25 Effect on the emission spectra of **1** dispersed in water upon incremental addition of 3-NP (inset: SV plots of 3-NP).

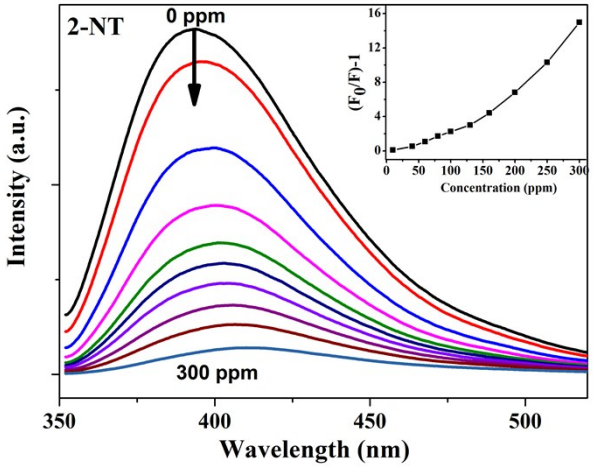


Fig. S26 Effect on the emission spectra of **1** dispersed in water upon incremental addition of 2-NT (inset: SV plots of 2-NT).

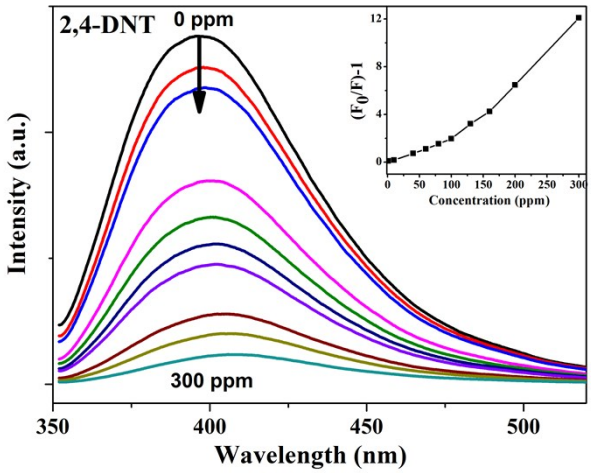


Fig. S27 Effect on the emission spectra of **1** dispersed in water upon incremental addition of 2,4-DNT (inset: SV plots of 2,4-DNT).

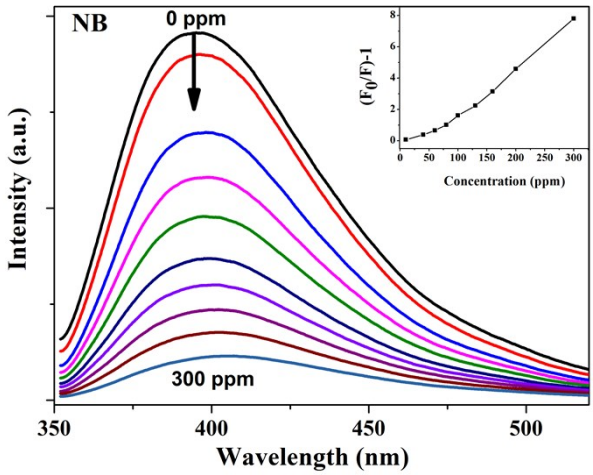


Fig. S28 Effect on the emission spectra of **1** dispersed in water upon incremental addition of NB (inset: SV plots of NB).

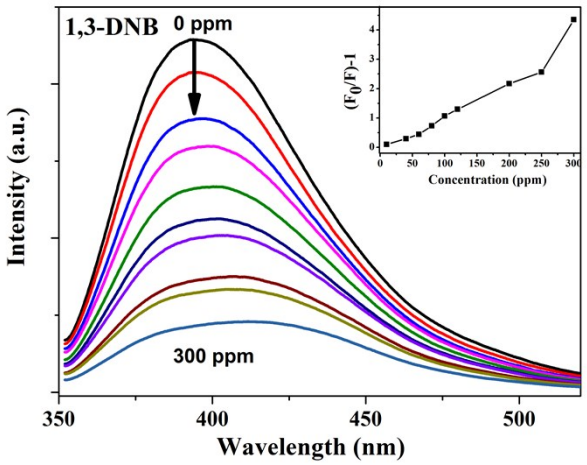


Fig. S29 Effect on the emission spectra of **1** dispersed in water upon incremental addition of 1,3-DNB (inset: SV plots of 1,3-DNB).

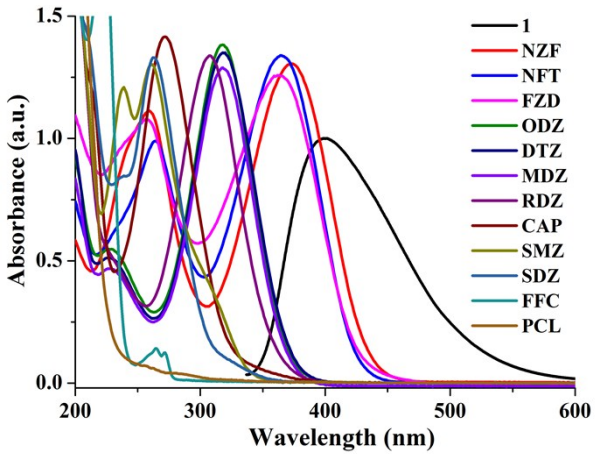


Fig. S30 Spectral overlap between normalized absorption spectra of selected antibiotics and the normalized emission spectra of **1** in water.

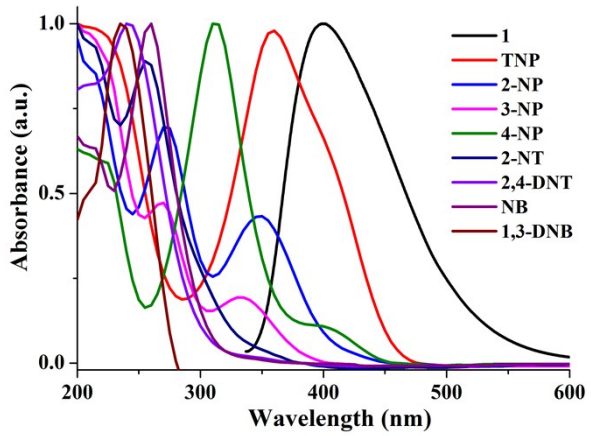


Fig. S31 Spectral overlap between normalized absorption spectra of selected nitroaromatics explosives and the normalized emission spectra of **1** in water.

Table S1. Crystallographic data and experimental details for **1**.

Complex	**1**
Empirical formula	$C_{60}H_{50}N_4O_{16}Zn_3$
Formula weight	1279
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.6166(4)
b/Å	14.4465(6)
c/Å	20.4967(10)
α/°	106.767(4)
β/°	98.427(4)
γ/°	101.203(4)
Volume/Å^3	2611.6(2)
Z	2
ρ_{calc}g/cm^3	1.273
μ/mm^{-1}	1.426
F(000)	1004.0
Crystal size/mm^3	0.27 × 0.24 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.934 to 50.998
Index ranges	-10 ≤ h ≤ 11, -17 ≤ k ≤ 17, -24 ≤ l ≤ 24
Reflections collected	19104
Independent reflections	9346 [R_{int} = 0.0352, R_{sigma} = 0.0565]
Data/restraints/parameters	9346/0/604
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0574, wR_2 = 0.1442
Final R indexes [all data]	R_1 = 0.0690, wR_2 = 0.1519
Largest diff. peak/hole / e Å^{-3}	1.00/-2.07

$R = [\sum || F_0| - |F_c|| / \sum |F_0|]$, $R_w = \sum_w [|F_0^2 - Fc^2|^2 / \sum_w (|F_w|^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O1	1.964(3)	Zn2	O9[5]	2.021(3)
Zn1	O4[1]	2.183(3)	Zn2	O12[6]	2.031(3)
Zn1	O7[2]	2.109(3)	Zn2	O13[7]	1.986(3)
Zn1	O10	1.977(3)	Zn3	O2[4]	2.011(3)
Zn1	O12[3]	2.271(3)	Zn3	O4[8]	2.031(3)
Zn1	O14[4]	2.095(3)	Zn3	O8	2.000(3)
Zn2	O5	1.976(3)	Zn3	O16[9]	1.989(3)

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	Zn1	O4[1]	88.47(12)	O14[4]	Zn1	O12[3]	86.99(11)
O1	Zn1	O7[2]	95.33(12)	O5	Zn2	O9[5]	101.70(13)
O1	Zn1	O10	177.12(13)	O5	Zn2	O12[6]	127.70(13)
O1	Zn1	O12[3]	91.47(12)	O5	Zn2	O13[7]	104.19(12)
O1	Zn1	O14[4]	84.29(12)	O9[5]	Zn2	O12[6]	111.85(12)
O4[1]	Zn1	O12[3]	179.41(10)	O13[7]	Zn2	O9[5]	105.43(13)
O7[2]	Zn1	O4[1]	87.53(11)	O13[7]	Zn2	O12[6]	104.03(12)
O7[2]	Zn1	O12[3]	91.90(10)	O2[4]	Zn3	O4[8]	110.90(11)
O10	Zn1	O4[1]	94.20(12)	O8	Zn3	O2[4]	104.90(12)
O10	Zn1	O7[2]	83.70(12)	O8	Zn3	O4[8]	102.96(12)
O10	Zn1	O12[3]	85.85(12)	O16[9]	Zn3	O2[4]	103.48(13)
O10	Zn1	O14[4]	96.62(12)	O16[9]	Zn3	O4[8]	128.67(13)
O14[4]	Zn1	O4[1]	93.59(11)	O16[9]	Zn3	O8	103.62(12)
O14[4]	Zn1	O7[2]	178.81(11)				

[1]1+X,+Y,+Z; [2]1+X,1+Y,+Z; [3]-1+X,+Y,+Z; [4]-1+X,-1+Y,+Z;

[5]-X,1-Y,-Z; [6]1-X,1-Y,-Z; [7]1-X,2-Y,-Z; [8]+X,-1+Y,+Z; [9]1-X,2-Y,1-Z.

Table S3. Summary of quenching constants (K_{sv}) of **1** for sensing different analytes at room temperature.

Analytes	K_{sv} (ppm^{-1})	Analytes	K_{sv} (ppm^{-1})
NZF	1.7×10^{-1}	TNP	5.3×10^{-1}
DTZ	1.6×10^{-1}	4-NP	3.8×10^{-1}
FZD	1.0×10^{-1}	2-NP	1.9×10^{-2}
ODZ	6.3×10^{-2}	3-NP	3.2×10^{-2}
NFT	9.1×10^{-2}	2-NT	2.8×10^{-2}
RDZ	4.6×10^{-2}	2,4-DNT	2.5×10^{-2}
CAP	6.4×10^{-3}	NB	2.1×10^{-2}
SMZ	1.7×10^{-2}	1,3-DNB	1.1×10^{-2}
MDZ	1.3×10^{-2}		
SDZ	3.3×10^{-3}		

Table S4. HOMO and LUMO energies calculated for the anlytes used at B3LYP/6-31G** level.

Analytes	HOMO (eV)	LUMO (eV)	Band gap
PCL[1]	-5.558	-1.777	3.781
SMZ[2]	-5.63	-1.82	3.81
SDZ[1]	-5.538	-2.26	3.278
FFC[2]	-6.62	-2.56	4.06
ODZ[2]	-4.97	-3.02	1.95
DTZ[2]	-6.37	-3.27	3.1
MDZ[2]	-6.41	-3.34	3.07
CAP[2]	-6.35	-3.42	2.93
RDZ[2]	-6.57	-3.52	3.05
NZF[2]	-5.99	-3.72	2.27
NFT[2]	-6.21	-3.94	2.27
FZD[2]	-6.37	-4.06	2.31
NB[2]	-6.59	-3.43	3.16
2-NT[2]	-6.51	-3.31	3.2
1,3-DNB[3]	-7.9855	-3.4311	4.5544
2,4-DNT[3]	-7.7645	-3.2174	4.5471
4-NP[2]	-6.34	-3.87	2.47
3-NP[2]	-6.32	-3.75	2.57
2-NP[2]	-6.24	-3.44	2.8
TNP[2]	-7.39	-4.97	2.42

1. B. Wang, X. L. Lv, D. W. Feng, L. H. Xie, J. Zhang, M. Li, Y. B. Xie, J. R. Li and H. C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 6204-6216.

2. H. R. Fu, L. B. Yan, N. T. Wu, L. F. Ma and S. Q. Zang, *J. Mater. Chem. A.*, 2018, **6**, 9183-9191.

3. S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem. Int. Ed.*, 2013, **52**, 2881-2885.