Supporting Information

An uncommon (5,5)-connected 3D metal organic material for selective and sensitive sensing of nitroaromatics and ferric ion: experimental studies and theoretical analysis

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Sensing Method

The photoluminescence sensing were performed as follows: the photoluminescence properties of **1** were investigated in N,N-dimethylformamide (DMF) emulsions at room temperature using a RF-5301PC spectrofluorophotometer. The **1**@DMF elusions were prepared by adding 5 mg of **1** powder into 3.00 mL of DMF and then ultrasonic agitation the mixture for 30 min before testing.

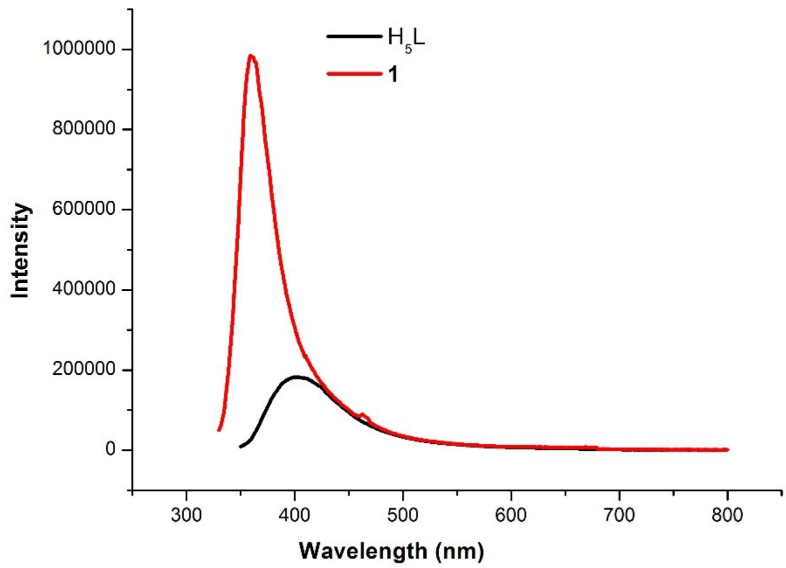


Fig. S1 view of the PL for solid state of **1** and H_5L at room temperature.

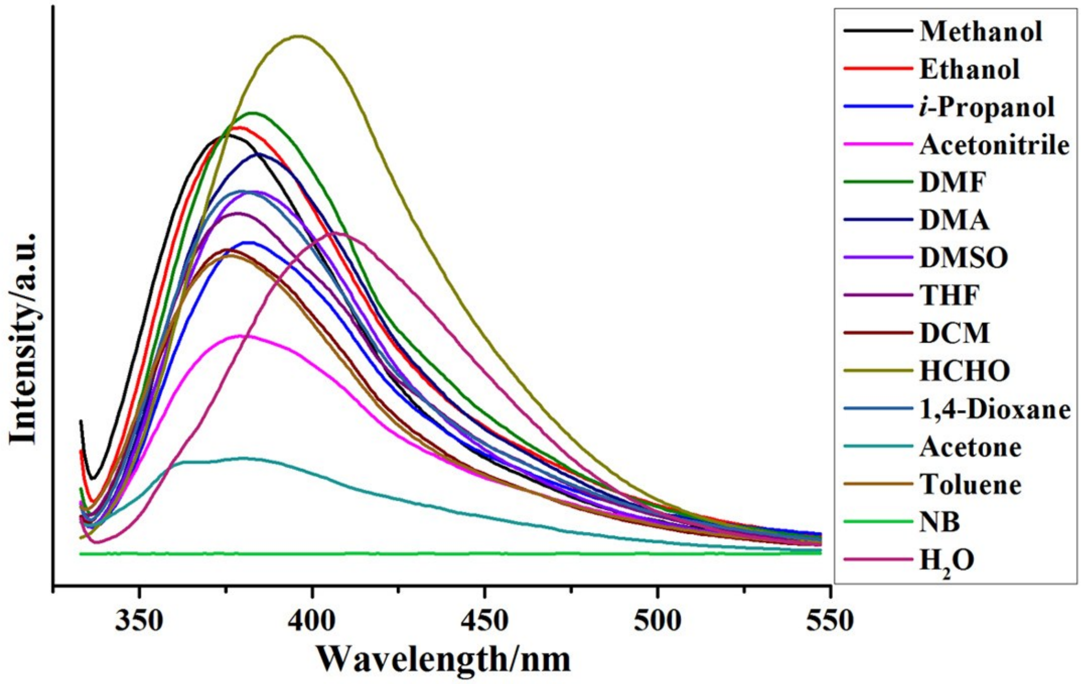


Fig. S2 Emission spectra of **1** at different solvents.

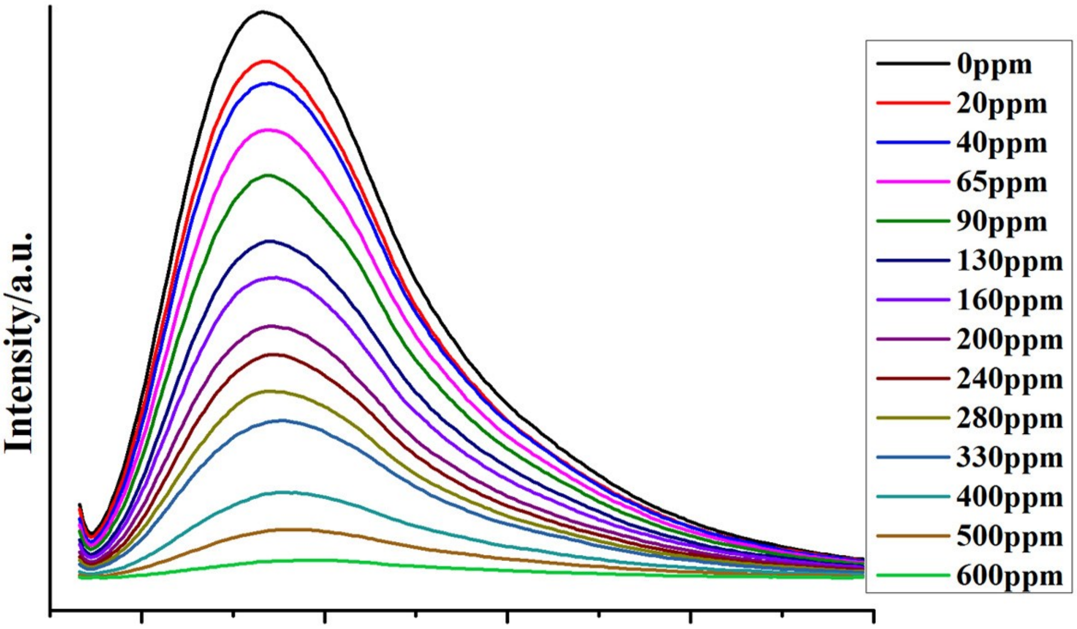


Fig. S3 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of 1,3-DNB in DMF.

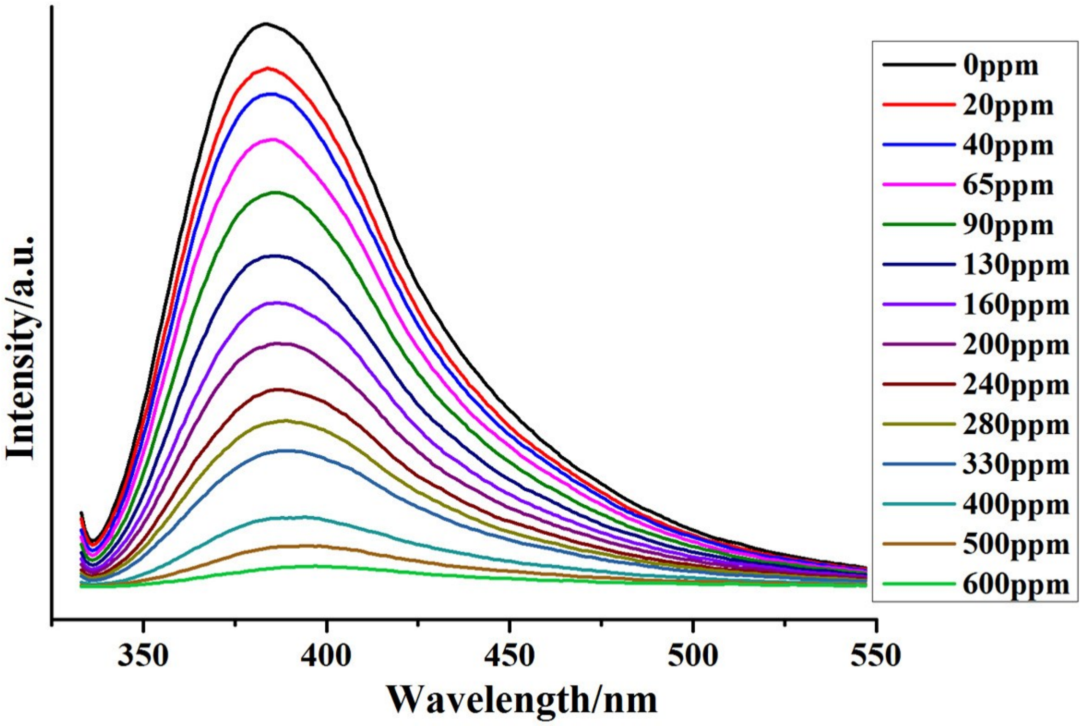


Fig. S4 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of 2,4-DNT in DMF.

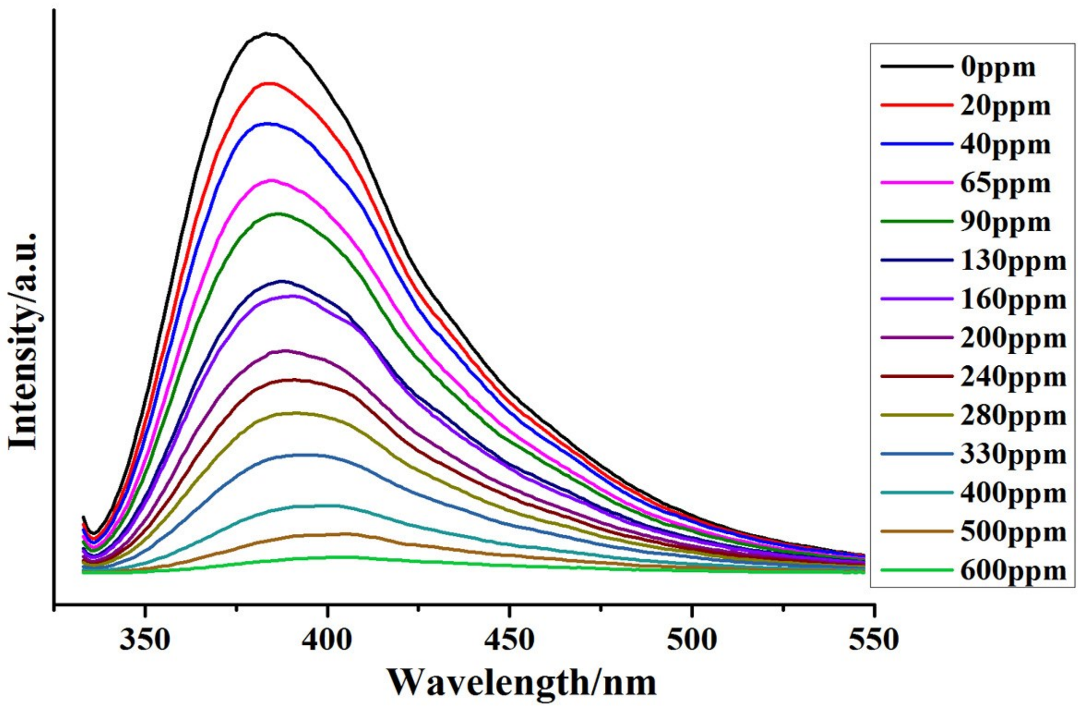


Fig. S5 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of 2,6-DNT in DMF.

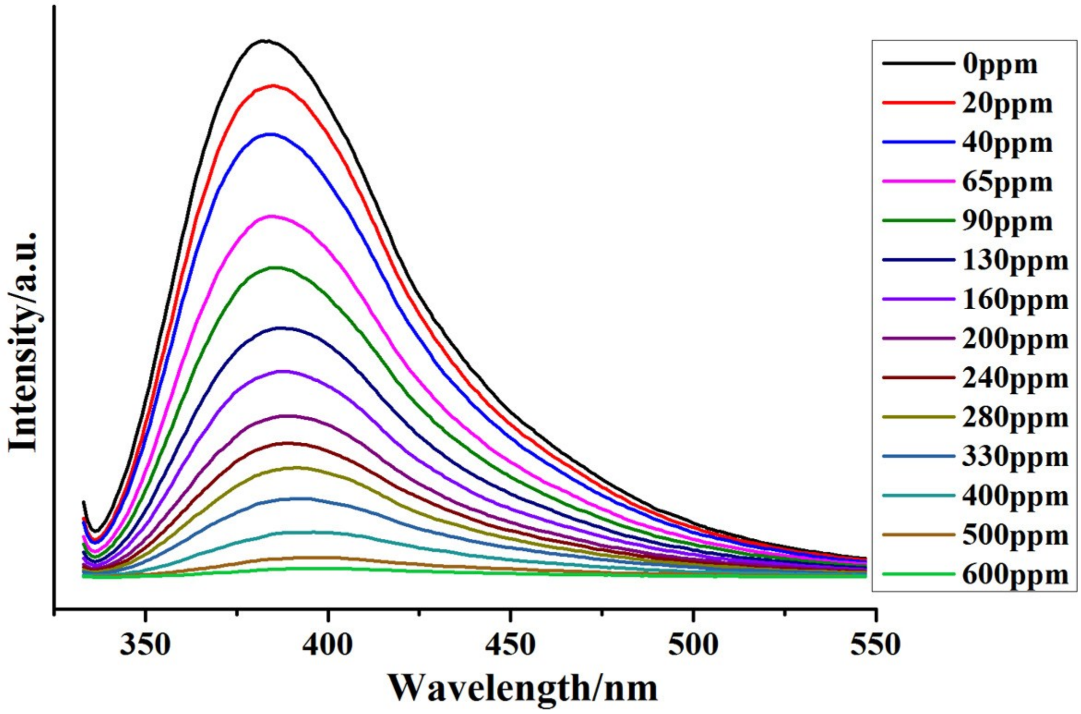


Fig. S6 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of 2-NT in DMF.

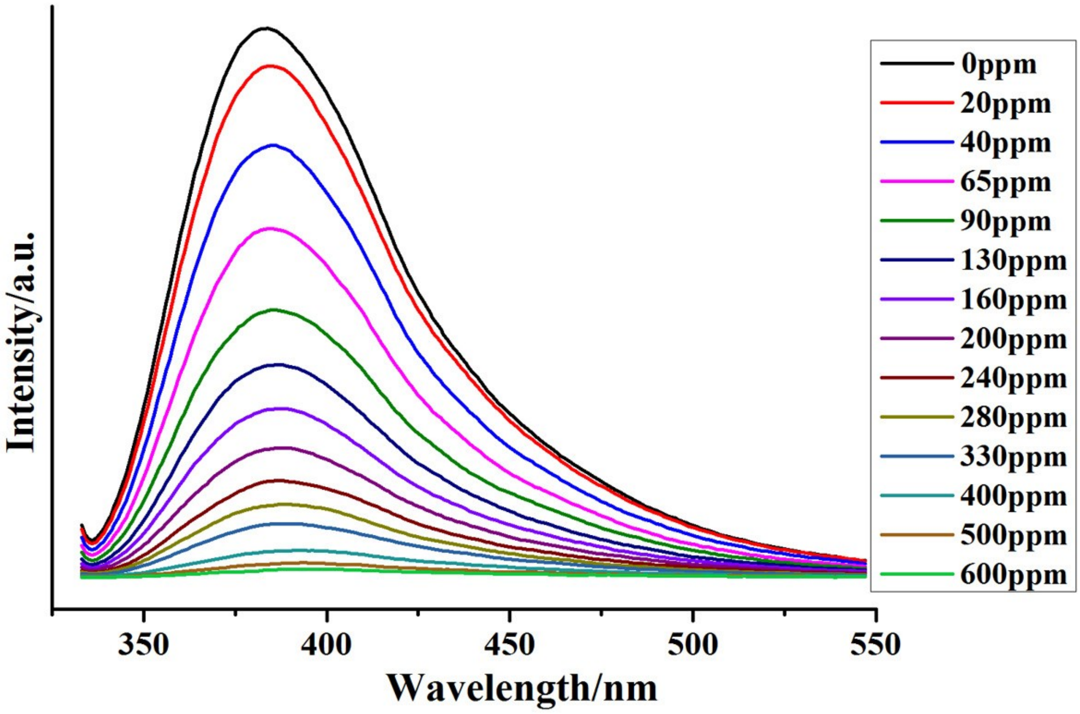


Fig. S7 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of 4-NT in DMF.

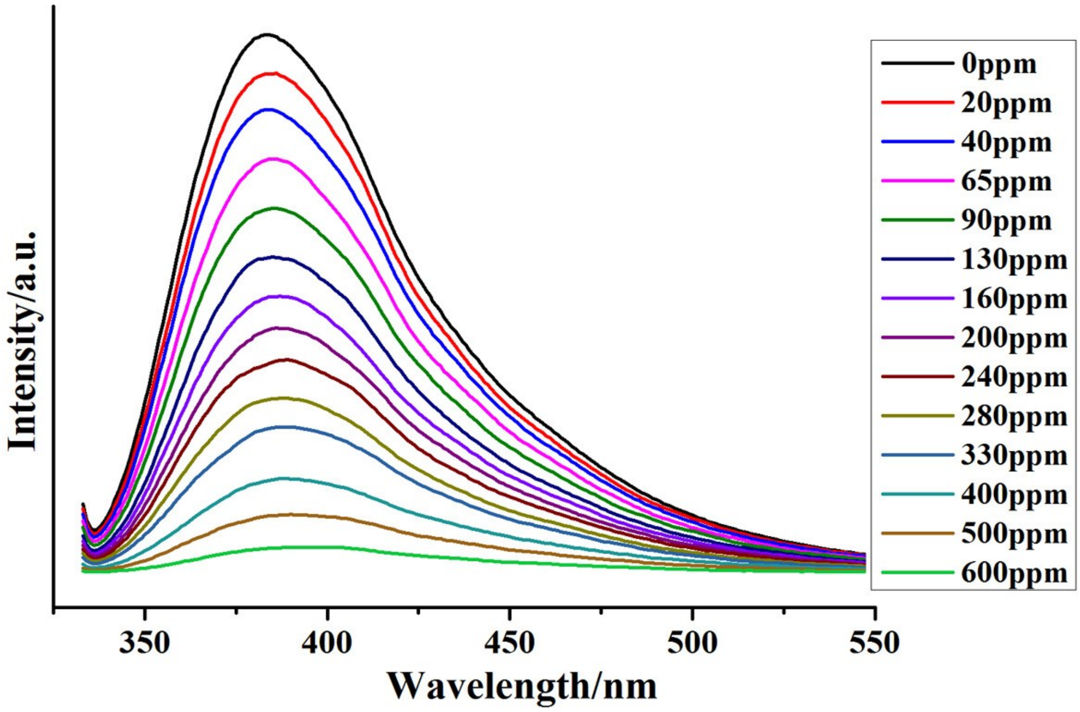


Fig. S8 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of NB in DMF.

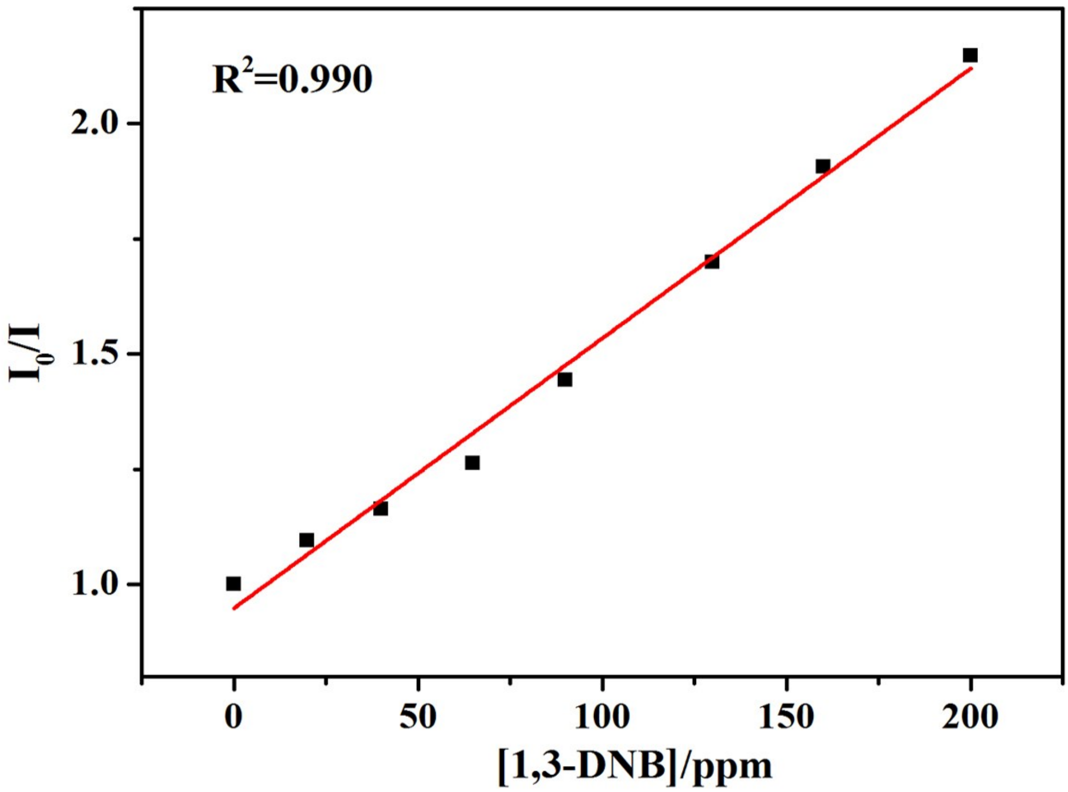


Fig. S9 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of 1,3-DNB.

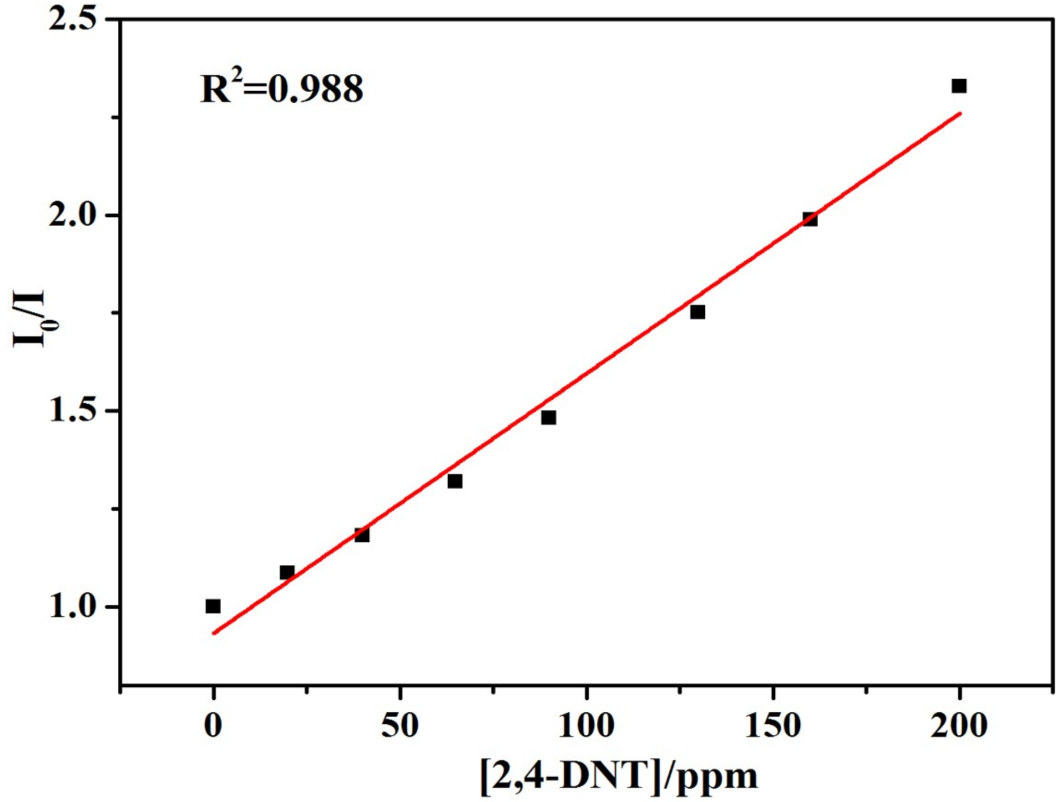


Fig. S10 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of 2,4-DNT.

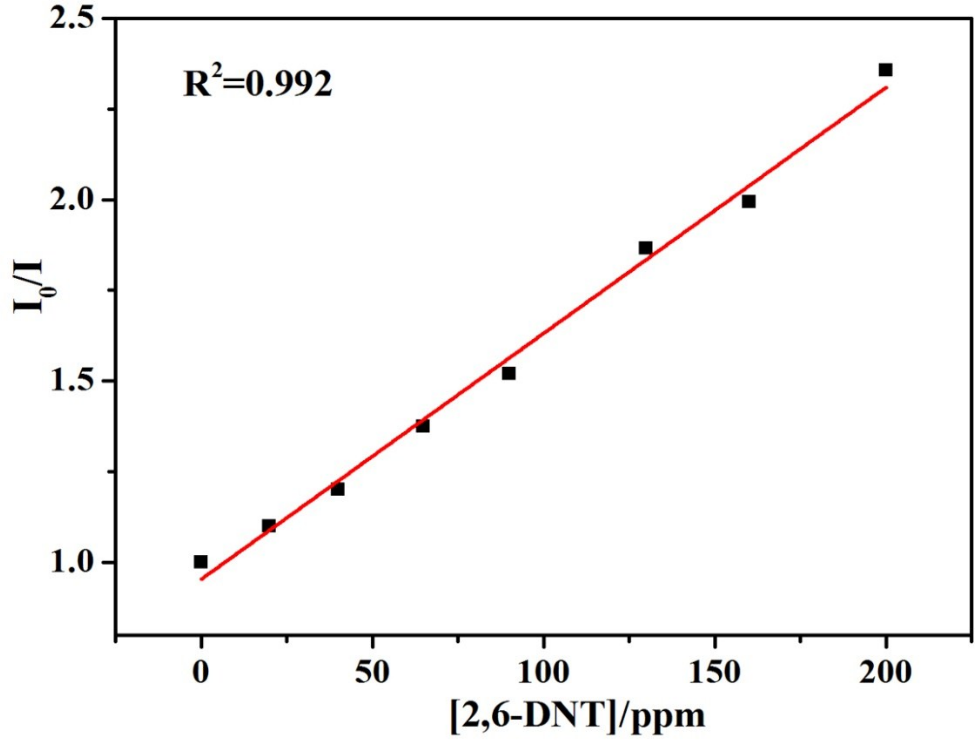


Fig. S11 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of 2,6-DNT.

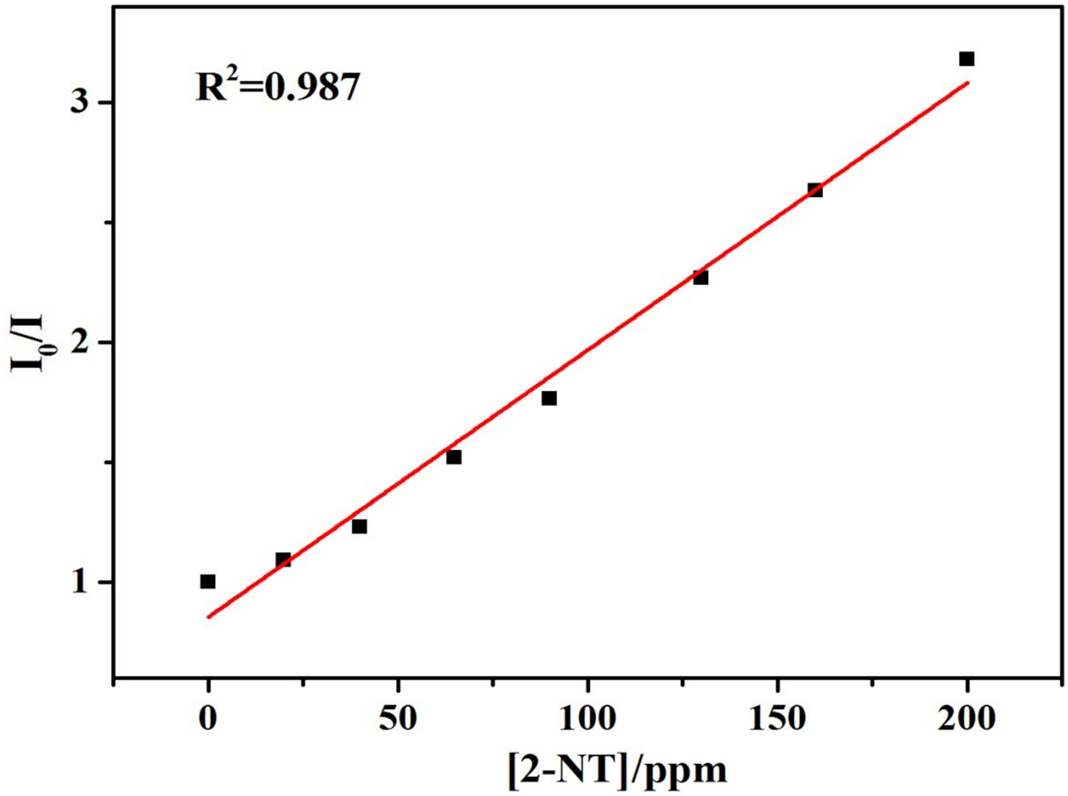


Fig. S12 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of 2-NT.

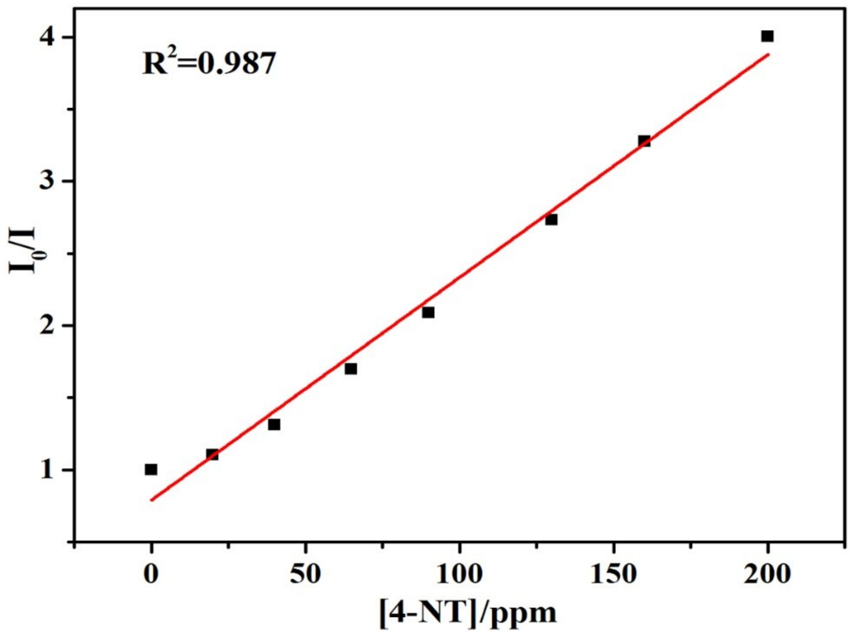


Fig. 13 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of 4-NT.

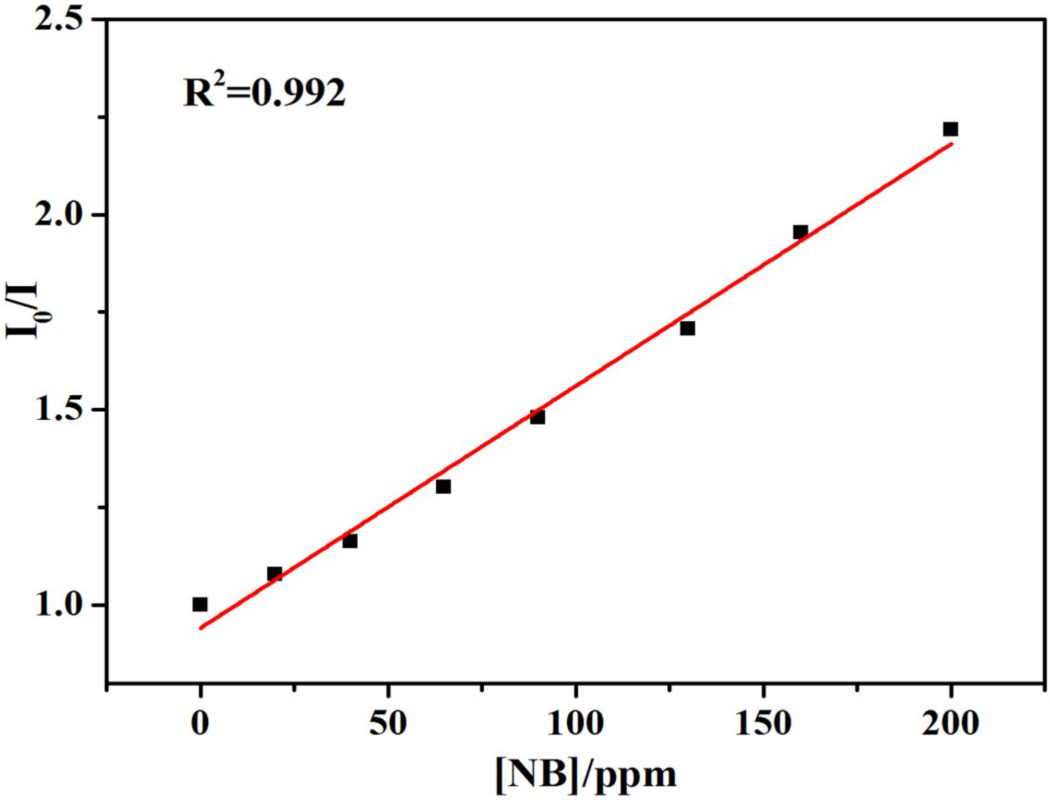
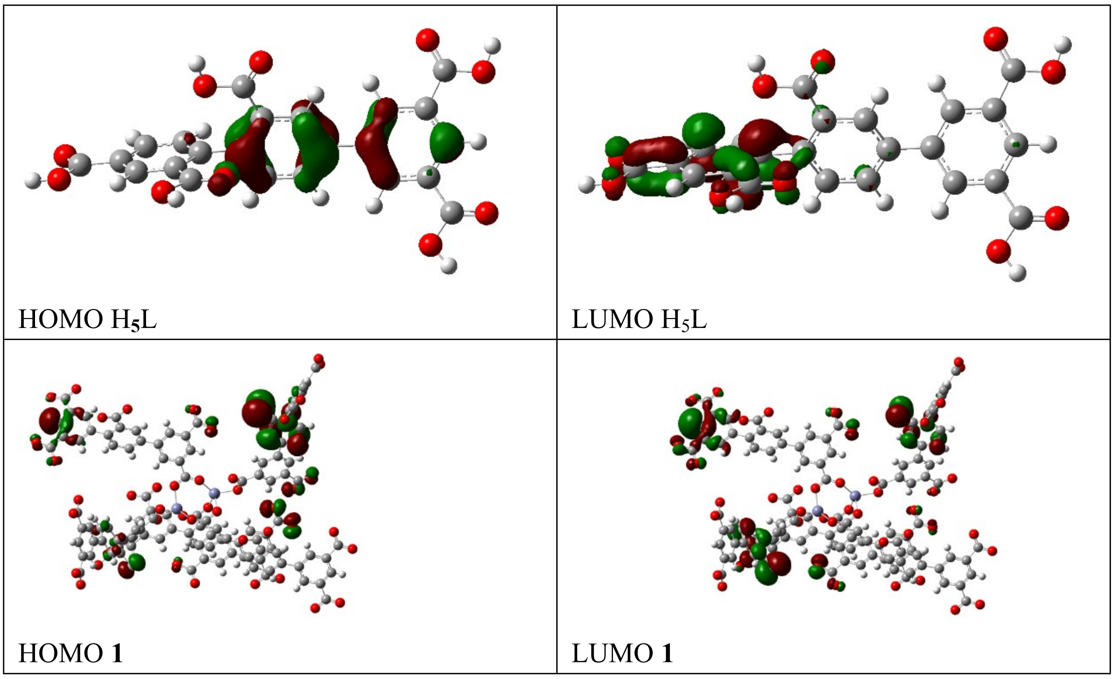
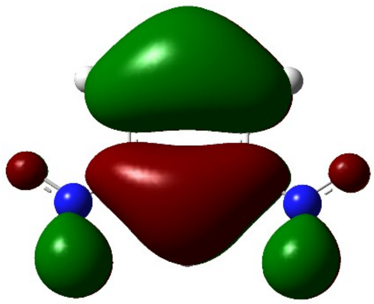
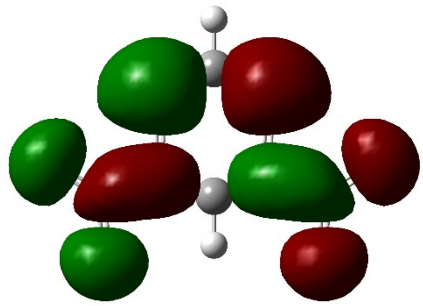
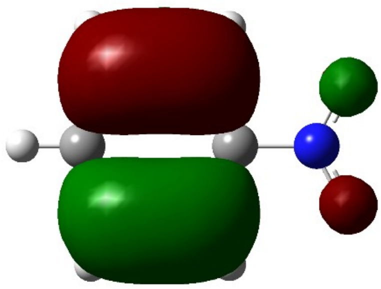
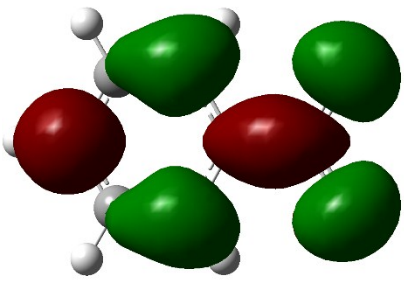
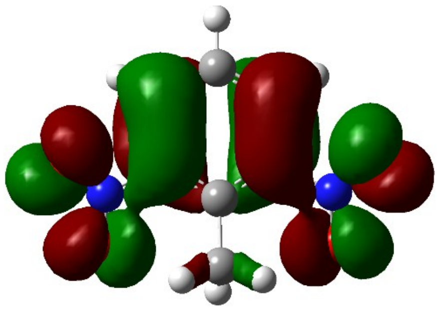
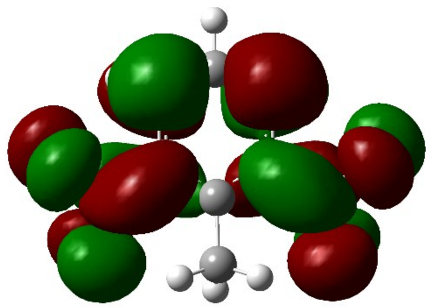
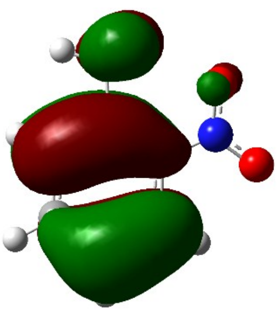
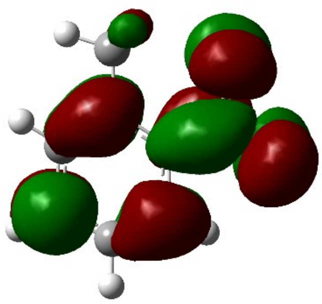
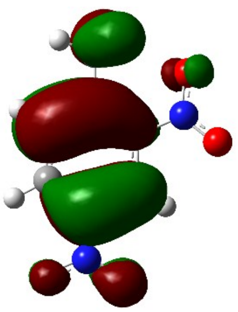
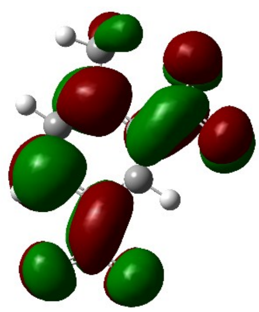


Fig. S14 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of NB.



 HOMO 1,3-DNB	 LUMO 1,3-DNB
 HOMO NB	 LUMO NB
 HOMO 2,6-DNT	 LUMO 2,6-DNT
 HOMO 2-NT	 LUMO 2-NT
	

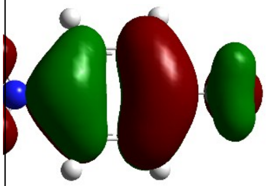
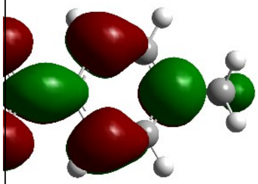
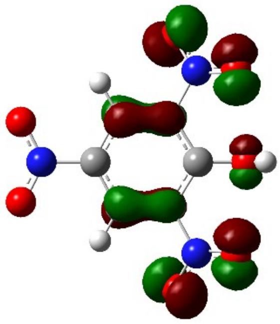
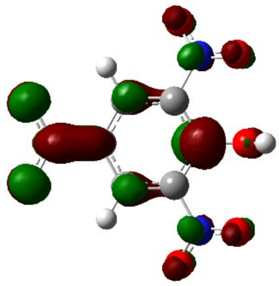
HOMO 2,4-DNT	LUMO 2,4-DNT
 HOMO 4-NT	 LUMO 4-NT
 HOMO TNP	 LUMO TNP

Fig. S15 HOMO-LUMO plots of H_5L, **1** and NACs

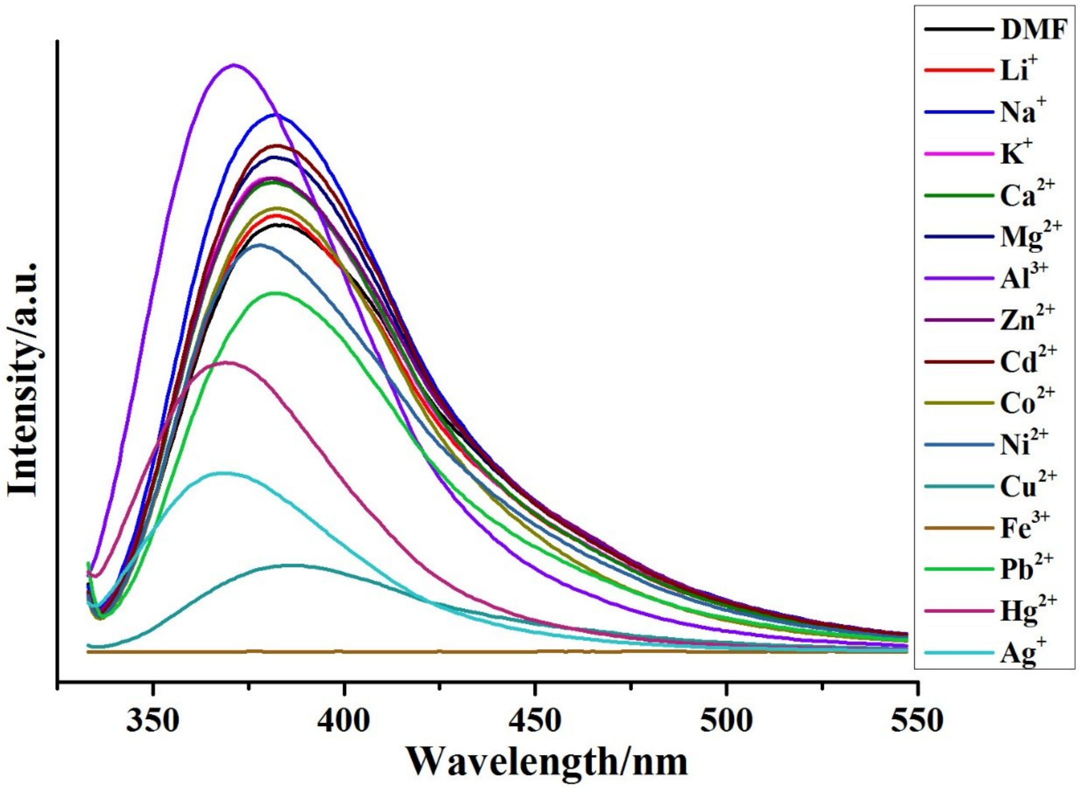


Fig. S16 Emission spectra of **1** at different metal ions.

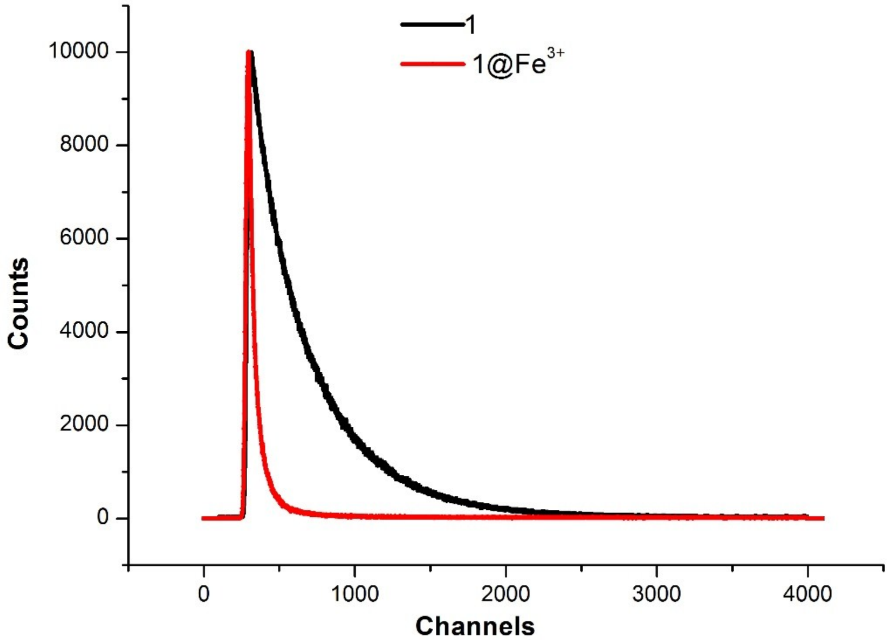


Fig. S17 Comparison of the fluorescence lifetime studies of original samples (black) and Fe^{3+}-infused **1** in 10^{-2} $Fe(NO_3)_3$ DMF solution (red).

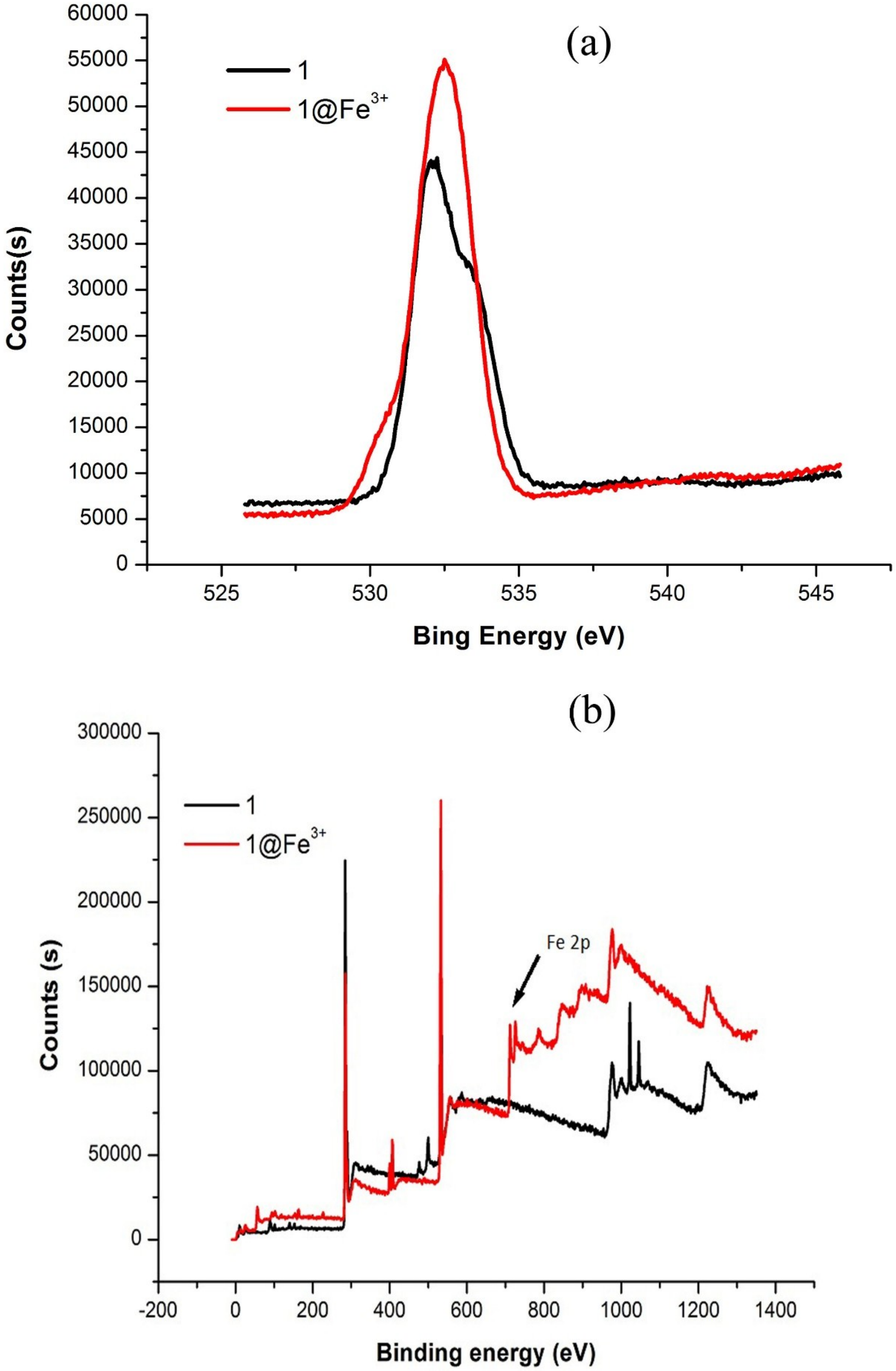


Fig. S18 (a) O1s XPS spectra of the original **1** (black) and **1**@Fe^{3+} (red); (b) XPS spectra of the **1**@Fe^{3+} (red) and original **1** (black).

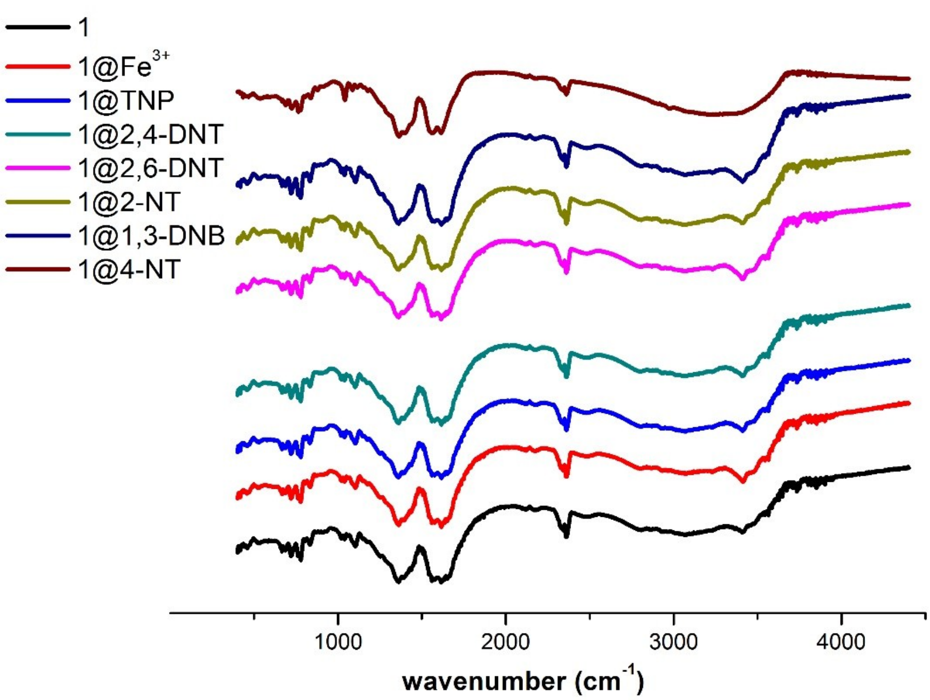


Fig. S19 view of IR spectra for different inclusion.

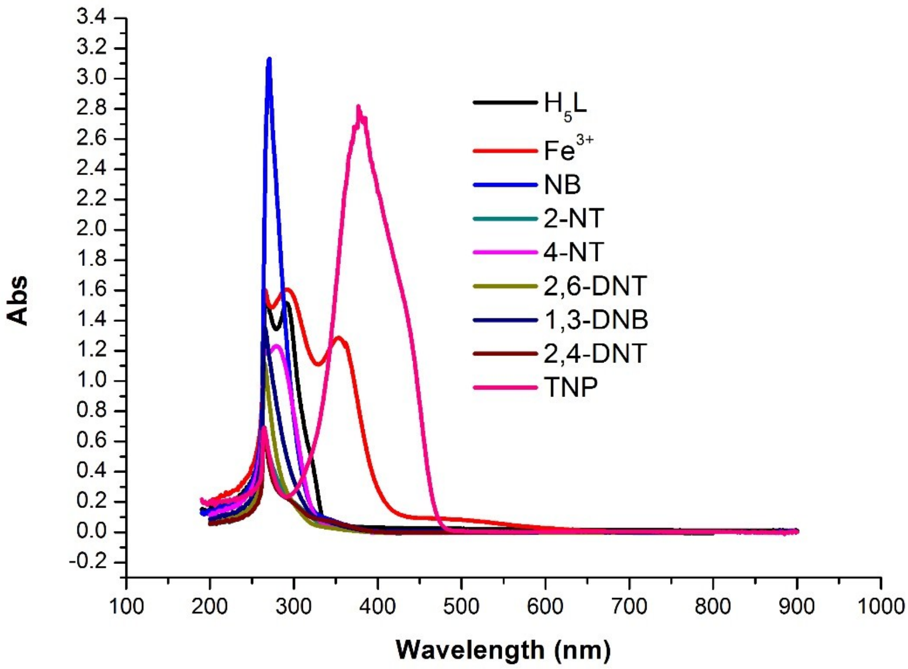


Fig. S20 view of spectra of the UV-vis for different analytes and ligand.

PXRD and thermal analysis

The PXRD pattern of the as-synthesized sample of **1** is uniform to that simulated from the single-crystal structure, showing the phase purity of the bulk samples (Fig. S21).

TGA of **1** displays a weight loss of 7.2% from 30 to 270 °C under a N2 atmosphere, resulting from the release of all DMF and water molecules per formula unit (calc. 7.3%). A plateau is followed within the temperature range 270–335 °C, which indicates that the framework's stability is up to 335 °C (Fig. S23). A further heating induces an abrupt weight loss owing to the decomposition of **1**. The weight loss ends at around 490 °C, leaving the white ZnO residua (obs. 25.7%, calc. 23.3%).

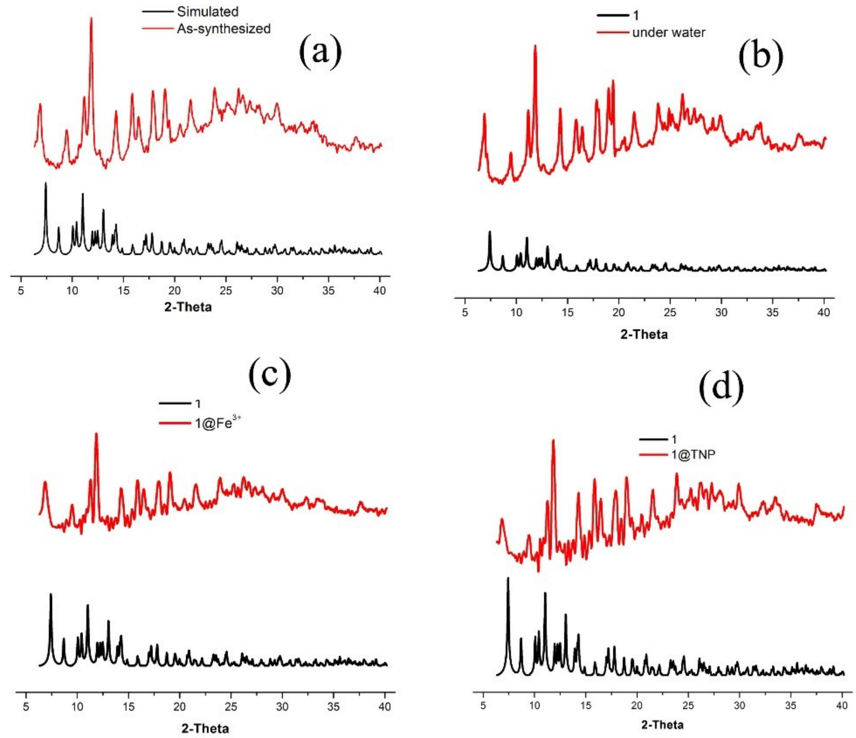


Fig. S21 XRD profiles of **1** (a) as-synthesized sample; (b) at water medium; and (c)-(d) after being soaked in Fe^{3+} and TNP solvents for 12 h.

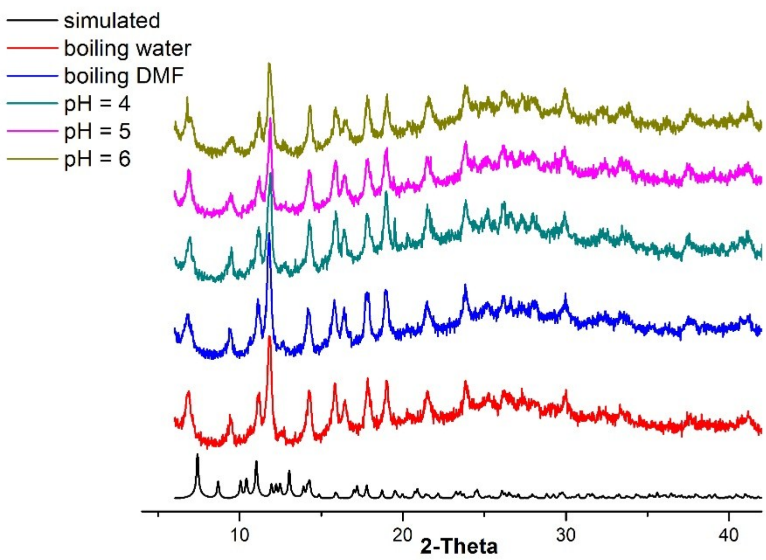


Fig. S22 XRD profiles of **1** after being soaked in acidic solutions for12 h.

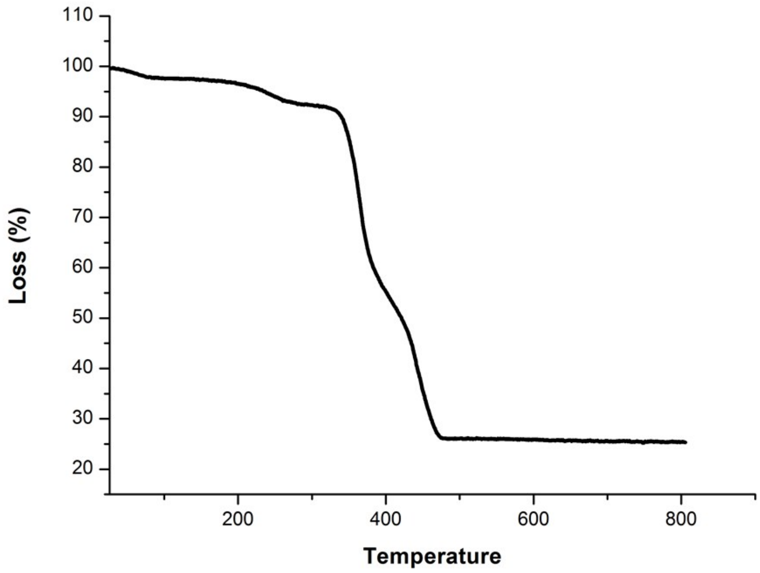


Fig. S23 view of TGA for sample **1**.

Table S1. Crystallographic data and structure refinement details for 1

Parameter	**1**
Formula weight	592.08
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Crystal color	colorless
a, Å	9.0940(6)
b, Å	12.7134(5)

c, Å	33.9463(14)
α, °	90
β, °	90
γ, °	90
V, Å ^{3}	3924.7(3)
Z	4
ρ_{calcd}, g/cm^3	1.002
μ, mm^{-1}	1.834
F(000)	1180
θ Range, deg	5.5-73.3
Reflection collected	5712
Independent reflections (R_{int})	0.063
Reflections with $I > 2\sigma(I)$	4743
Number of parameters	326
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0878, 0.2365
R_1, wR_2 (all data)**	0.0983, 0.2531

* $R = \sum(F_o - F_c)/\sum(F_o)$, ** $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$.

Table S2. Selected bond distances (Å) and angles (deg) for **1**

	1		
Zn(1)-O(1)	1.989(12)	Zn(1)-O(2)	2.551(15)
Zn(1)-O(11)	2.149(19)	Zn(1)-O(3)#1	1.952(9)
Zn(1)-O(5)#2	1.955(13)	Zn(1)-O(7)#3	2.007(11)
Zn(2)-O(8)	1.915(11)	Zn(2)-O(4)#4	1.945(7)
Zn(2)-O(6)#5	1.953(9)	Zn(2)-O(9)#6	1.925(7)

	1		
O(1)-Zn(1)-O(2)	54.2(5)	O(1)-Zn(1)-O(11)	85.7(7)
O(1)-Zn(1)-O(3)#1	127.1(6)	O(1)-Zn(1)-O(5)#2	104.3(5)

O(1)-Zn(1)-O(7)#3	97.4(5)	O(2)-Zn(1)-O(11)	96.6(6)
O(2)-Zn(1)-O(3)#1	78.1(5)	O(2)-Zn(1)-O(5)#2	158.2(4)

Material	K_{sv} (M^{-1})	Reference
$Zn_2(TZBPDC)(\mu_3\text{-}OH)(H_2O)_2$	4.9×10^4	1
$\{[Zn(tcbp)_{0.5}(bpe)_{0.5}]\cdot0.5(bpe).2H_2O\}_n$	8.1×10^4	2
$\{[Tb(L1)_{1.5}(H_2O)]\cdot3H_2O\}_n$	7.47×10^4	3
$[Y_2(PDA)_3(H_2O)]\cdot2H_2O$	7.09×10^4	4
$[Zn_2(L)_2(dpyb)]$	2.4×10^4	5
$[Cd(NDC)_{0.5}(PCA)]\cdot G_x$	3.5×10^4	6
$Zr_6O_4(OH)_4(L)_6$	2.9×10^4	7
$[Cd_2Cl(H_2O)(L)]\cdot4.5DMA$	3.6×10^4	8
$(Me_2NH_2)_6[In_{10}(TTCA)_{12}]\cdot24DMF\cdot15H_2O$	1.36×10^4	9
1	1.42×10^4	In this work

O(3)#1-Zn(1)-O(11)	77.6(8)	O(7)#3-Zn(1)-O(11)	176.8(6)
O(4)#4-Zn(2)-O(8)	118.7(5)	O(6)#5-Zn(2)-O(8)	103.4(5)
O(8)-Zn(2)-O(9)#6	100.4(4)		

symmetry codes: #1 = -x, -1/2+y, 1/2-z; #2 = -x, 1/2+y, 1/2-z; #3 = 1-x, 1/2+y, 1/2-z; #4 = 1+x, -1+y, z; #5 = 1+x, y, z; #6 = 1/2+x, 1/2-y, 1-z.

Table S3 Listed the parameters for the analytes in this work.

Analyte		**Results**
$Fe(NO_3)_3$	**K_{sv}**	**7.83×10^3**
	LOD	**0.81**
TNP	**K_{sv}**	**1.42×10^4**
	LOD	**0.54**

Table S4 Comparison of the detective sensitivity in various TNP sensors.

Table S5 Comparison of the detective sensitivity in various Fe^{3+}sensors.

Material	Sensitivity	Reference
$Eu(acac)_3@Zn(C_{15}H_{12}NO_2)_2$	5×10^{-3} M	1
$Eu(C_{33}H_{24}O_{12})(H_2NMe)(H_2O)$	2×10^{-4} M	2
$Eu(C_{22}H_{14}O_2)_3$	10^{-4} M	3
$[Eu(BTPCA)(H_2O)]\cdot 2DMF\cdot 3H2O$	10^{-5} M	4
MIL-53(Al)	0.9×10^{-6} M	5
$[Tb(BTB)(DMF)]\cdot 1.5DMF\cdot 2.5H_2O$	10^{-5} M	6
carbon nanoparticles (CNPs)	0.32×10^{-6} M	7
Fluorescent Gold Nanoclusters	5.4×10^{-6} M	8
1	1.44×10^{-5} M	In this work

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