Supporting Information

A new Zn(II) metal-organic framework having 3D $CdSO_4$ topology as luminescent sensor and photocatalyst for degradation of organic dyes

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Photoluminescence measurements

The photoluminescence sensing experiments were performed as follows: the photoluminescence properties of **1** were investigated in DMF/H_2O emulsions at room temperature using a RF-5301PC spectrofluorophotometer. The suspensions were prepared by adding 5 mg of **1** powders into 3 mL of DMF/H_2O and then ultrasonic agitation the mixture for 30 min before testing. For the titration experiments of TNP, **1** powder (5 mg) was immersed in DMF solutions with the dropped addition of different concentrations of TNP in DMF. The photomultiplier tube (PMT) voltage was 700 V, the scan speed was 1200 nm min^{-1}, the slit width of excitation and emission is 5 nm.

Photocatalytic Method

The photocatalytic reactions were performed as follows: 50mg of **1** were dispersed in 50 mL aqueous solution of RhB/MV (10 mg/L) under stirring in the dark for 30 min to ensure the establishment of an adsorption-desorption equilibrium. Then the mixed solution was exposed to UV irradiation from an Hg lamp (250 W) and kept under continuous stirring during irradiation for 100 min. Samples of 5mL were taken out every 10 min and collected by centrifugation for analysis by UV-Vis spectrometer. By contrast, the simple control experiment was also performed under the same condition without adding any catalysts. The photocatalytic activity studies were carried out in a Shimadzu UV-Vis 2501PC recording spectrophotometer.

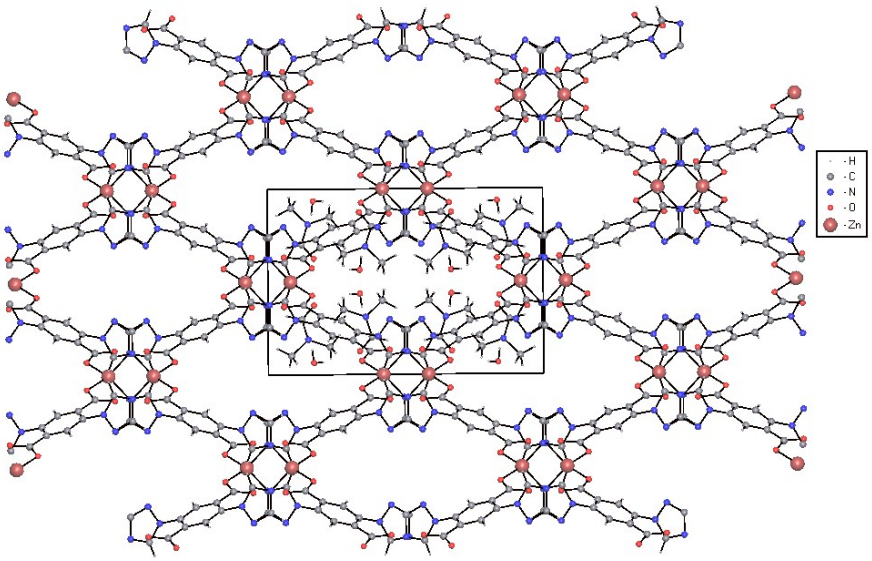


Fig. S1 3D packing pattern in **1,** solvents are included in the voids.

Thermogravimetric analysis (TGA) were carried out under nitrogen atmosphere from room temperature up to 800 °C with a heating rate of 10 °C min^{-1} (Fig. S2) to study the thermal stability of **1**. The first weight loss takes place at 130–252 °C and corresponds to the loss of guest DMF molecules (obsd, 33.2 %; calcd, 33.7%). After 252 °C, the material exhibits a striking weight loss, indicating the complete decomposition of the structure.

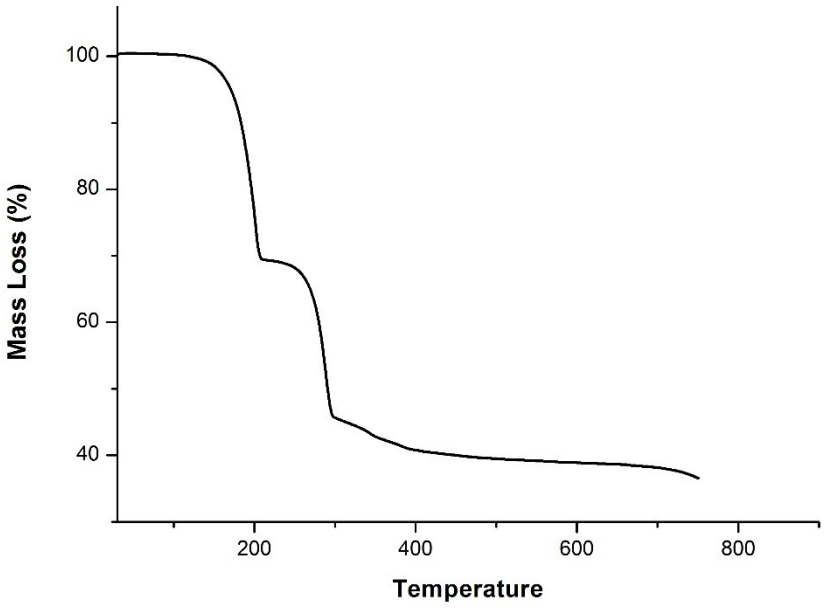


Fig. S2 view of TGA in **1**.

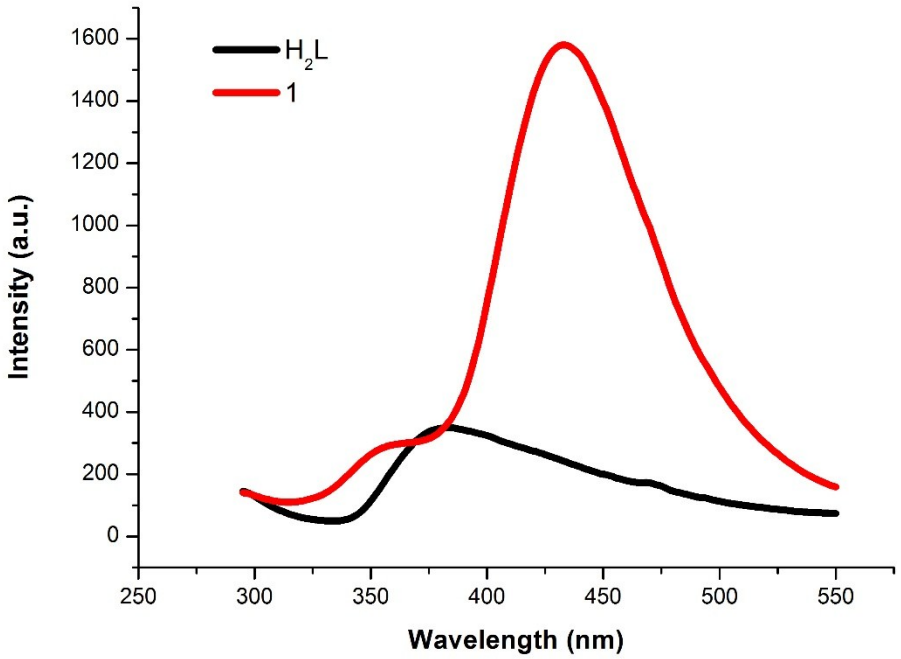


Fig. S3 The photoluminescence spectra of solid samples of H_2L ligand and **1** recorded at room temperature (λ_{ex} =280 nm).

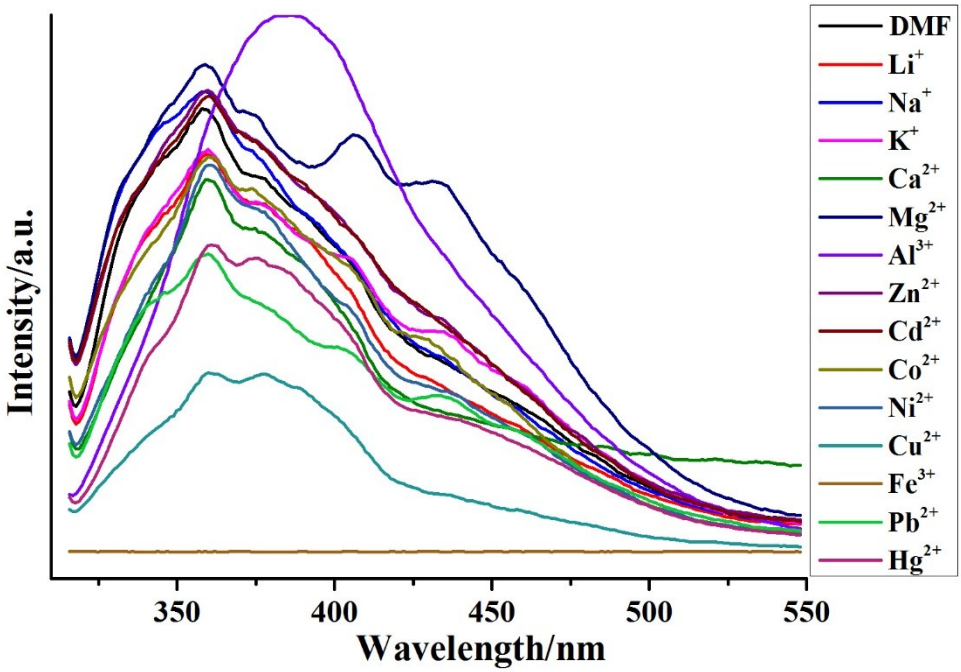


Fig. S4 The photoluminescence intensities spectra of **1** that was dispersed in the solutions of

different metal ions.

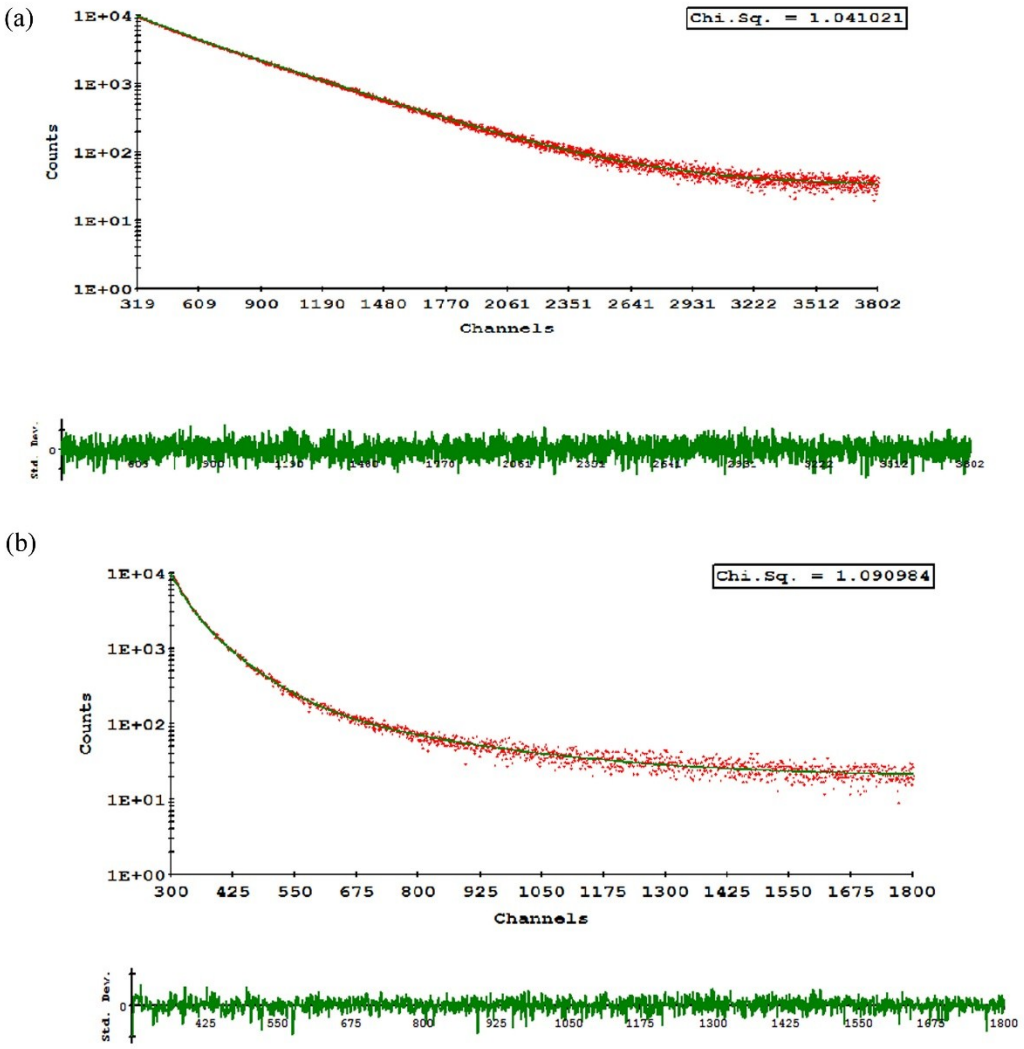


Fig. S5 Comparison of the fluorescence lifetime of **1** (above) and Fe^{3+}@ **1** (below).

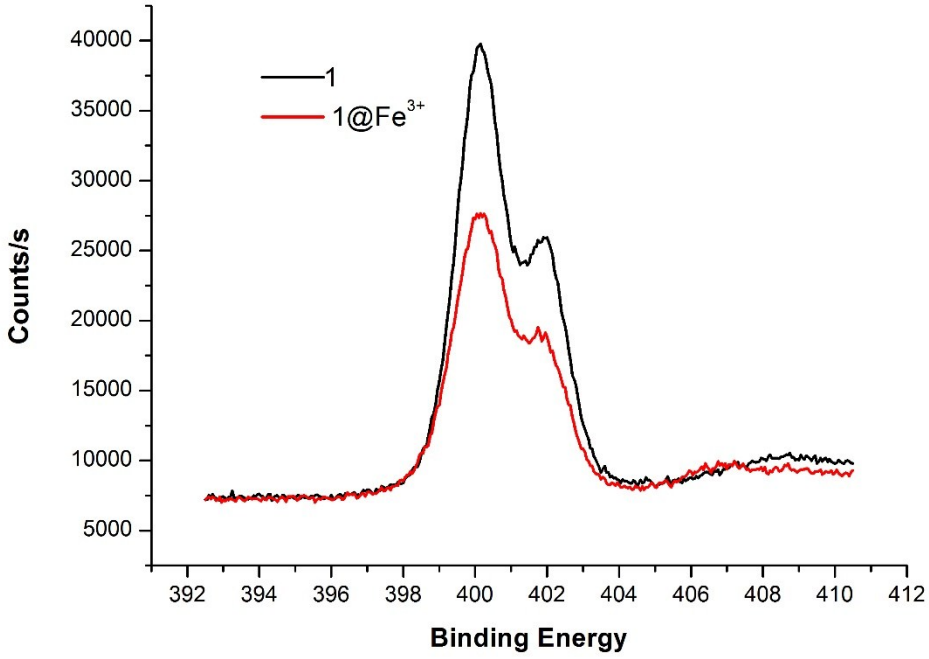


Fig. S6 The N1s XPS spectra of the **1** (black) and **1**@Fe^{3+} (red).

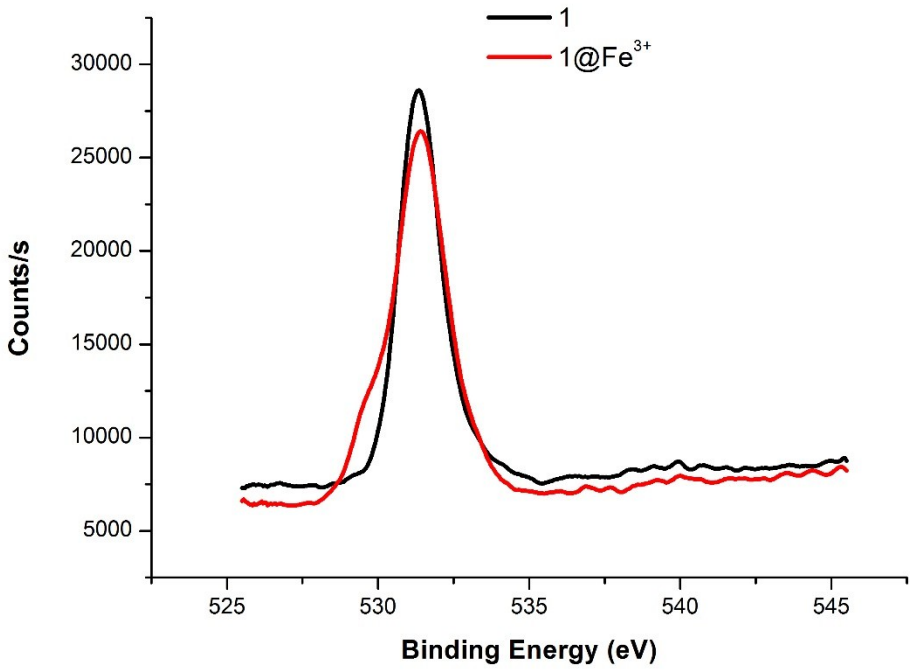


Fig. S7 The O1s XPS spectra of the **1** (black) and **1**@Fe^{3+} (red).

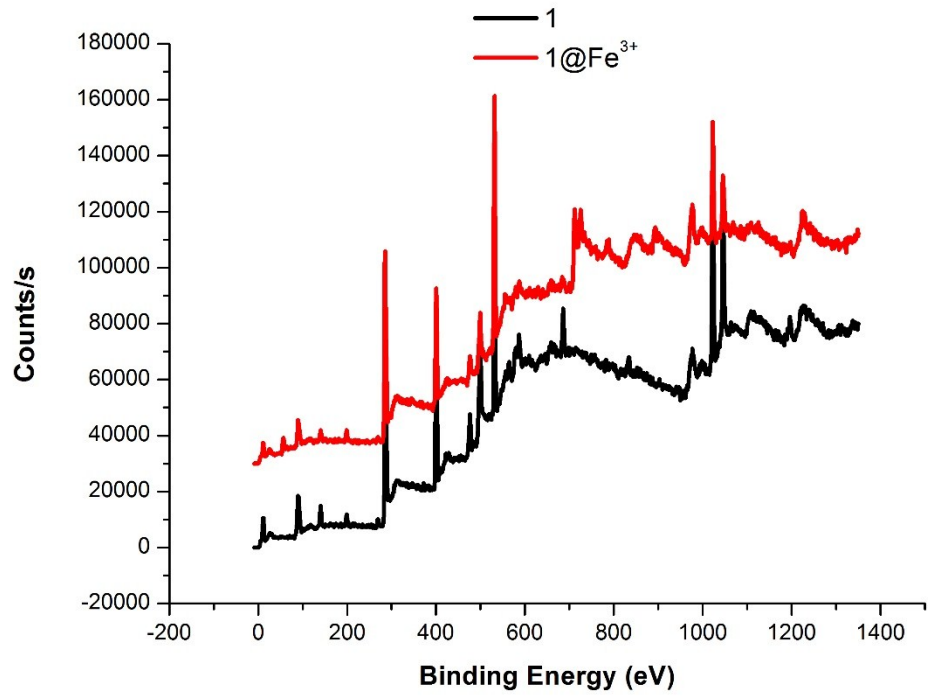


Fig. S8 The XPS spectra of the **1**@Fe^{3+} (red) and **1** (black).

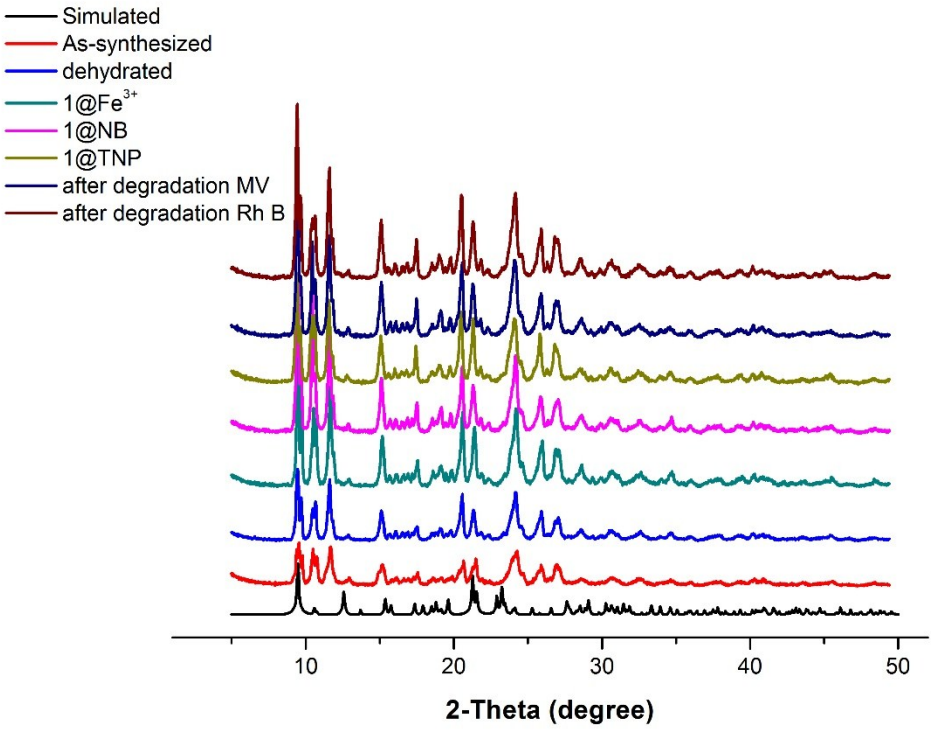


Fig. S9 view of the PXRD for the sample **1** (black: simulated; red: as-synthesized) and its suspensions of analytes.

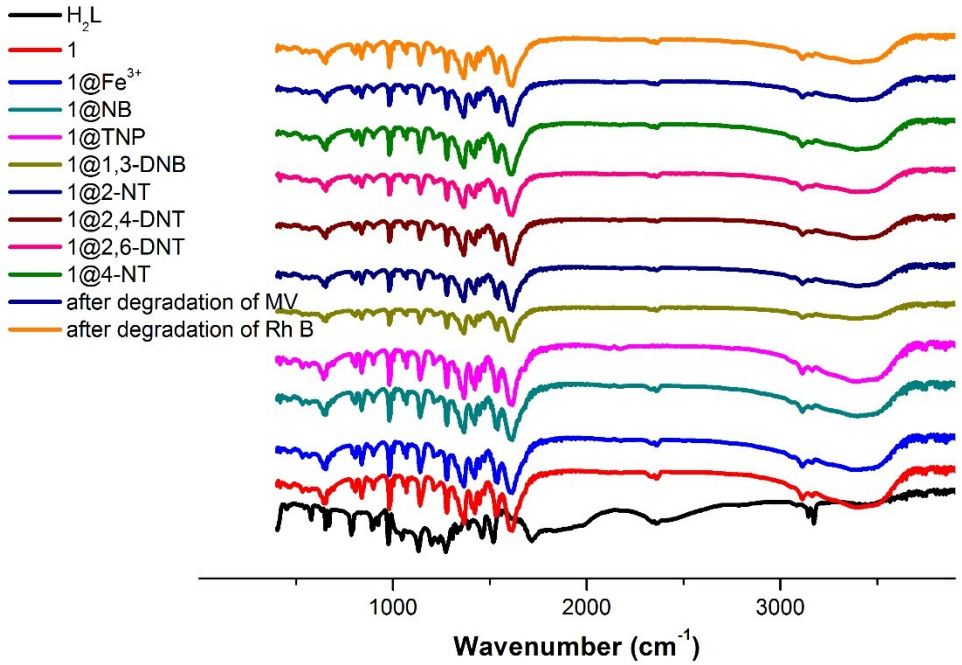


Fig. S10 The IR spectra of **1**, H_2L, **1**@Fe^{3+}, **1**@ACs (ACs = nitro-aromatic and aromatic compounds) and the samples after degradation of dyes.

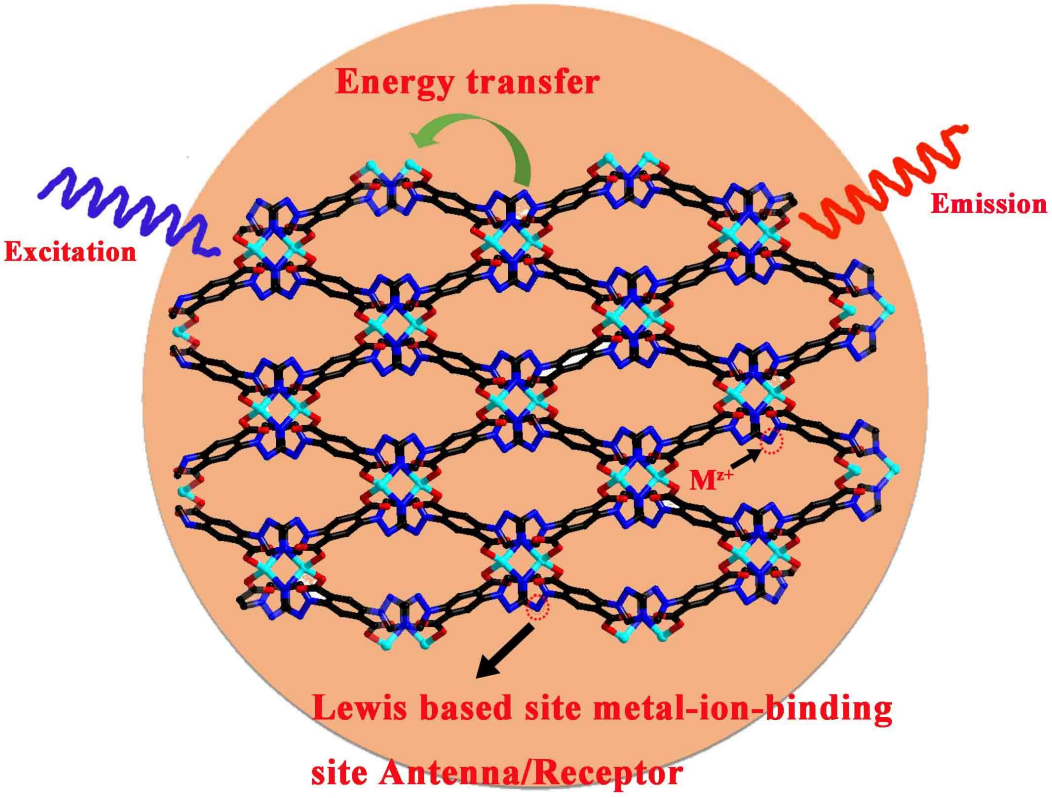


Fig. S11 Pictorial description of energy-transfer processes in **1**.

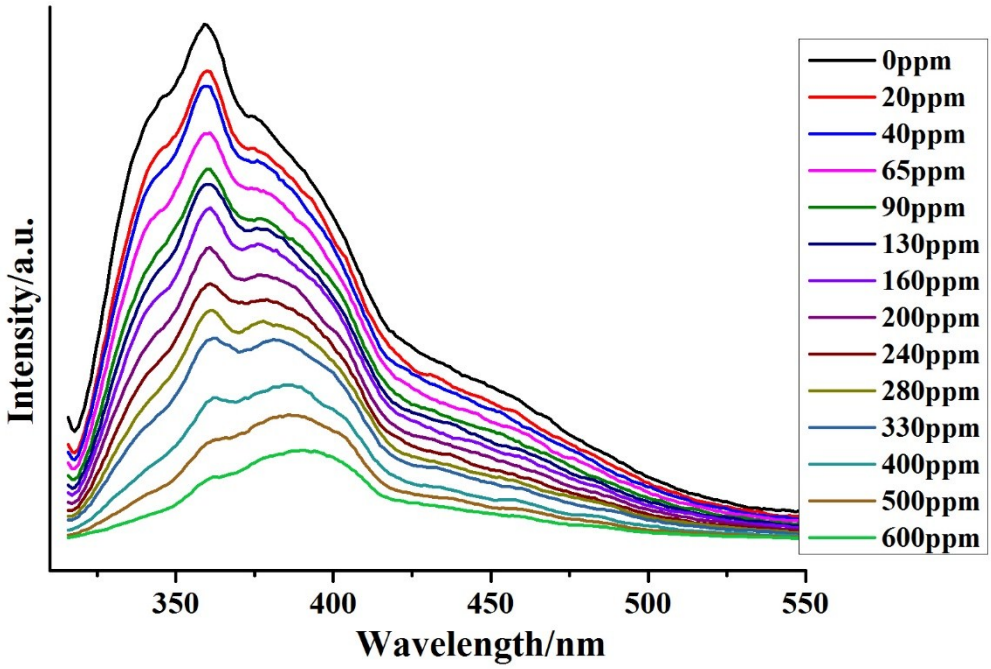


Fig. S12 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of 1,3-DNB in DMF.

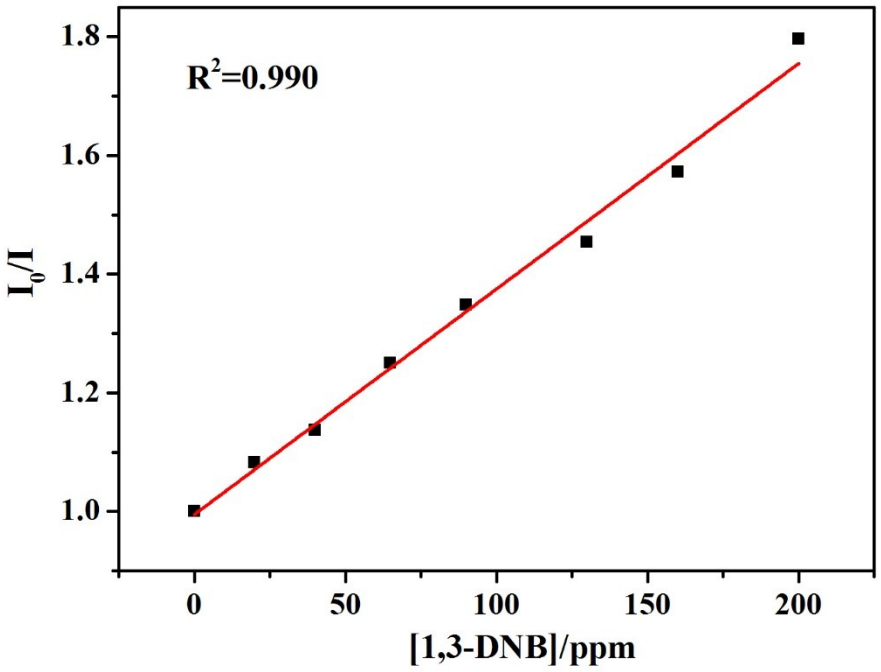


Fig. S13 The Stern–Volmer plot of **1** against 1,3-DNB.

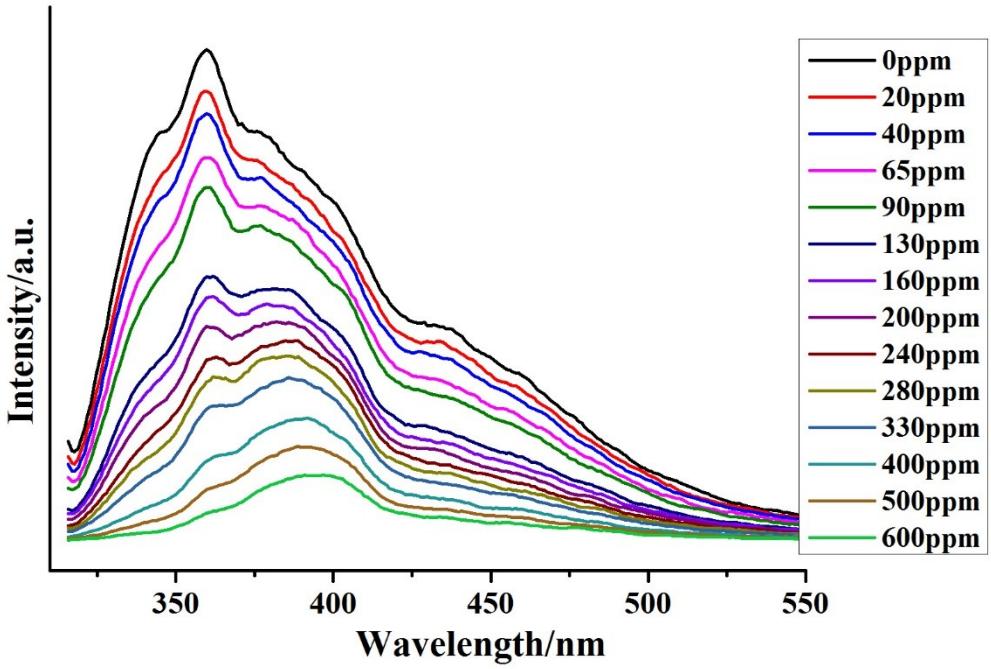


Fig. S14 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of 2,4-DNT in DMF.

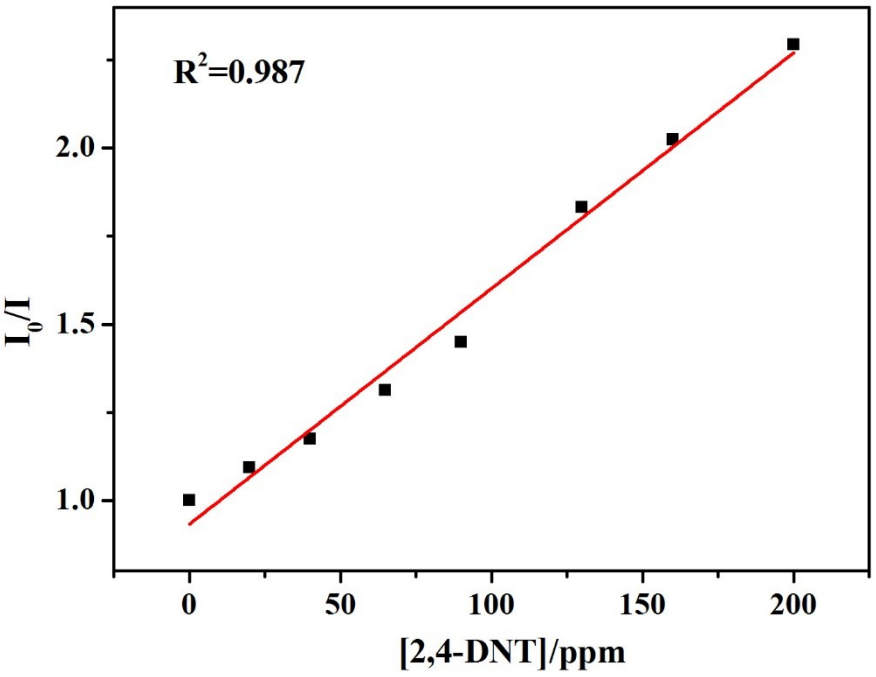


Fig. S15 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of 2,4-DNT.

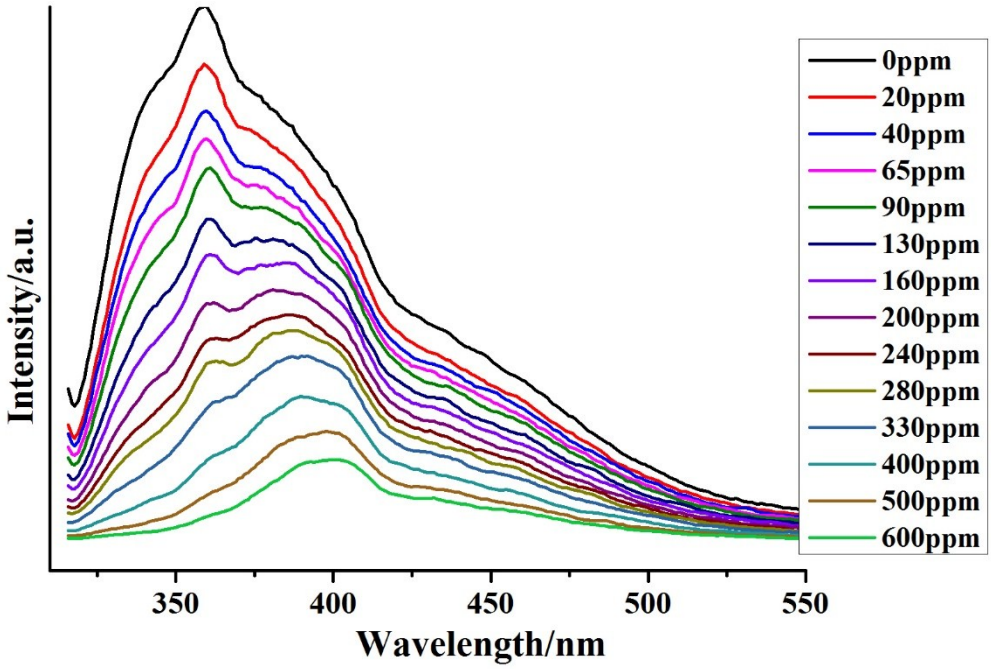


Fig. S16 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of 2,6-DNT in DMF.

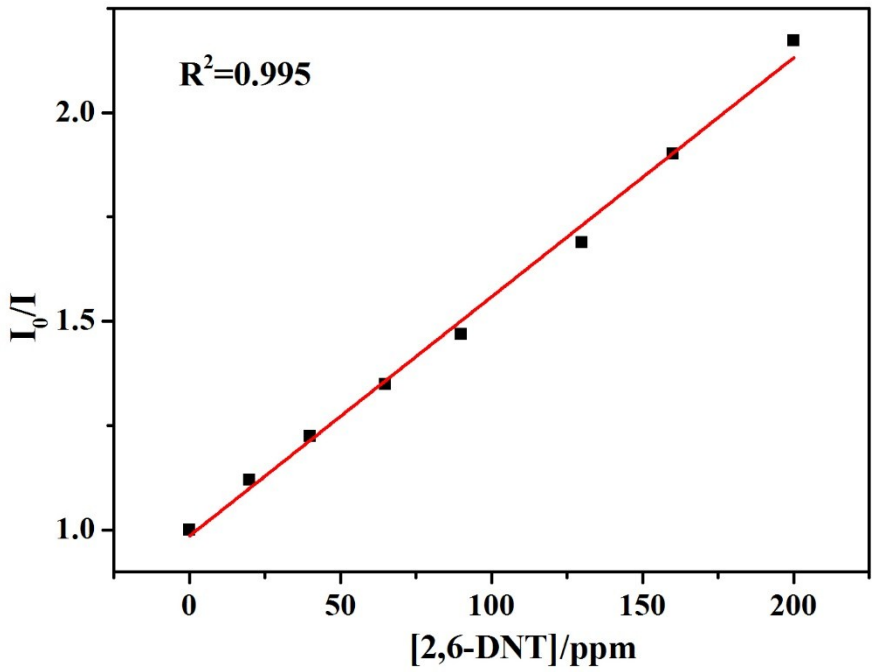


Fig. S17 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of 2,6-DNT.

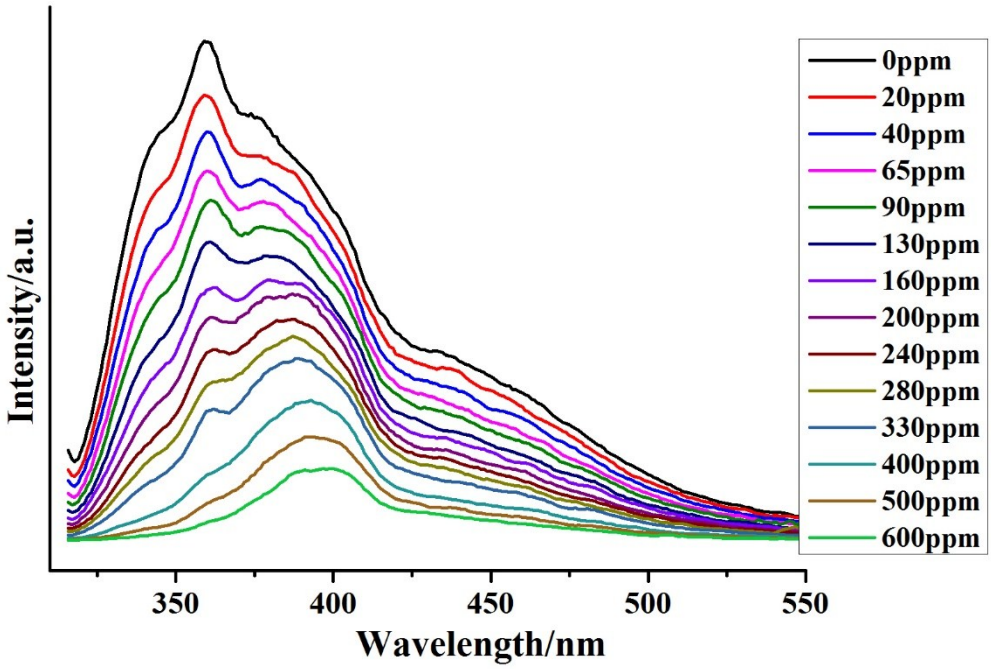


Fig. S18 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of 2-NT in DMF.

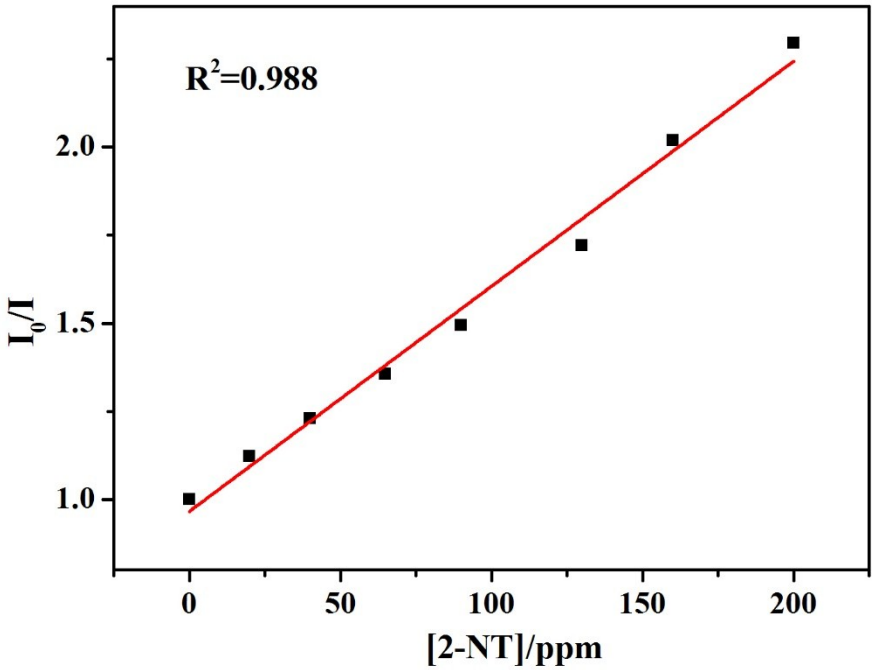


Fig. S19 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of 2-NT.

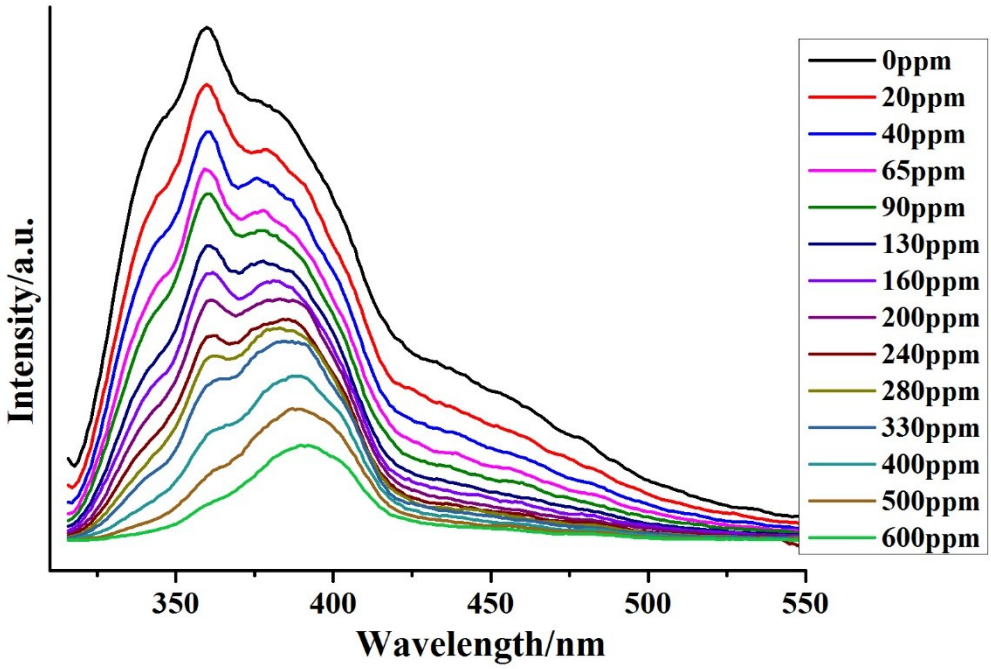


Fig. S20 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of 4-NT in DMF.

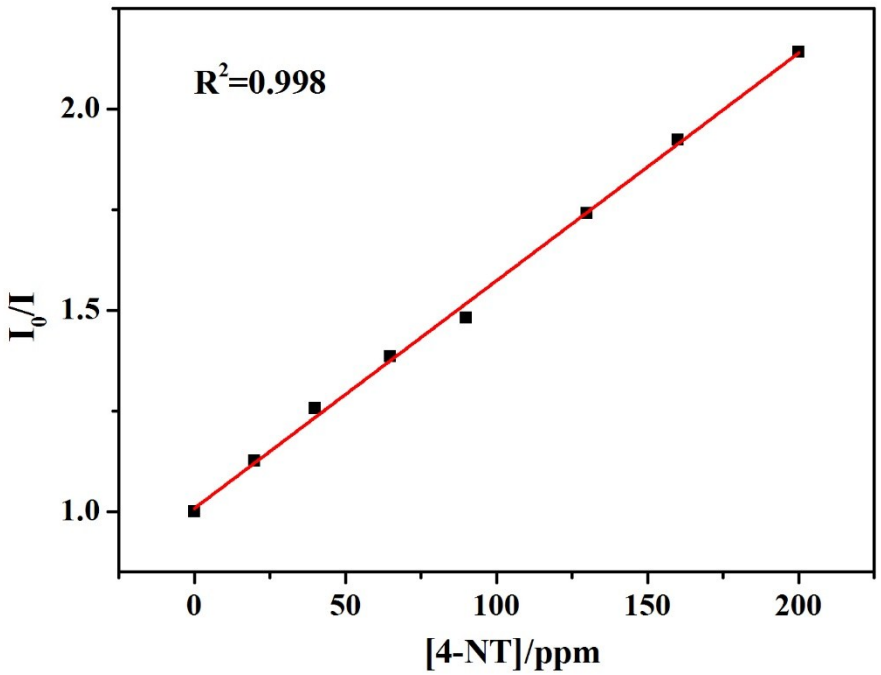


Fig. S21 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of 4-NT.

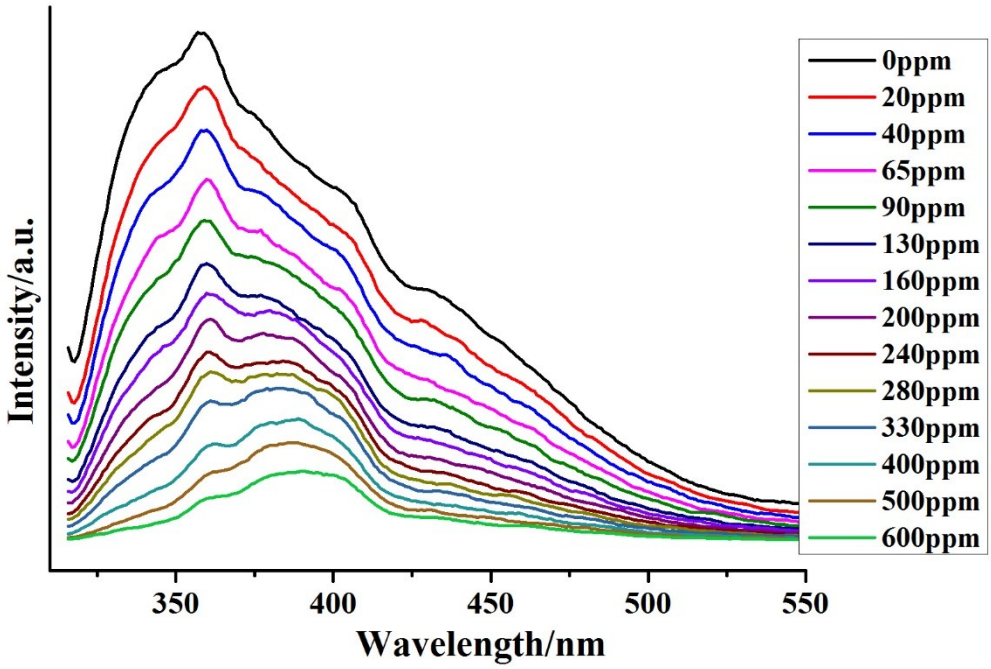


Fig. S22 Luminescent quenching of **1** dispersed in ethanol by the gradual addition of 1 mM solution of NB in DMF.

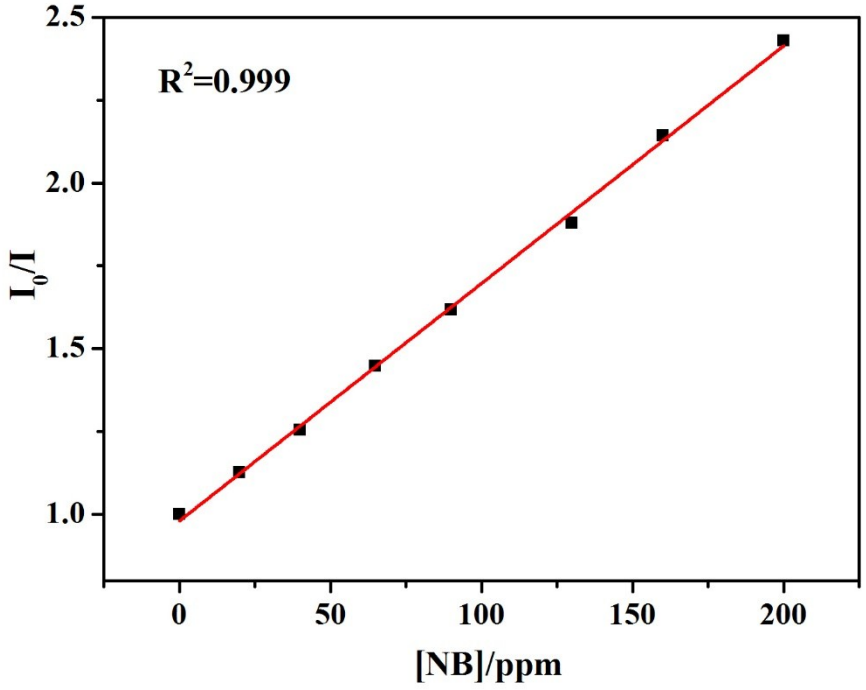


Fig. S23 Stern–Volmer plot for the fluorescence quenching of **1** upon the addition of NB.

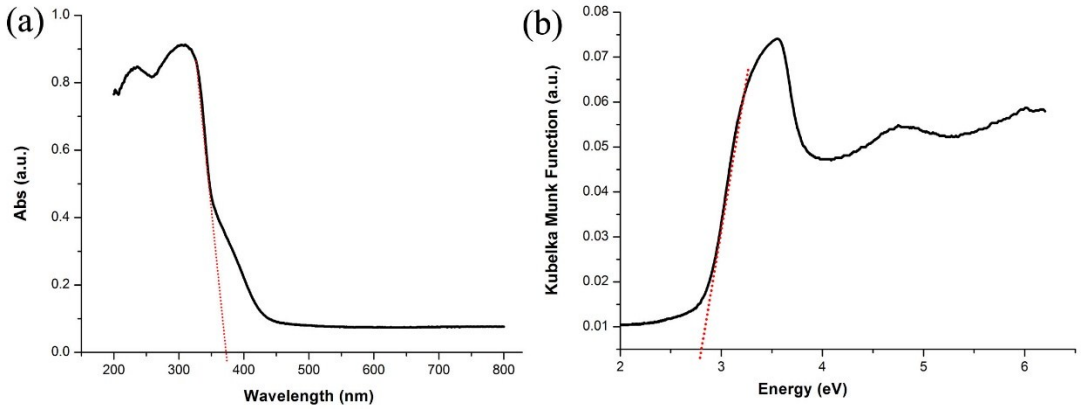
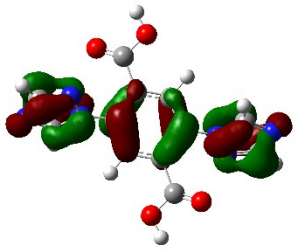
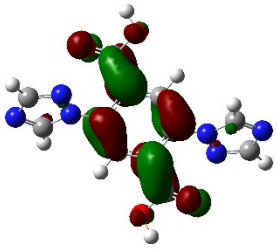
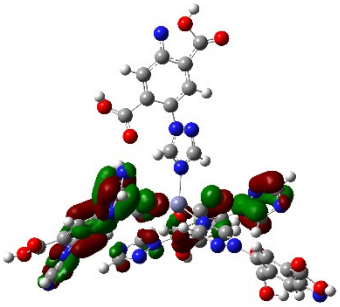
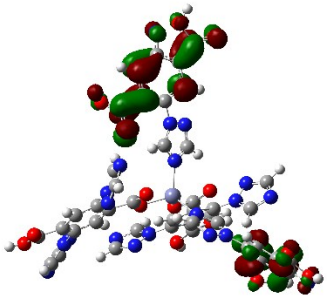
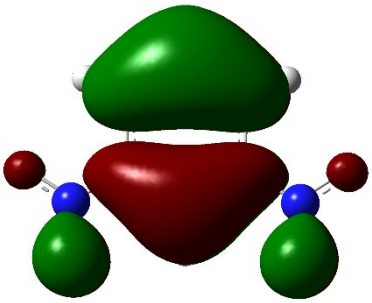
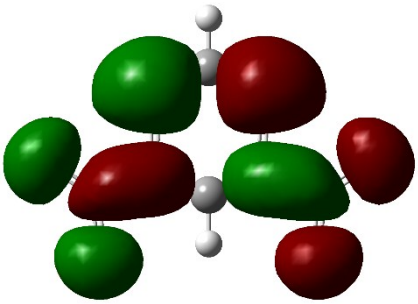
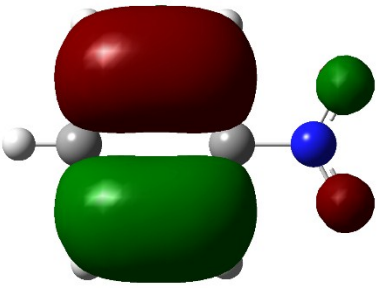
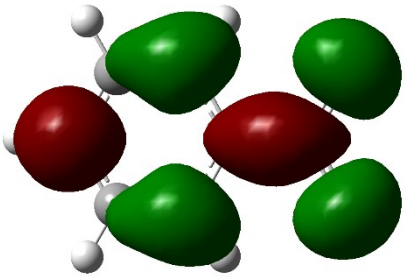
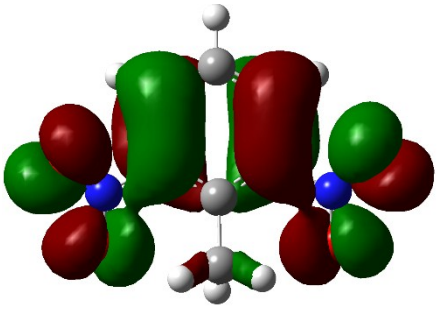
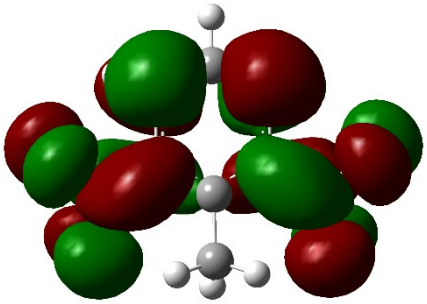


Fig. S24. (a) UV–vis diffuse-reflectance spectra of **1** with $BaSO_4$ as background. (b) Solid-state optical diffuse-reflection spectra of **1** derived from diffuse reflectance data at ambient temperature. The intercept of the extrapolated absorption edge on the energy scale (x axis) gives the band gap of the sample.

 HOMO H_2L	 LUMO H_2L
 HOMO **1**	 LUMO **1**
 HOMO 1,3-DNB	 LUMO 1,3-DNB
 HOMO NB	 LUMO NB
 HOMO 2,6-DNT	 LUMO 2,6-DNT

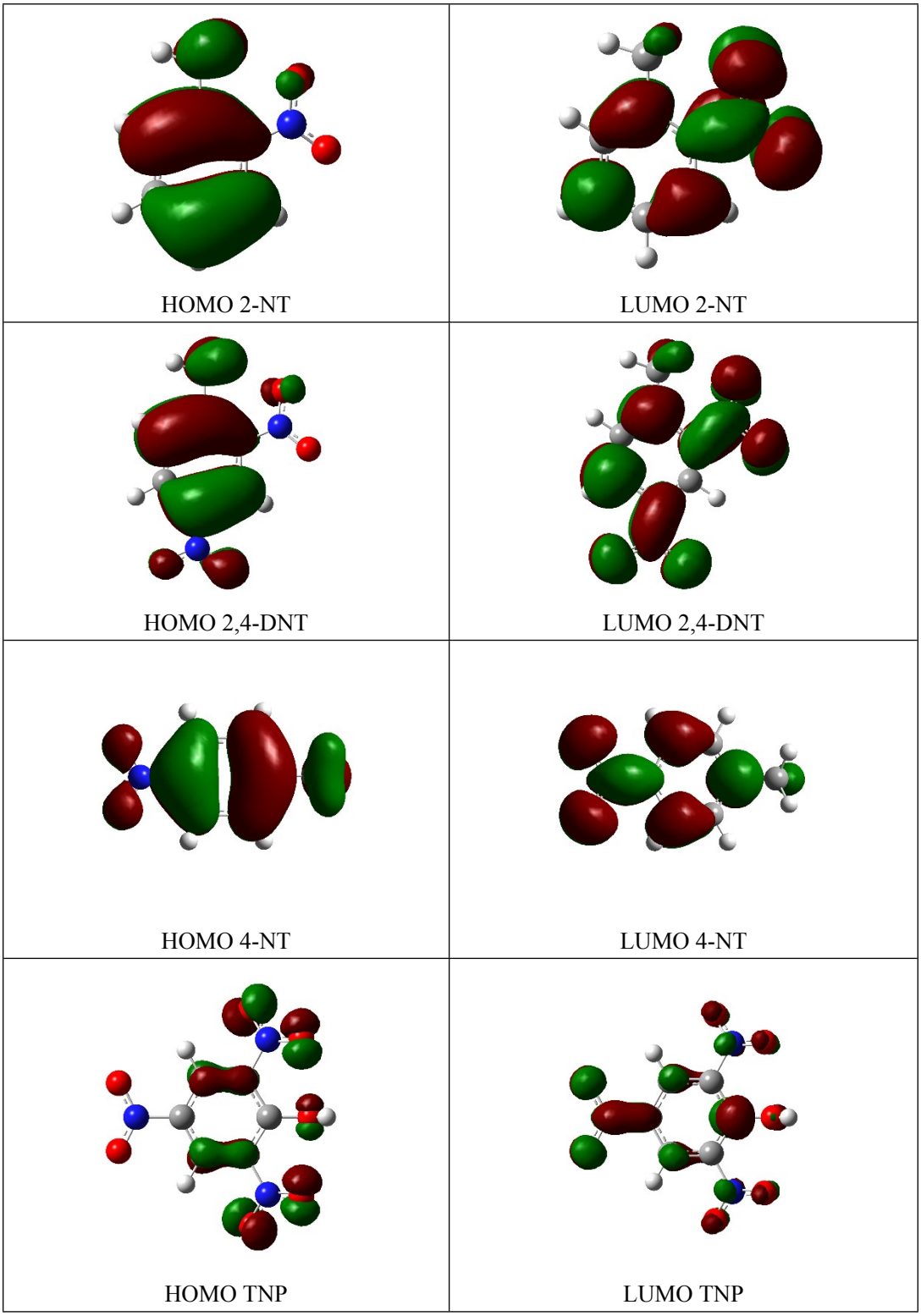


Fig. S25 HOMO–LUMO energies of the NACs along with MOF **1** and H_2L.

Measurements

The activated samples were prepared by soaking the as-synthesized samples in CH_3OH for two days, then in CH_2Cl_2 for three days and subsequent heating at 100 ºC in a quartz tube under high vacuum for 20 h to remove the solvent molecules prior to

measurements. The nitrogen adsorption-desorption measurements were carried out at liquid nitrogen temperature (77 K) by using automatic volumetric adsorption equipment (Micromeritics, ASAP2020).

The N_2 sorption for **1** has been measured at 77 K and exhibits type I isotherm (Fig. S26), indicating that **1** is a microporous material with pore volume of 1600 cm^3 (STP) g^{-1} and the BET surface area is 1997 m^2/g.

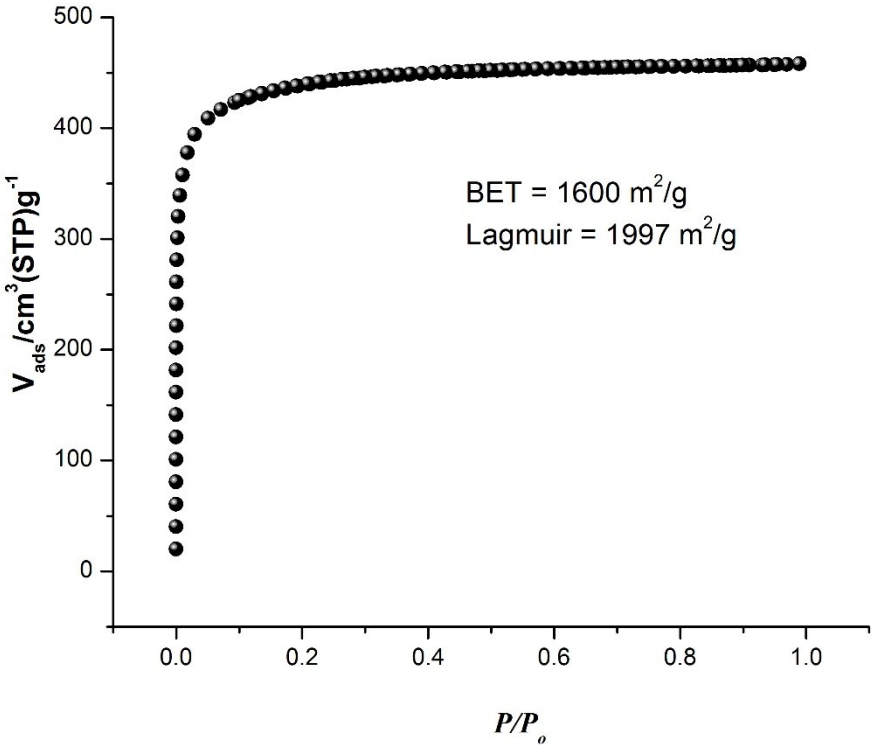


Fig. S26 The N_2 adsorption isotherms at 77 K for **1.**

Table S1. Crystal data and structure refinement information for **1**

Compound	**1**
Formula	$C_{20.7}H_{24.9}N_{8.7}O_{6.7}Zn$
Crystal system	monoclinic
Space group	*C*2/c
Crystal color	colorless
a, [Å]	11.4591(5)
b, [Å]	16.6924(6)
c, [Å]	13.1556(5)
α, [°]	90
β, [°]	101.234(4)
γ, [°]	90
V, Å ^{3}	2468.19(17)
Z	4
ρ_{calcd}, g/cm^3	1.372
μ, mm^{-1}	1.804
F(000)	1048
θ Range, deg	2.03-25.69
Reflection collected	4731/0.0307
Goodness-of-fit on F^2	1.020
R_1, $wR_2(I > 2\sigma(I))^*$	0.0478, 0.1223
R_1, wR_2 (all data)**	0.0538, 0.1258

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

Table S2. Selected bond distances (Å) and angles (°) of **1**

1

Zn(1)-O(1)#1	1.952(2)	Zn(1)-N(2)#2	2.013(3)
O(1)-Zn(1)-O(1)	96.55(13)	O(1)-Zn(1)-N(2)	110.30(10)

N(2)-Zn(1)-N(2)	101.43(15)		

Symmetric codes: #1: 1-x,y,1/2-z; #2: 1/2+x,-1/2+y,z