A Luminescent Heterometallic Metal-Organic Framework for Naked-eye Discrimination of Nitroaromatic Explosives

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1. Material and methods

All chemicals were obtained from commercial sources and used as received without further purification. Room temperature and temperature-dependence powder X-ray diffraction data were collected using Rigaku D/MAX-rA and D/MAX-2200-3KW diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å), respectively. IR spectra (KBr pellets) were conducted on a Nicolet Impact 410 FTIR spectrometer in the range of 400-4000 cm⁻¹. Themo-gravimetric analysis with heating from room temperature to 800 °C was performed using a Netzsch STA 449c analyzer in a flow of N₂ with a heating rate of 10 °C min⁻¹. Elemental analysis (C, H, and N) was measured with a Euro EA3000 analyzer. The gas adsorption measurements were performed on ASAP 2020 apparatuses, after the sample was degassed for 4 h at 180 °C. Fluorescent spectra were performed on a PTI QM-40 luminescence spectrometer equipped with a 450 W xenon lamp.UV-vis spectra were conducted on a PerkinElmer Lambda 35 UV-Vis spectrometer. The maximum of valance band (VB) and the minimum of conduction bond (CB) energies of compound 1, the lowest unoccupied molecular orbitals (LUMOs) and the highest occupied molecular orbitals (HOMOs) energies of the nitro compounds were calculated viaDmol3 program Perdew-Burke-Ernzerh of package.

2. Synthesis of the heterometallic MOF

[Li]₄[Cd₃Li₂(BDC)₆] (1):A mixture of Cd(OAc)₂·2H₂O (99 mg, 0.37 mmol), Li₂CO₃ (5 mg, 0.068 mmol), 9-AC (9-anthracencarboxylic acid, 55 mg, 0.25 mmol), H₂BDC (42 mg, 0.25 mmol), methanol (1 mL) and DMA (4 mL) was mixed and sealed in a 25

mL Teflon-lined stainless steel autoclave and heated at 150 °C for 4 days. Colourless crystals were recovered by filtration, washed with DMA and ethanol, and finally dried at ambient temperature (85.20wt% yield based on H₂BDC). CHN elemental analysis: anal. for 1: C 42.04 wt%, H 1.86 wt%; calc. for 1: C 42.28 wt%, H 1.77 wt%.IR (KBr, cm⁻¹): 3427 (s), 1563 (s), 1506(w),1478 (w), 1398 (s), 1313 (w), 1154 (w), 1012 (w), 950 (m), 887 (s), 841 (m), 750 (s), 517 (m).

3. X-ray crystallographic structure

The single-crystal data were collected on an Oxford Xcalibur diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) using a ω scan for 1 at room temperature. The crystal structure was resolved by direct methods and refined using full-matrix least-squares methods on F2 using *SHELXTL* program package and anisotropic refinement was applied to non-hydrogen atoms (Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.*2008, **64**, 112–122).The crystallographic data for 1 are summarized in Table S1.The CCDC numbers for **1**is1561462.

	1
Empirical formula	C ₄₈ H ₂₄ O ₂₄ Cd ₃ Li ₆
Formula weight	1363.51
Crystal system	monoclinic
Space group	C2/c
<i>a</i> , Å	6.5914(11)
<i>b</i> , Å	34.784(6)
<i>c</i> , Å	30.396(5)
α, °	90.00
β, °	90.00
γ, ⁰	90.20
Volume, Å ³	6969(2)
Ζ	4

Table S1 Crystallographic data for compound 1

100
1.300
2664.0
3.56 to 50.02
26340
6140
1.045
0.0613
0.2448

4. Sensing of nitroaromatic explosives

Eight common nitro explosives (i.e,PA, TNB, 1,3-dinitrobenzene(DNB), 1,3,5trinitrotoluene (TNT), cyclotetramethylenetetranitramine (HMX), 2,4-dinitroanisole (DNAN), cyclotrimethylenetrinitramine (RDX), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.0.0] dodecane (CL-20)) were used to study the sensitivity and selectivity of 1.In typical experimental step, 3 mg of 1was dispersed in 20 mL acetonitrile, and treated by ultrasonication for 1 h and then aged for 3 days. The fluorescence of the 1-baseddispersions upon excitation at 355 nm was measured *in-situ* after incremental addition of freshly prepared analyte solutions (1mM) to 3 mL the acetonitrile dispersion of 1.

Caution:Some nitro compounds used in this work aredangerous and should be handled carefully and in small amounts.

5. the asymmetric unit of 1



Figure S1the asymmetric unit of 1.

6. the PXRD and TGA results of 1



Figure S2thePXRD patterns of simulated, experimental and degassed samples of compound 1.



Figure S3 PXRD patterns of compound 1 at different experiment conditions.



Figure S4 the TGA and DSC curves of compound 1.

7. the solid-state fluorescence of 1



Figure S5Solid-state fluorescent spectra of compound 1at room temperature.

8. the selective detection property of 1



Figure S6the emission spectra of 1-based dispersion upon increment addition of a TNT acetonitrile solution (1 mM).



Figure S7the emission spectra of 1-based dispersion upon increment addition of a DNAN acetonitrile solution (1 mM).



Figure S8the emission spectra of 1-based dispersion upon increment addition of a HMXacetonitrile solution (1 mM).



Figure S9the emission spectra of 1-based dispersion upon increment addition of a RDX acetonitrile solution (1 mM).



Figure S10the emission spectra of 1-based dispersion upon increment addition of a CL-20 acetonitrile solution (1 mM).



Figure S11the emission spectra of 1-based dispersion upon increment addition of a DNB acetonitrile solution (1 mM).



Figure S12the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM).



Figure S13the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of TNB.



Figure S14the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of TNT.



Figure S15the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of DNAN.



Figure S16the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of HMX.



Figure S17the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of RDX.



Figure S18the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of CL-20.



Figure S19the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of DNB.

9. RETand PET study



Figure S20Spectral overlap between the normalized emission spectrum of 1-based dispersion and normalized absorption spectra of different nitro compounds.



Figure S21HOMO and LUMO energies for explosive analytes and CB and VB of 1.