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 Kα radiation (λ = 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. Thermo-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 via Dmol3 program Perdew-Burke-Ernzerh of package.

2. Synthesis of the heterometallic MOF

\[[\text{Li}]_4\text{Cd}_3\text{Li}_2(\text{BDC})_6\] (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 (85.20 wt% yield based on H$_2$BDC). 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-Kα radiation ($\lambda = 0.71073$ Å) using a $\omega$ 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 SHELXL 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 is 1561462.

<table>
<thead>
<tr>
<th>Table S1 Crystallographic data for compound 1</th>
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<tr>
<td><strong>Empirical formula</strong></td>
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<td><strong>Formula weight</strong></td>
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<td><strong>Crystal system</strong></td>
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<td><strong>$Z$</strong></td>
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4. Sensing of nitroaromatic explosives

Eight common nitro explosives (i.e., PA, TNB, 1,3-dinitrobenzene (DNB), 1,3,5-trinitrotoluene (TNT), cyclotetramethylenetetranitramine (HMX), 2,4-dinitroanisole (DNAN), cyclotrimethylenetetranitramine (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 1 was dispersed in 20 mL acetonitrile, and treated by ultrasonication for 1 h and then aged for 3 days. The fluorescence of the 1-based dispersions upon excitation at 355 nm was measured \textit{in-situ} after incremental addition of freshly prepared analyte solutions (1 mM) to 3 mL the acetonitrile dispersion of 1.

\textit{Caution: Some nitro compounds used in this work are dangerous and should be handled carefully and in small amounts.}
5. the asymmetric unit of 1

Figure S1 the asymmetric unit of 1.

6. the PXRD and TGA results of 1

Figure S2 the PXRD patterns of simulated, experimental and degassed samples of compound 1.

Figure S3 PXRD patterns of compound 1 at different experiment conditions.
7. the solid-state fluorescence of 1

8. the selective detection property of 1

Figure S4 the TGA and DSC curves of compound 1.

Figure S5 Solid-state fluorescent spectra of compound 1 at room temperature.

Figure S6 the emission spectra of 1-based dispersion upon increment addition of a TNT acetonitrile solution (1 mM).
Figure S7: The emission spectra of 1-based dispersion upon increment addition of a DNAN acetonitrile solution (1 mM).

Figure S8: The emission spectra of 1-based dispersion upon increment addition of a HMX acetonitrile solution (1 mM).

Figure S9: The emission spectra of 1-based dispersion upon increment addition of a RDX acetonitrile solution (1 mM).
Figure S10 the emission spectra of 1-based dispersion upon increment addition of a CL-20 acetonitrile solution (1 mM).

Figure S11 the emission spectra of 1-based dispersion upon increment addition of a DNB acetonitrile solution (1 mM).

Figure S12 the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM).
Figure S13 the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of TNB.

Figure S14 the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of TNT.

Figure S15 the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of DNAN.
Figure S16 the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of HMX.

Figure S17 the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of RDX.

Figure S18 the emission spectra of 1-based dispersion upon increment addition of a PA acetonitrile solution (1 mM) in the presence of CL-20.
1. **Figure S19**

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

2. **Figure S20**

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

3. **Figure S21**

HOMO and LUMO energies for explosive analytes and CB and VB of 1.