

Supporting Information

A Lanthanide Metal-organic Framework Containing Hydrazine Group for Highly Sensitive Luminescent Sensing of Formaldehyde Gas

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1. Materials and methods

All of the solvents and reagents in this article were purchased from commercial companies and used without further purification unless otherwise stated. The organic ligand 2-hydrazine-terephthalic acid ($\text{H}_2\text{BDC-NH-NH}_2$) was purchased from Jilin Scientific Research Technology Co., Ltd. $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and Hexanal were purchased from Anhui Zesheng Technology Co., Ltd. 2-fluorobenzoic acid (2-FBA) was purchased from Saen Chemical Technology (Shanghai) Co., Ltd. Nitric acid, n-hexane, anhydrous methanol, ethanol, isopropyl alcohol, acetone, benzene, toluene, ethylbenzene, formaldehyde and N,N-dimethylformamide (DMF, AR) were purchased from Sinopharmate Chemical Reagent Co., Ltd.

Single Crystal X-Ray Diffraction (SC-XRD) data were collected on a Bruker SMART APEX-II diffractometer equipped with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure data of Eu-BDC-NH-NH₂ was analyzed and refined by the direct method and full-matrix least-squares on F^2 using the SHELX-2013 package. All nonhydrogen atoms were refined by Anisotropic thermal parameters, and all hydrogen atoms attached to C atoms were restrained with isotropic thermal parameters. Powder X-Ray Diffraction (PXRD) patterns were measured on an X'Pert PRO diffractometer at the range of 2~45° for 2θ with Cu $K\alpha$ radiation at room temperature. The contents of C, H, and N in the as-synthesized crystals were analyzed applying a thermo scientific flash 2000 CHNS/O elemental analyzer. 77 K Nitrogen adsorption-desorption curves were recorded on a Micromeritics ASAP 2460 surface area analyzer. Thermogravimetric Analysis (TGA) were tested on a TG209 F3 Thermogravimetric Analyzer with a heating rate of 5 °C·min⁻¹ under a nitrogen atmosphere. Fourier Transform Infrared (FT-IR) spectra were characterized by a Thermo Fisher Nicolet iS10 spectrometer using potassium bromide pellet method. The low-temperature (77 K) time-resolved phosphorescent spectra of Gd-BDC-NH-NH₂ were recorded using an Edinburgh Instrument F920 transient fluorescence spectrometer. Photoluminescence (PL) spectra at room temperature for different samples were performed on a Hitachi F4600 fluorescence spectrometer. The fluorescent images of Eu-BDC-NH-NH₂ crystals were taken with Olympus IX-71 fluorescent inverted microscope ($\lambda_{\text{ex}} = 365 \text{ nm}$). The mass spectrum (ESI-MS) was measured with an Agilent 7890A-5975C temperament combination instrument. Prior to the ESI-MS measurement, 15 mg of Eu-BDC-NH-NH₂ and FA-treated Eu-

BDC-NH-NH₂ were separately digested in 2 mL of HPLC grade methanol by the treatment with 200 μL of 48% HF. For HCHO-treated Eu-BDC-NH-NH₂, the required amount of NaHCO₃ was added to the medium to attain neutral pH, filtered and then HCHO was introduced into the filtrate. For both samples, the organic layer was collected by filtration after 15 min of sonication. Then, the samples were further diluted by adding HPLC grade methanol for the ESI-MS measurements. Ultraviolet-Visible Absorption (UV-vis) spectra were performed on a Hitachi UV-2600 spectrometer.

2. Supplementary Tables.

Table S1. Crystallographic data and structure refinement results for Tb-BDC-NH-NH₂ (CCDC number: 2348622)

Unit cell parameters	Tb-BDC-NH-NH ₂
Formula	C ₄₈ H ₁₈ Tb ₆ N ₁₂ O ₁₉
Temperature/K	299(2)
Crystal system	Cubic
Space group	<i>Fm</i> $\bar{3}$ <i>m</i>
<i>a</i> (Å)	21.5579(5)
<i>b</i> (Å)	21.5579(5)
<i>c</i> (Å)	21.5579(5)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	10018.9(7)
<i>Z</i>	2
<i>D_c</i> (g/cm ³)	1.386
μ (mm ⁻¹)	1.54178
<i>F</i> (000)	3880
Θ range (°)	3.551 to 67.969
Index ranges	-20 ≤ <i>h</i> ≤ 20, -25 ≤ <i>k</i> ≤ 13, -21 ≤ <i>l</i> ≤ 22
Crystal size(mm ³)	0.03 × 0.04 × 0.03
GOF on <i>F</i> ²	1.071
<i>R</i> _{int}	0.0849
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2σ (<i>I</i>)]	0.0692, 0.1889
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0727, 0.1855
Largest diff. peak and hole (e Å ⁻³)	1.296, -1.087

Table S2. MOF-based formaldehyde fluorescence sensors.

Materials	Detection limit	Medium	Sensing mode	Ref.
Eu-BDC-NH-NH₂	41.7 ppb	gas	Turn-on	This work
Ag ⁺ /Eu ³⁺ -1	51 ppb	gas	Ratiometric	[1]
Eu/Zr-MOF	200 ppb	water	Turn-on	[2]
Eu ³⁺ @BioMOF-1	5500 ppb	water	Turn-on	[3]
JNU-100	0.6 ppb	Aqueous solution	Turn-on	[4]
JNU-105-(NH ₂) ₂	1.87 ppb	Aqueous solution	Turn-on	[5]
Al-MIL-53-N ₂ H ₃	250 ppb	HEPES (pH = 7.4)	Turn-on	[6]
Eu-based MOF	30 ppb	CH ₃ OH solution	Turn-off	[7]

3. Supplementary Figures.

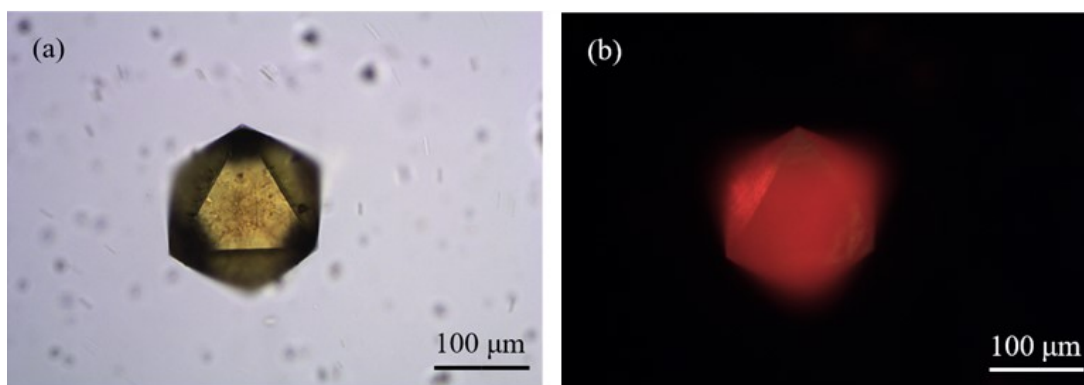


Figure S1. Micrographs of Eu-BDC-NH-NH₂ under (a) light and (b) dark field.

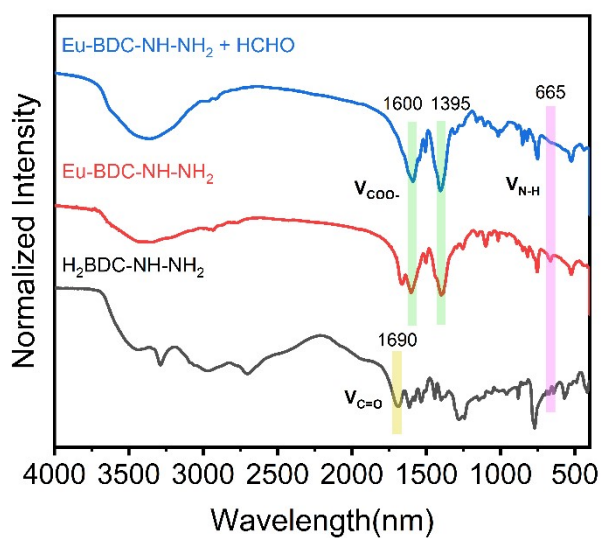


Figure S2. FTIR spectra of H₂BDC-NH-NH₂, Eu-BDC-NH-NH₂ and Eu-BDC-NH-NH₂ + HCHO.

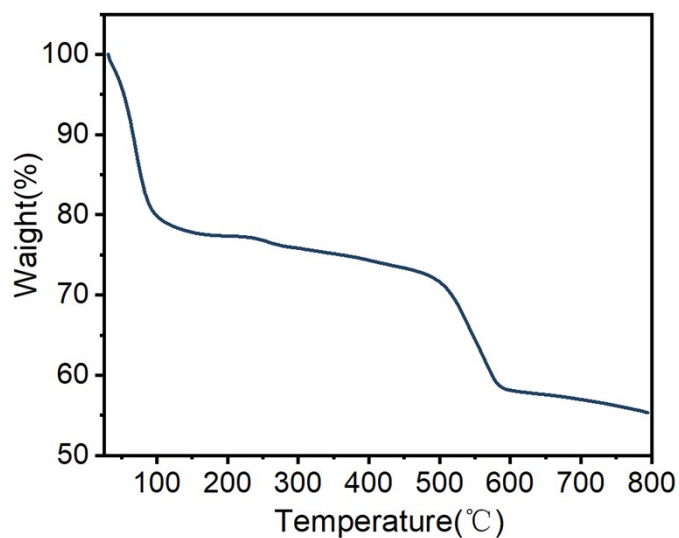


Figure S3. TGA curves for Eu-BDC-NH-NH₂.

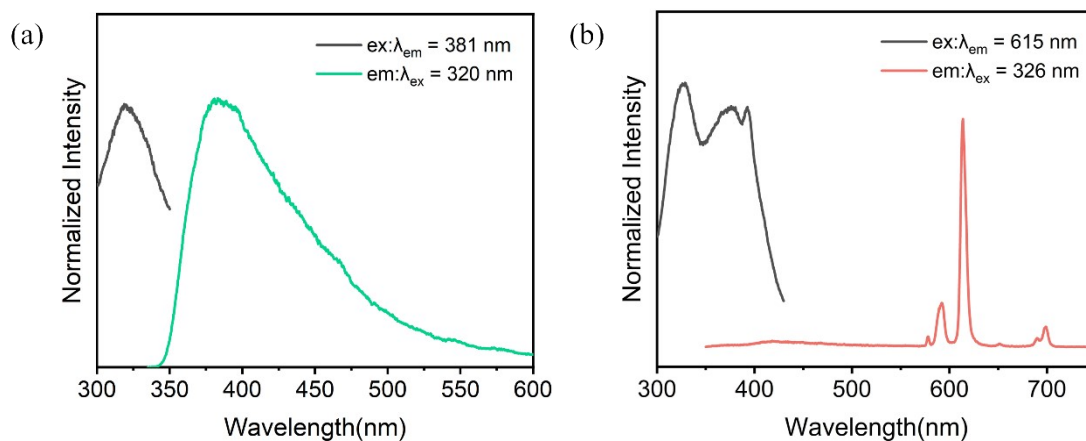


Figure S4. Solid-state excitation and emission spectra of (a) organic ligand H₂BDC-N₂H₃ and (b) Eu-BDC-NH-NH₂.

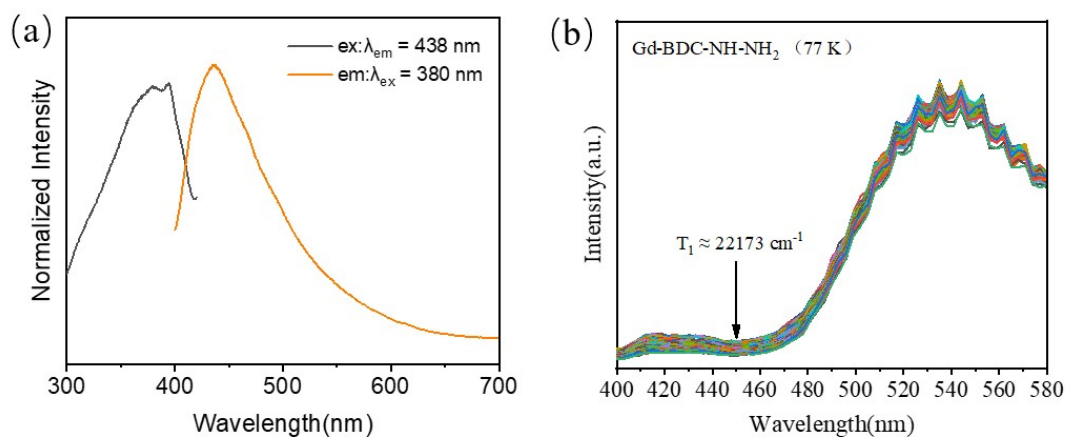


Figure S5. (a) Solid-state excitation and emission spectra of Gd-BDC-NH-NH₂. (b) The phosphorescence spectrum of Gd-BDC-NH-NH₂ under 77 K.

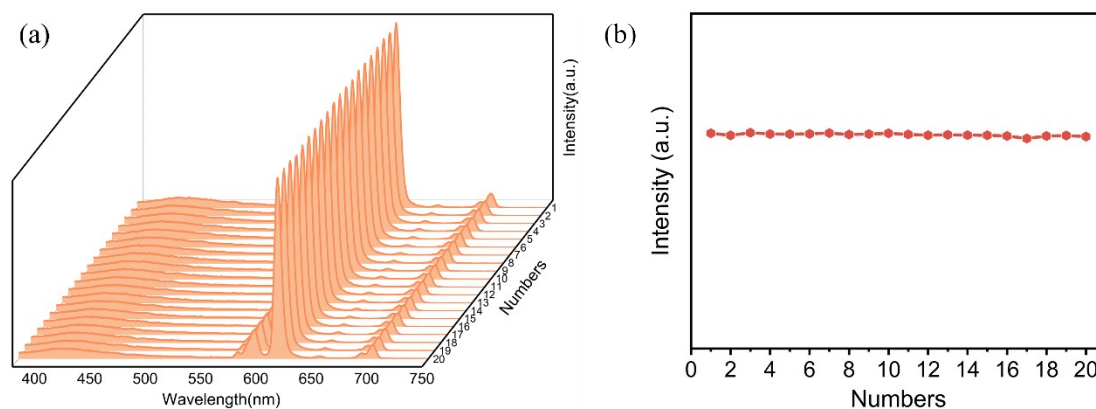


Figure S6. (a) The fluorescence spectra of Eu-BDC-NH-NH₂ in air were tested for 20 times under the excitation of 326 nm ultraviolet light. (b) The fluorescence intensity I_{615} of Eu-BDC-NH-NH₂ with the number of times.

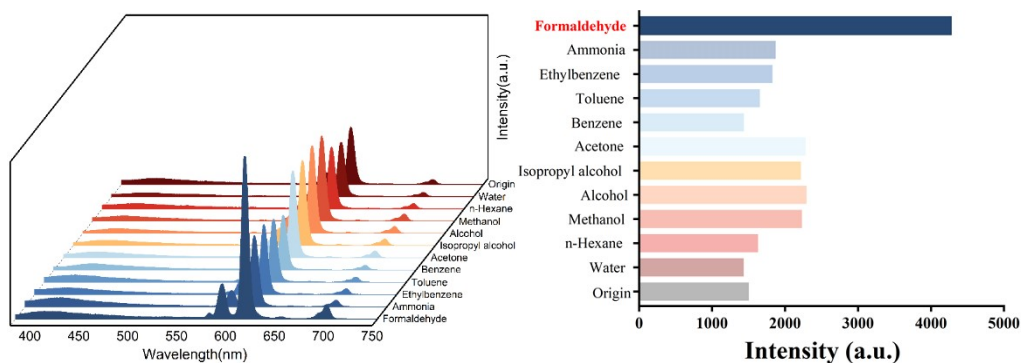


Figure S7. The emission spectra of Eu-BDC-NH-NH₂ exposed to different gases ($\lambda_{ex} = 326$ nm).

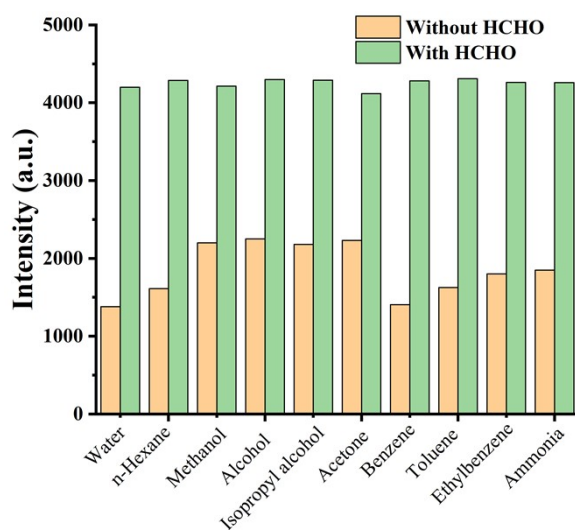


Figure S8. The response of the Eu-BDC-NH-NH₂ towards HCHO in the presence of interfering gases.

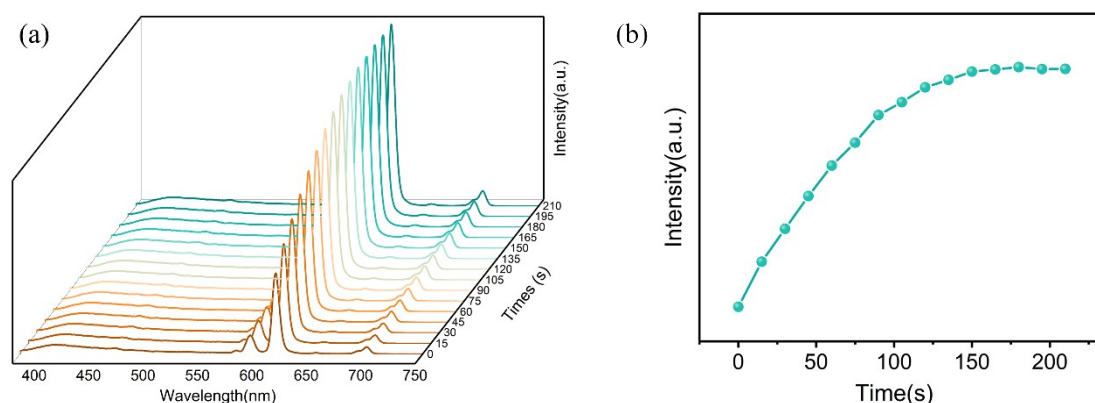


Figure S9. (a) Time dependent emission spectra of Eu-BDC-NH-NH₂ exposed to 200 ppb formaldehyde gas. (b) Fluorescence intensity of Eu-BDC-NH-NH₂ at 615 nm changes with time after exposed to 200 ppb formaldehyde gas. ($\lambda_{ex} = 326$ nm)

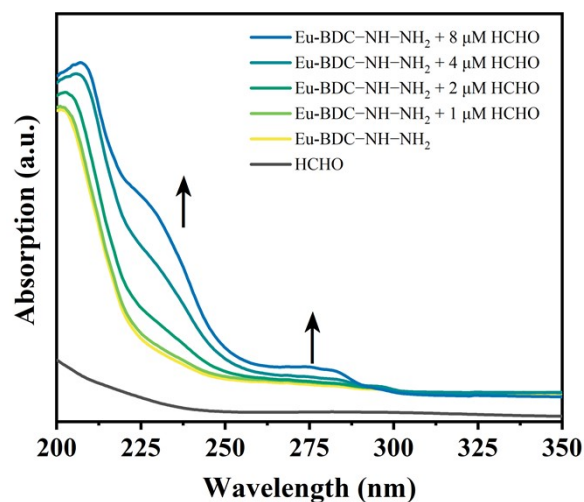


Figure S10. UV-vis absorption spectra of Eu-BDC-NH-NH₂ after adding different concentrations of formaldehyde (0–8 μM).

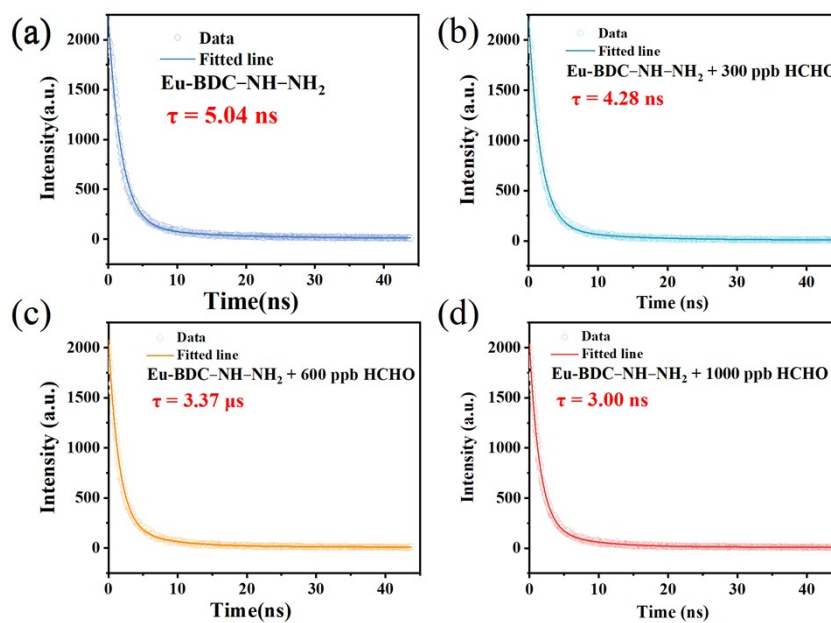


Figure S11 Time-resolved radioluminescence decay curves at 440 nm emission of Eu-BDC-NH-NH₂ reacting with different concentration formaldehyde gas.

References

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