Supporting Information

Two luminescent metal-organic frameworks for sensing of nitroaromatic explosives and DNA strand

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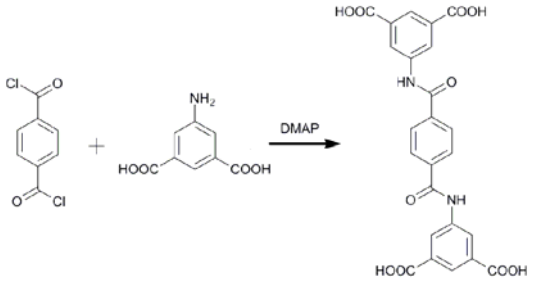
1. Synthesis of H_4L and general characterizations



5-Aminoisophthalic acid (62 mmol, 11.23g) and 4-(dimethylamino)pyridine (DMAP, 6.2 mmol, 0.76g) were dissolved in 150 mL of anhydrous *N*,*N*'-dimethylacetamide under N_2. Terephthaloyl chloride (30 mmol, 6.09g) was dissolved with 50 mL of anhydrous *N*,*N*'-dimethylacetamide and added dropwise. The mixture was stirred under nitrogen for 48h, and then 200 mL of 5% HCl was added to precipitate the product and dissolve the excess 5-aminoisophthalic acid and DMAP. The solid was washed by another 100 mL of 5% HCl followed by 50 mL of water and 50 mL ethanol. The damp product was kept in oven overnight to give white powder. Yield = 13.28 g (90%). Data for H_4L: Selected IR (KBr, cm^{-1}): 3376(b), 1716(s), 1678(m), 1558(vs), 1508(s), 1338(m), 1282(m), 1252(m), 1196(s), 759(m), 667(m). ^1H NMR (DMSO-d_6, δ ppm): 13.32 (4H, COOH), 10.77 (2H, CONH), 8.70 (4H, ArH), 8.24(2H, ArH), 8.17(4H, ArH). ^1H NMR spectrum of H_4L was shown in Fig. S1.

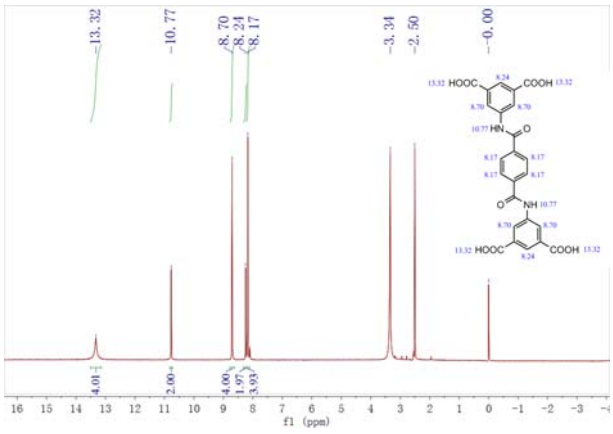


Fig. S1 ^1H NMR spectrum of H_4L.

Table S1. Crystal data and structure refinement for compounds **1** and **2**.

	Compound **1**	Compound **2**
Empirical formula	$C_{31}H_{41}CdN_5O_{14}$	$C_{31}H_{41}N_5O_{14}Zn$
Formula weight	820.10	773.08
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, *P*-1	Triclinic, *P*-1
Unit cell dimensions	a = 10.217(2) Å α = 102.53(3) deg. b = 10.362(2) Å β = 99.35(3) deg. c = 18.118(4) Å γ = 93.79(3) deg.	a = 10.004(2) Å α = 103.66(3) deg. b = 10.293(2) Å β = 99.58(3) deg. c = 17.914(4) Å γ = 93.45(3) deg.
Volume	1837.3(6) $Å^3$	1757.9(6) $Å^3$
Z, Calculated density	2, 1.482 g/cm^3	2, 1.461 g/cm^3
Absorption coefficient	0.666 mm^{-1}	0.773 mm^{-1}
F(000)	844	808
Theta range for data collection	2.99 to 27.49 deg.	3.06 to 27.48 deg.
Reflections collected / unique	19200 / 8444 [R_{int} = 0.0751]	18509 / 8001 [R_{int} = 0.0621]
Completeness to theta	98.7 %	99.5 %
Max. and min. transmission	0.869 and 0.847	0.857 and 0.824
Goodness-of-fit	1.098	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0706, wR2 = 0.1494	R1 = 0.0678, wR2 = 0.1302
R indices (all data)	R1 = 0.0963, wR2 = 0.1599	R1 = 0.1090, wR2 = 0.1461

Table S2. Selected bond Lengths and angles for compounds **1** and **2**.

	Bond	Length (Å)	Angle	Deg. (°)
1	Cd(1)-O(4)#4	2.240(4)	O(4)#4-Cd(1)-O(9)#5	116.19(15)
	Cd(1)-O(9)#5	2.268(3)	O(4)#4-Cd(1)-O(7)#6	111.65(14)
	Cd(1)-O(7)#6	2.303(4)	O(9)#5-Cd(1)-O(7)#6	89.10(13)
	Cd(1)-O(1)	2.367(3)	O(4)#4-Cd(1)-O(1)	84.05(13)
	Cd(1)-O(2)	2.432(3)	O(9)#5-Cd(1)-O(1)	131.37(13)
	Cd(1)-O(8)#6	2.589(4)	O(7)#6-Cd(1)-O(1)	125.81(14)
			O(4)#4-Cd(1)-O(2)	138.28(13)
			O(9)#5-Cd(1)-O(2)	91.61(13)
			O(7)#6-Cd(1)-O(2)	98.44(13)
			O(1)-Cd(1)-O(2)	54.56(11)
			O(4)#4-Cd(1)-O(8)#6	83.97(16)
			O(9)#5-Cd(1)-O(8)#6	141.67(12)
			O(7)#6-Cd(1)-O(8)#6	52.59(12)
			O(1)-Cd(1)-O(8)#6	80.09(13)
			O(2)-Cd(1)-O(8)#6	92.78(14)
2	O(1)-Zn(1)	2.000(2)	O(1)-Zn(1)-O(7)#4	107.52(11)
	O(3)-Zn(1)#1	2.213(3)	O(1)-Zn(1)-O(10)#5	107.06(11)
	O(4)-Zn(1)#1	2.266(3)	O(7)#4-Zn(1)-O(10)#5	100.78(10)
	O(7)-Zn(1)#2	2.020(2)	O(1)-Zn(1)-O(3)#6	145.39(10)
	O(10)-Zn(1)#3	2.035(2)	O(7)#4-Zn(1)-O(3)#6	97.38(11)
			O(10)#5-Zn(1)-O(3)#6	90.97(10)
			O(1)-Zn(1)-O(4)#6	87.62(10)
			O(7)#4-Zn(1)-O(4)#6	121.80(10)
			O(10)#5-Zn(1)-O(4)#6	128.52(10)
			O(3)#6-Zn(1)-O(4)#6	58.52(10)

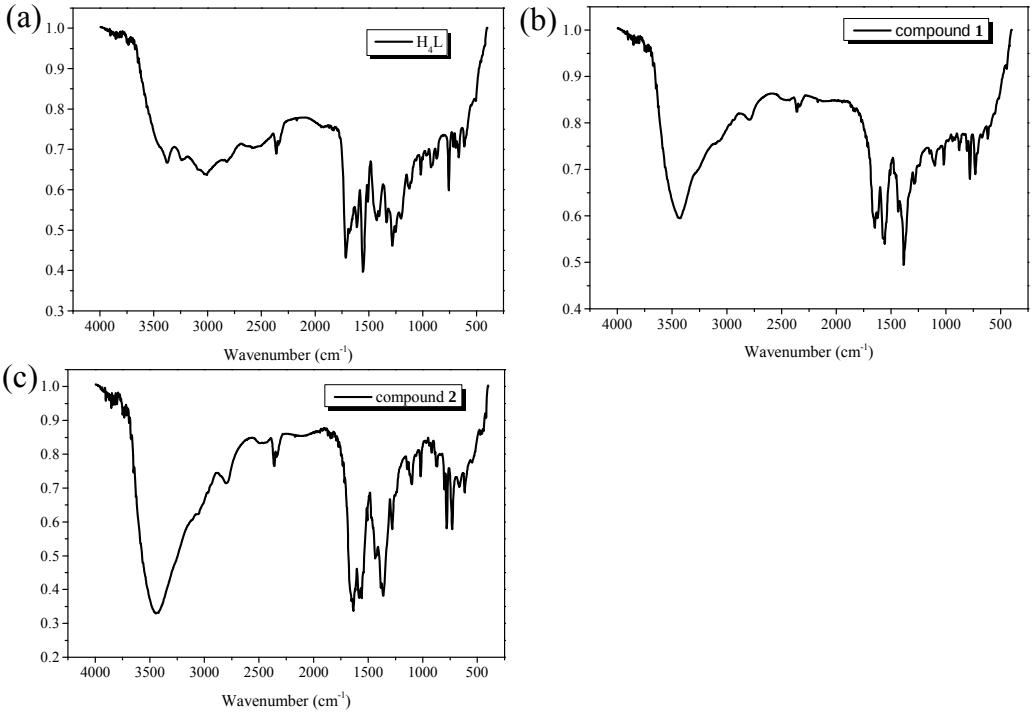


Fig. S2 IR spectra of the free ligand, compounds **1** and **2**.

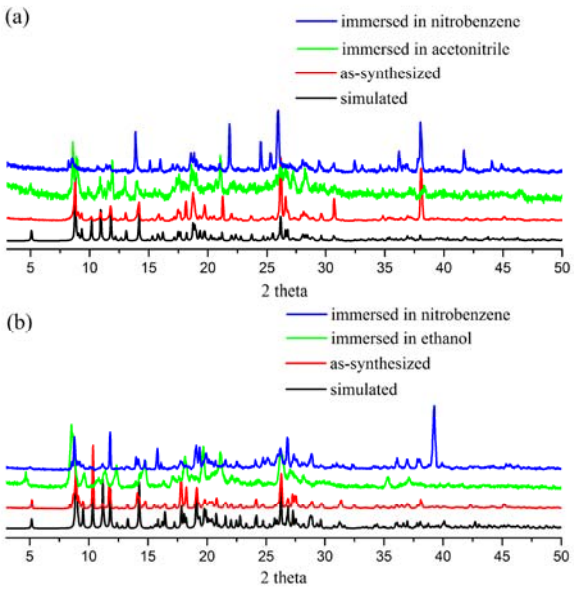


Fig. S3 PXRD patterns of compounds **1** (a) and **2** (b).

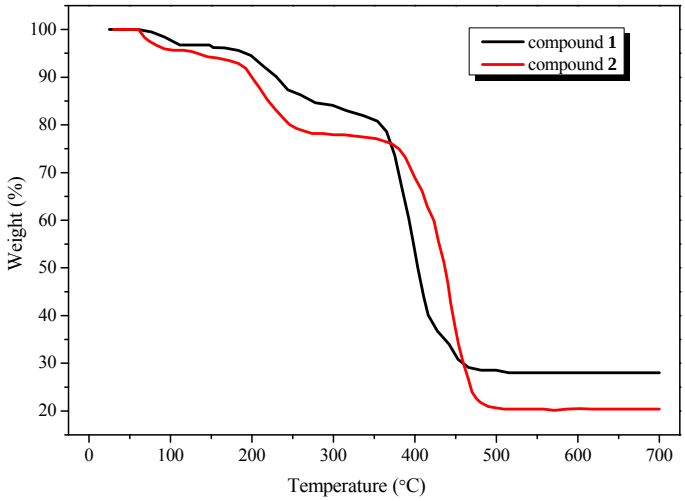


Fig. S4 Thermogravimetric analyses (TGA) curves for compounds **1** and **2**.

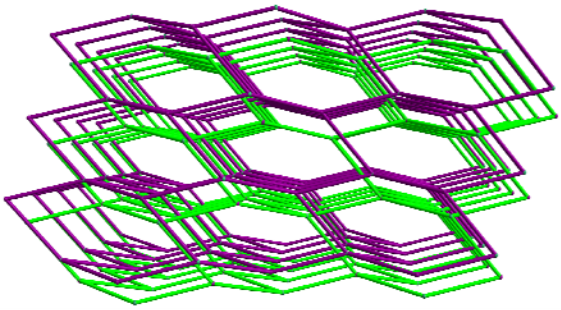


Fig. S5 The simplified 2-fold interpenetrating **dia** network of compounds **1** and **2**.

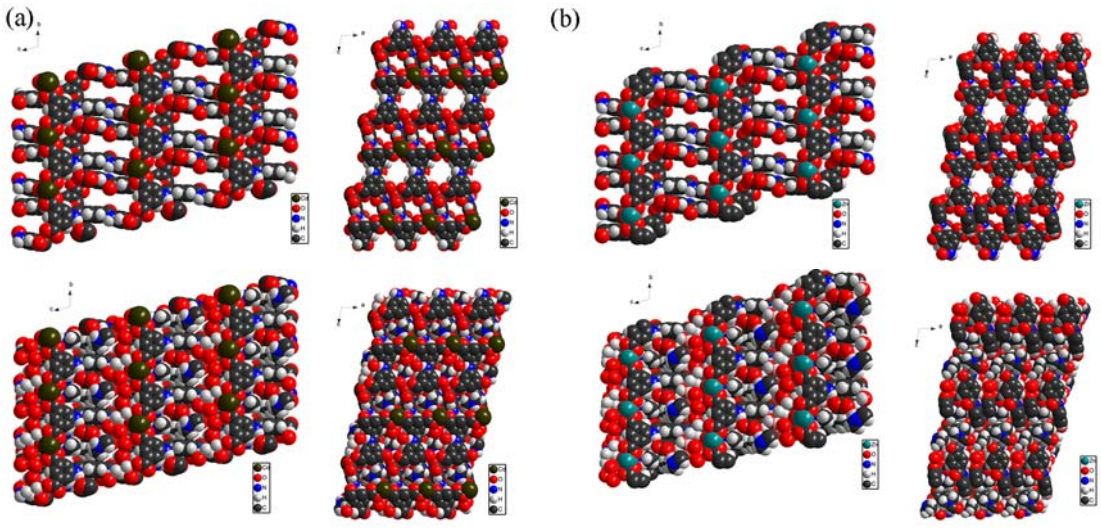


Fig. S6 Comparison of the space-filling representations of compounds **1** (a) and **2** (b) between solvent-free channels (top row) and actual pore (down row) along the *a* axis and *b* axis.

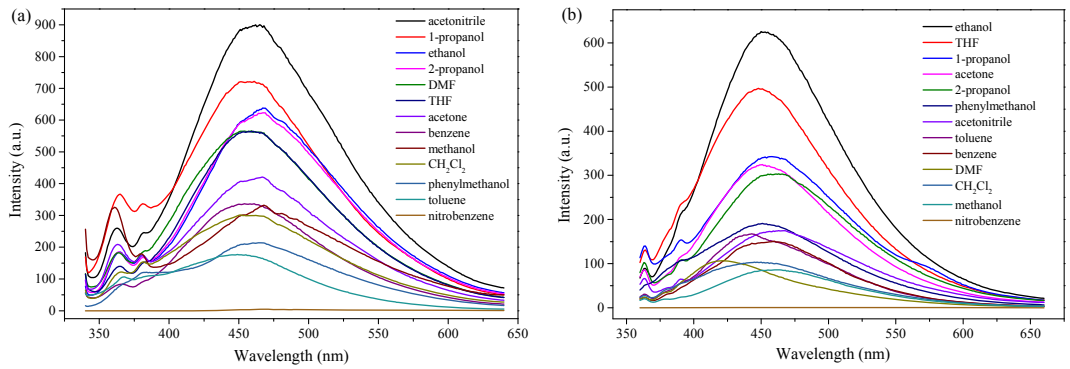


Fig. S7 Emission spectra of **1** (a) and **2** (b) in different solvents when excited at 330 and 340 nm, respectively.

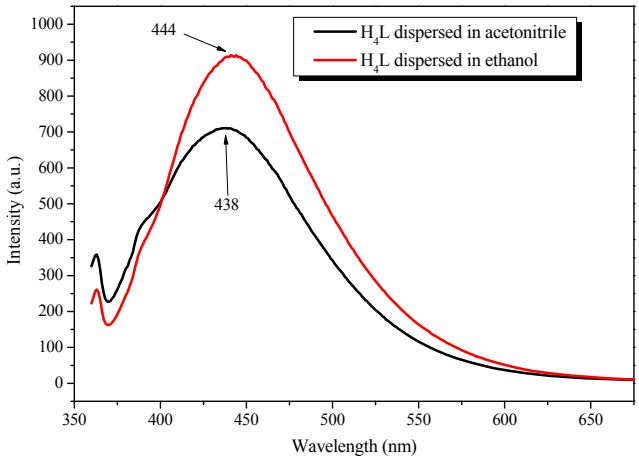


Fig. S8 Emission spectra of free H_4L ligand dispersed in acetonitrile and ethanol when excited at 340 nm.

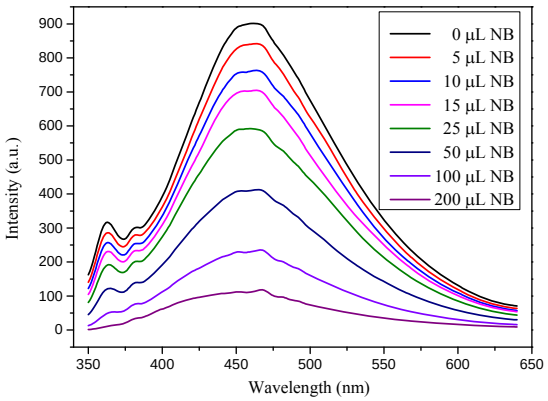


Fig. S9 Fluorescence titration of compound **1** dispersed in acetonitrile with the addition of different volume of 0.2 M acetonitrile solution of NB. Excitation wavelength was 330 nm and fluorescence emission was monitored from 350 nm to 640 nm. The slit width for both excitation and emission was 5 nm.

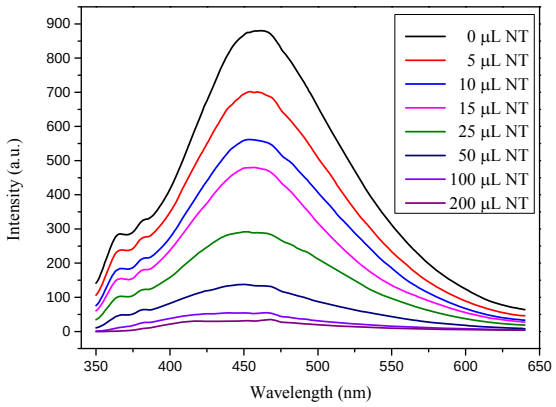


Fig. S10 Fluorescence titration of compound **1** dispersed in acetonitrile with the addition of different volume of 0.2 M acetonitrile solution of NT. Excitation wavelength was 330 nm and fluorescence emission was monitored from 350 nm to 640 nm. The slit width for both excitation and emission was 5 nm.

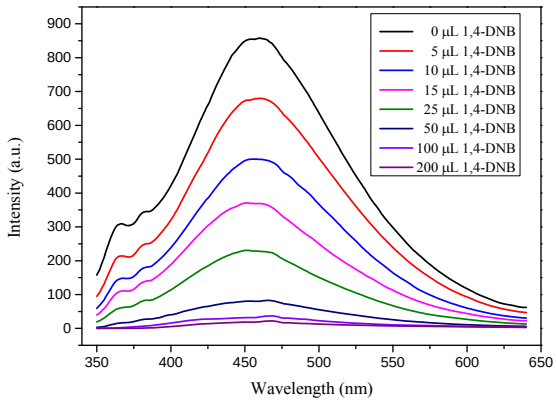


Fig. S11 Fluorescence titration of compound **1** dispersed in acetonitrile with the addition of different volume of 0.2 M acetonitrile solution of 1,4-DNB. Excitation wavelength was 330 nm and fluorescence emission was monitored from 350 nm to 640 nm. The slit width for both excitation and emission was 5 nm.

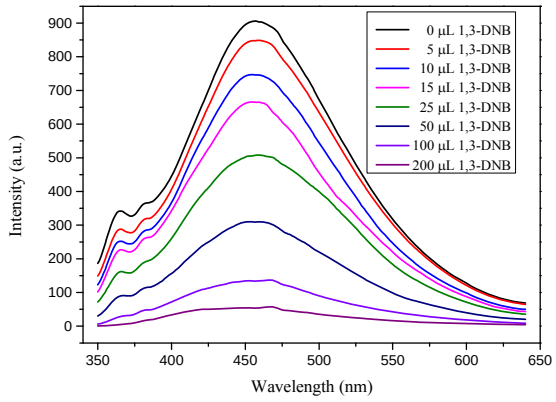


Fig. S12 Fluorescence titration of compound **1** dispersed in acetonitrile with the addition of different volume of 0.2 M acetonitrile solution of 1,3-DNB. Excitation wavelength was 330 nm and fluorescence emission was monitored from 350 nm to 640 nm. The slit width for both excitation and emission was 5 nm.

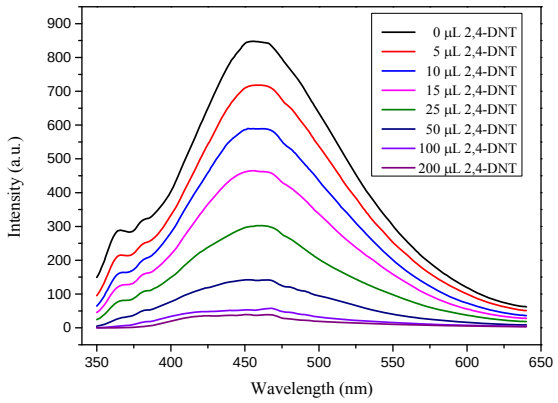


Fig. S13 Fluorescence titration of compound **1** dispersed in acetonitrile with the addition of different volume of 0.2 M acetonitrile solution of 2,4-DNT. Excitation wavelength was 330 nm and fluorescence emission was monitored from 350 nm to 640 nm. The slit width for both excitation and emission was 5 nm.

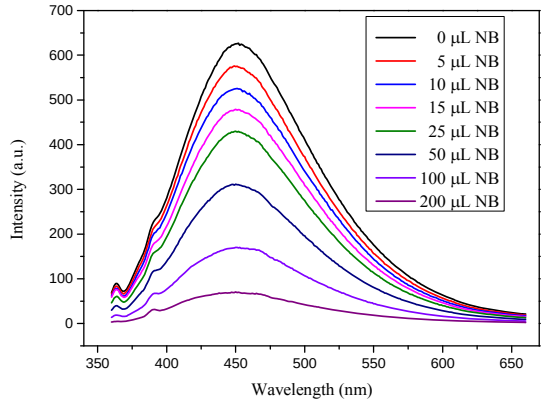


Fig. S14 Fluorescence titration of compound **2** dispersed in ethanol with the addition of different volume of 0.2 M ethanol solution of NB. Excitation wavelength was 330 nm and fluorescence emission was monitored from 350 nm to 640 nm. The excitation slit width was 3 nm, and emission slit width was 5 nm.

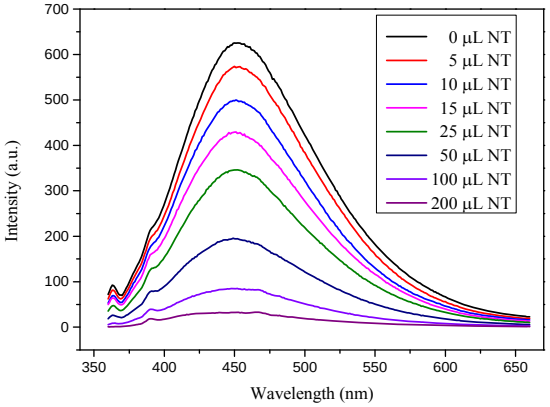


Fig. S15 Fluorescence titration of compound **2** dispersed in ethanol with the addition of different volume of 0.2 M ethanol solution of NT. Excitation wavelength was 330 nm and fluorescence emission was monitored from 350 nm to 640 nm. The excitation slit width was 3 nm, and emission slit width was 5 nm.

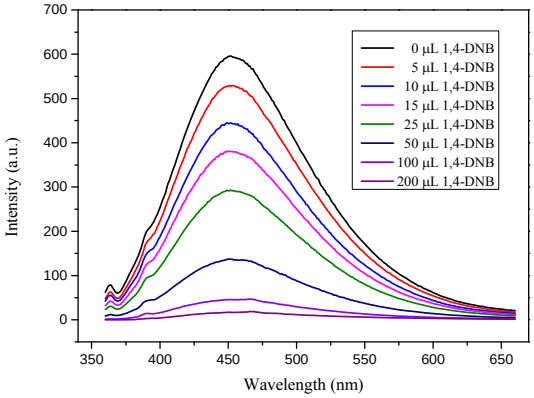


Fig. S16 Fluorescence titration of compound **2** dispersed in ethanol with the addition of different volume of 0.2 M ethanol/acetone (v/v = 1:1) solution of 1,4-DNB. Excitation wavelength was 330 nm and fluorescence emission was monitored from 350 nm to 640 nm. The excitation slit width was 3 nm, and emission slit width was 5 nm.

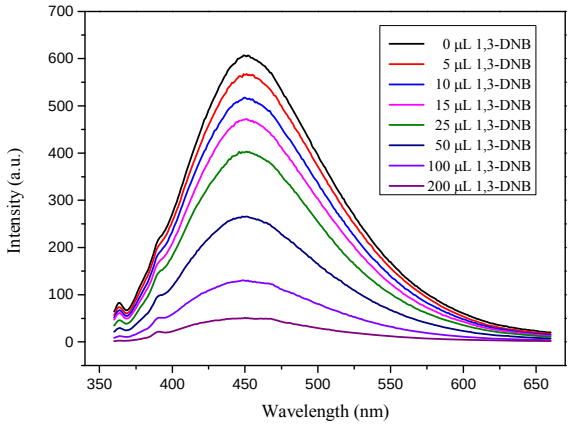


Fig. S17 Fluorescence titration of compound **2** dispersed in ethanol with the addition of different volume of 0.2 M ethanol solution of 1,3-DNB. Excitation wavelength was 330 nm and fluorescence emission was monitored from 350 nm to 640 nm. The excitation slit width was 3 nm, and emission slit width was 5 nm.

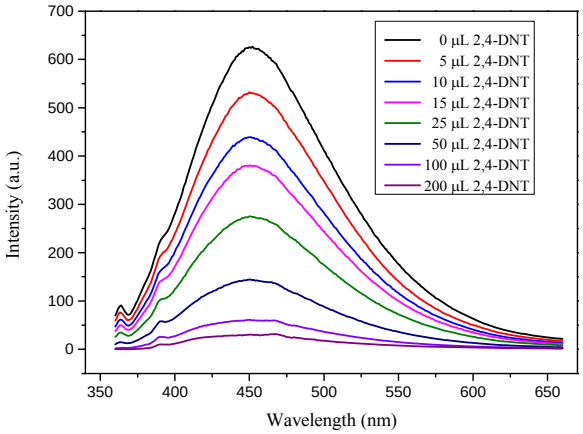


Fig. S18 Fluorescence titration of compound **2** dispersed in ethanol with the addition of different volume of 0.2 M ethanol solution of 2,4-DNT. Excitation wavelength was 330 nm and fluorescence emission was monitored from 350 nm to 640 nm. The excitation slit width was 3 nm, and emission slit width was 5 nm.

Table S3. HOMO and LUMO energies calculated for explosive analytes at B3LYP/6-31G* level of theory.

Analytes	HOMO (eV)	LUMO (eV)	Band gap (eV)
NT	-7.36454	-2.31722	5.04732
NB	-7.59261	-2.43017	5.16244
2,4-DNT	-8.11463	-2.97750	5.13713
1,3-DNB	-8.41456	-3.13562	5.27893
1,4-DNB	-8.35250	-3.49679	4.85571

2. Details of the biomacromolecule sensing experiments

Chemicals and Reagents. All oligonucleotides were purchased from Sangon Biotech. Co. Ltd. (Shanghai, China) and their sequences are listed in Table S4. The concentrations of the oligonucleotides were represented as single-stranded concentrations. Single-stranded concentrations were determined by measuring the UV absorbance at 260 nm. Other chemicals were of analytical grade and used without further purification.

Table S4. The sequences used in this work.

Name	Sequence (5' to 3')
Probe DNA	GGA AGT GTT GAT AAG ATA-(FAM)
Target DNA	TAT CTT ATC AAC ACT TCC
Single-base mismatch T1	TAT CTT ATC **T**AC ACT TCC
Two-base mismatch T2	TAT CTT **T**TC **T**AC ACT TCC
Three-base mismatch T3	TAT CTT **T**TC **T**AC **T**CT TCC

Apparatus and measurements. All fluorescence measurements of samples were carried out on a SHIMADZU RF-5301PC spectrofluorimeter with 1cm-path-length micro quartz cell (40 μL, Starna Brand, England). The emission spectra were collected from 490 nm to 600 nm with an excitation wavelength of 480 nm at room temperature. Both the excitation and emission slit widths were set at 5 nm.

Probe DNA (100 nM) and target DNA (150 nM) were prepared in 25 mM Tris-HCl buffer (pH 7.4) containing 100 mM NaCl and 5 mM $MgCl_2$. Each solution was heated to 95 °C for 5min, cooled slowly to 25 °C and incubated at 25 °C for 30 min. Then, compounds were added to a final volume of 100 μL. Upon vortexing for 1 min, the solutions were incubated with rocking at 37 °C for 4 hours. Finally, the fluorescence signal was recorded.

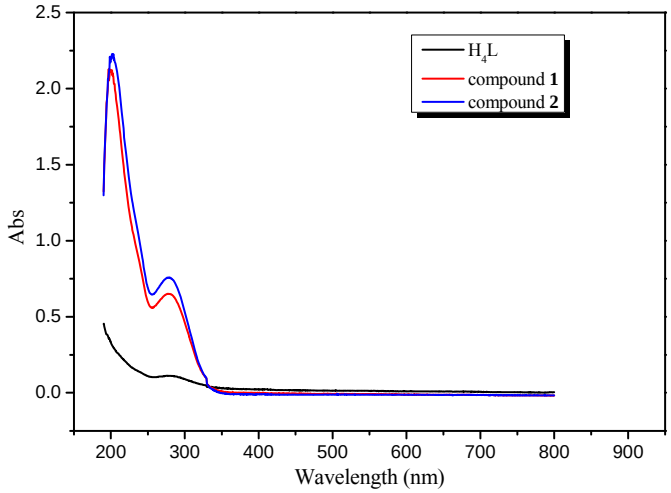


Fig. S19 Absorption spectra of the dispersion of H_4L ligand and compounds in Tris-HCl buffer.

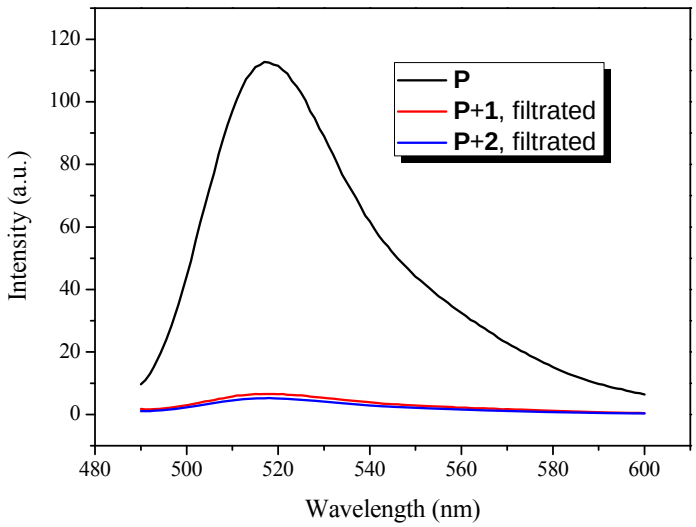


Fig. S20 The comparison between the fluorescence spectra of the orginal and adsorbed **P** solutions. Compound **1** or **2** (0.05 μg/μL) was dispersed in the solution of **P** (100 nM) in Tris-HCl buffer. The suspension was incubated for 30 min, and then filtrated to remove dispersed MOF and adsorbed **P**. The fluorescence of the original **P** solution and the filtrate were recorded.

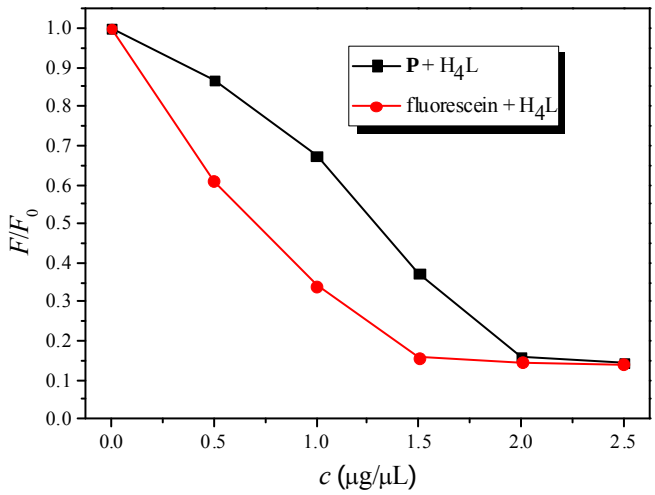


Fig. S21 Fluorescence quenching efficiency of **P** and fluorescein in the presence of different concentrations of H_4L ligand. The fluorescence intensities were measured at 522 and 512 nm, respectively. All measurements were carried out in Tirs-HCl buffer (pH = 7.4).

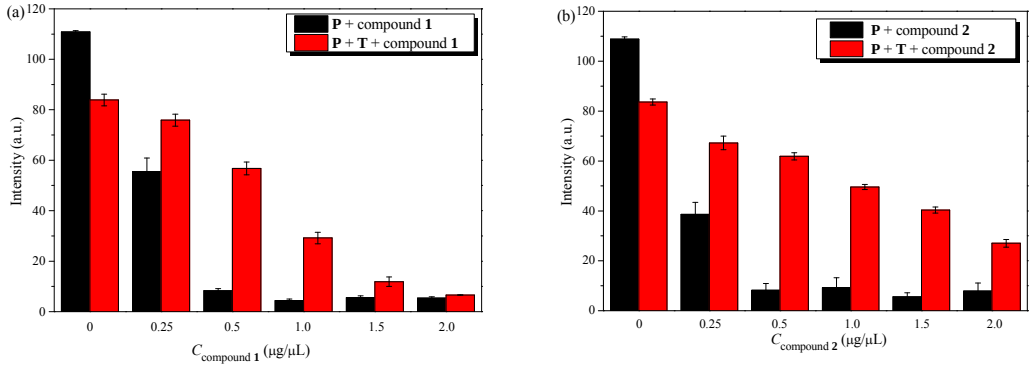


Fig. S22 Fluorescence intensity histograms of probe DNA (**P**, 100 nM) and **P** (100 nM) + target DNA (**T**, 150nM) in the presence of different concentrations of compound **1** (a) or **2** (b).

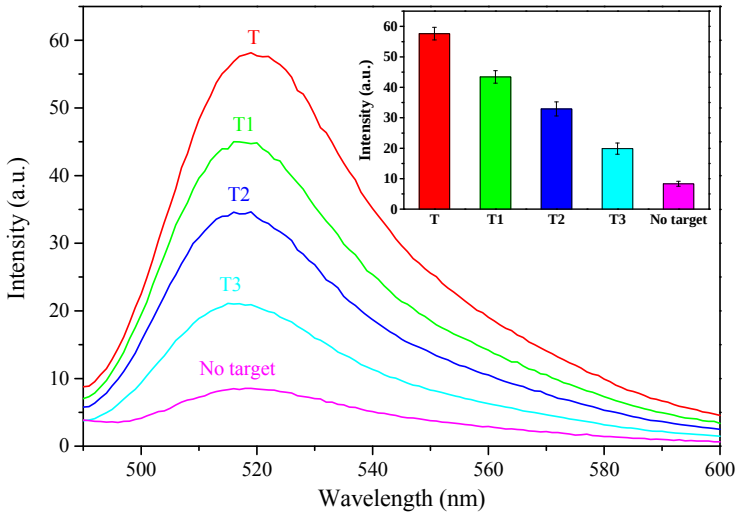


Fig. S23 Fluorescence emission spectra of **P** under different conditions: (a) **P** + **1** + **T** (perfectly matched target DNA); (b) **P** + **1** + **T1** (single-base mismatched DNA); (c) **P** + **1** + **T2** (two-base mismatched DNA); (d) **P** + **1** + **T3** (three-base mismatched DNA); (e) **P** + **1**. The concentrations of **T**, **T1**, **T2**, and **T3** are 150 nM. Concentrations of **P** and **1** are 100 nM and 0.5 μg/μL, respectively. Inset: the corresponding fluorescence intensity histograms at 522 nm.

Table S5. List of the detection limit with different analytic methods for the nucleic acid detection.

Detection Limit (nm)	Reference
0.05	**This work**
0.05	1
0.185	2
~2	3
1	4
3	5

References

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