Electronic Supplementary Information

for

Formaldehyde Recognition through Aminal Formation in a Luminescent Metal-Organic Framework

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Experimental

Materials and physical measurement

All the reagents and solvents were purchased from commercial sources without further purification. 4,4'-dicarboxylic acid (BPDC) was purchased from Energy Chemical. HCHO aqueous solution (analytical grade, 40 wt.%) was purchased from Guangzhou Chemical Reagent Factory. Fourier transform infrared (FT-IR) spectra were collected on Thermo Scientific FT-IR Nicolet iS10 spectrophotometer. UV-Vis spectra were obtained on Bio-Logic MOS-450/AF-CD Spectrometer in the range of 200 to 800 nm. Photoluminescence spectra were measured on Horiba FluoroLog-3 spectrofluorometer with a 400 nm UV cut. Powder X-ray diffraction (PXRD) patterns were recorded on Rigaku Ultima IV X-ray Diffractometer (Cu Kα, $\lambda = 1.5418$ Å) in a step of 0.02° at 40 kV and 40 mA. Thermogravimetric analyses (TGA) were measured on Mettler-Toledo thermal analyser in range of 40 to 800 °C with 10 °C/min heating rate in a nitrogen atmosphere at a flow rate of 50 mL/min.

Synthesis of JNU-105, JNU-105-$(NH_2)_2$, and JNU-105-$(NH)_2CH_2$

JNU-105. $Zn(NO_3)_2 \cdot 6H_2O$ (14.9 mg, 0.05 mmol), BPDC (6.05 mg, 0.025 mmol), and xanthine (2.85 mg, 0.019 mmol), 40 μL of concentrated HNO_3, 2 mL of mixed solvent (DEF : H_2O = 10 : 1) were added into a 10 mL glass tube. After ultrasonic treatment for 30 min, the tube was sealed and placed into an oven at 120 °C for 3 days. Colorless crystals were filtered and washed with DEF and acetone three times (yield: 48%, based on the xanthine). Elemental analysis (%): calculated for $Zn_8(\mu_3\text{-}O)_4(\text{xanthine})_4(BPDC)_2(DEF)_{2.5}(H_2O)_{10}$: C, 34.87; H: 3.41; N: 12.43. found: C, 34.77; H, 3.19; N, 11.98.

JNU-105-$(NH_2)_2$. 2,2'-diamino-[1,1'-biphenyl]-4,4'-dicarboxylic acid ($(NH_2)_2$-BPDC) was synthesized according to the reported work.[1-3] $Zn(NO_3)_2 \cdot 6H_2O$ (14.9 mg, 0.05 mmol), $(NH_2)_2$-BPDC (6.8 mg, 0.025 mmol), xanthine (3.8 mg, 0.025 mmol), 15 μL of concentrated HNO_3, and 2 mL of mixed solvent (DEF : H_2O = 10 : 1) were added into a 10 mL glass tube. After ultrasonic treatment for 30 min, the tube was sealed and placed into an oven at 120 °C for 5 days. Yellow to brown crystals were filtered and washed with DEF and acetone three times (yield: 53%, based on the xanthine). Elemental analysis (%): calculated for $Zn_4(\mu_3\text{-}O)_2(\text{xanthine})_2[(NH_2)_2\text{-}BPDC](DEF)_{1.5}(H_2O)_3$: C, 34.47; H, 3.72; N, 14.67. found: C, 33.71; H, 3.47; N, 14.19.

JNU-105-$(NH)_2CH_2$. 20 mg of **JNU-105-$(NH_2)_2$** and 2 mL HCHO aqueous solution (40 wt.%) were mixed in a 10 mL quartz vial at room temperature for 4 days. The crystals were collected and washed with deionized water and acetone three times, and then dried in 80 °C vacuum oven overnight to afford **JNU-105-$(NH)_2CH_2$**.

X-ray crystallography

The as-synthesized petal-like crystal clusters of JNU-105, JNU-105-$(NH_2)_2$, and JNU-105-$(NH)_2CH_2$ were cut into suitable sizes for single-crystal X-ray diffraction (SCXRD) analysis. The SCXRD data were collected by Oxford Cryostream system on a XtaLAB PRO MM007-

DW diffractometer equipped with a graphite monochromator Cu Kα radiation (λ = 1.54184 Å) at 100 or 298 K. The structures of JNU-105, JNU-105-$(NH_2)_2$ and JNU-105-$(NH)_2CH_2$ were solved by using Olex2 software with ShelXT program and refined by ShelXL program. The intensively disordered solvent molecules in voids were removed by the SQUEEZE/PLATON program. CCDC Nos. 2164136-2164138 contain the supplementary crystallographic data for JNU-105, JNU-105-$(NH_2)_2$ and JNU-105-$(NH)_2CH_2$. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Photoluminescence measurement

HCHO titration experiment. 10 mg of dried **JNU-105** and **JNU-105-$(NH_2)_2$** were finely ground, immersed into 20 mL deionized water and ultrasonicated for 15 min to afford 0.5 mg/mL MOF suspension. In a 3.5 mL quartz cell, 2.7 mL of MOF suspension was added as the blank sample. 20 μL of HCHO aqueous solution (1 mM) was added into suspension each time until the concentration of HCHO in suspension reached to 0.1 mM. The luminescence emission was recorded after mixing and shaking.

VOCs sensing experiment. In luminescence response experiment of **JNU-105-$(NH_2)_2$** for individual VOC, a certain amount of 13 different kinds of aqueous solution of VOCs was individually added into MOF suspension (0.1 M for VOCs, 0.25 mg/mL for MOF, total 3mL). In luminescence response experiment for mixed VOCs, 5 μL of each VOCs (THF, methanol, iso-propanol, ethanol, DMSO, DMF, DMA, acetonitrile, acetone, 1,4-dioxane) were added together into 2.7 mL MOF suspension. The luminescence emission was measured after shaking.

MOF-based test papers. 0.5 mg/mL of MOF-dichloromethane suspension was dropped on the filter paper stripes (1 × 4 cm) and dried in air. The test paper was used for the detection of HCHO in aqueous solutions under the UV (365 nm) irradiation.

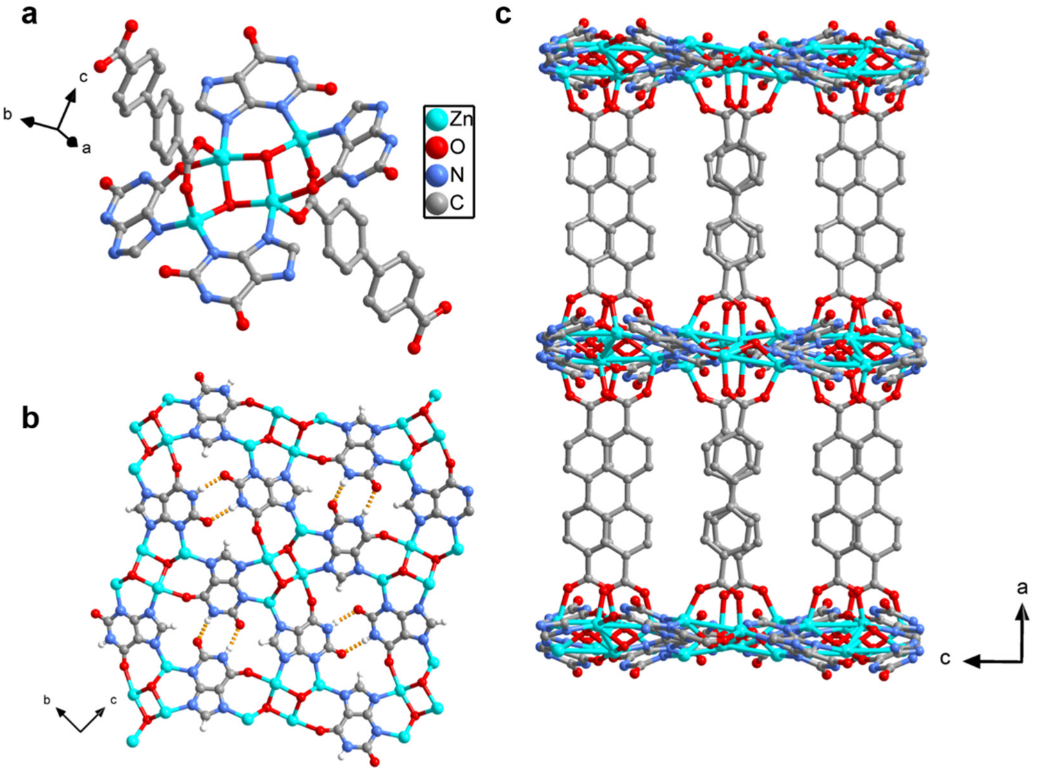

Fig. S1. (a) Tetranuclear zinc nuclear SBU in **JNU-105**. (b) The dense *ab* layer formed by xanthine linkers and zinc ions. (c) 3D pillar-layer framework.

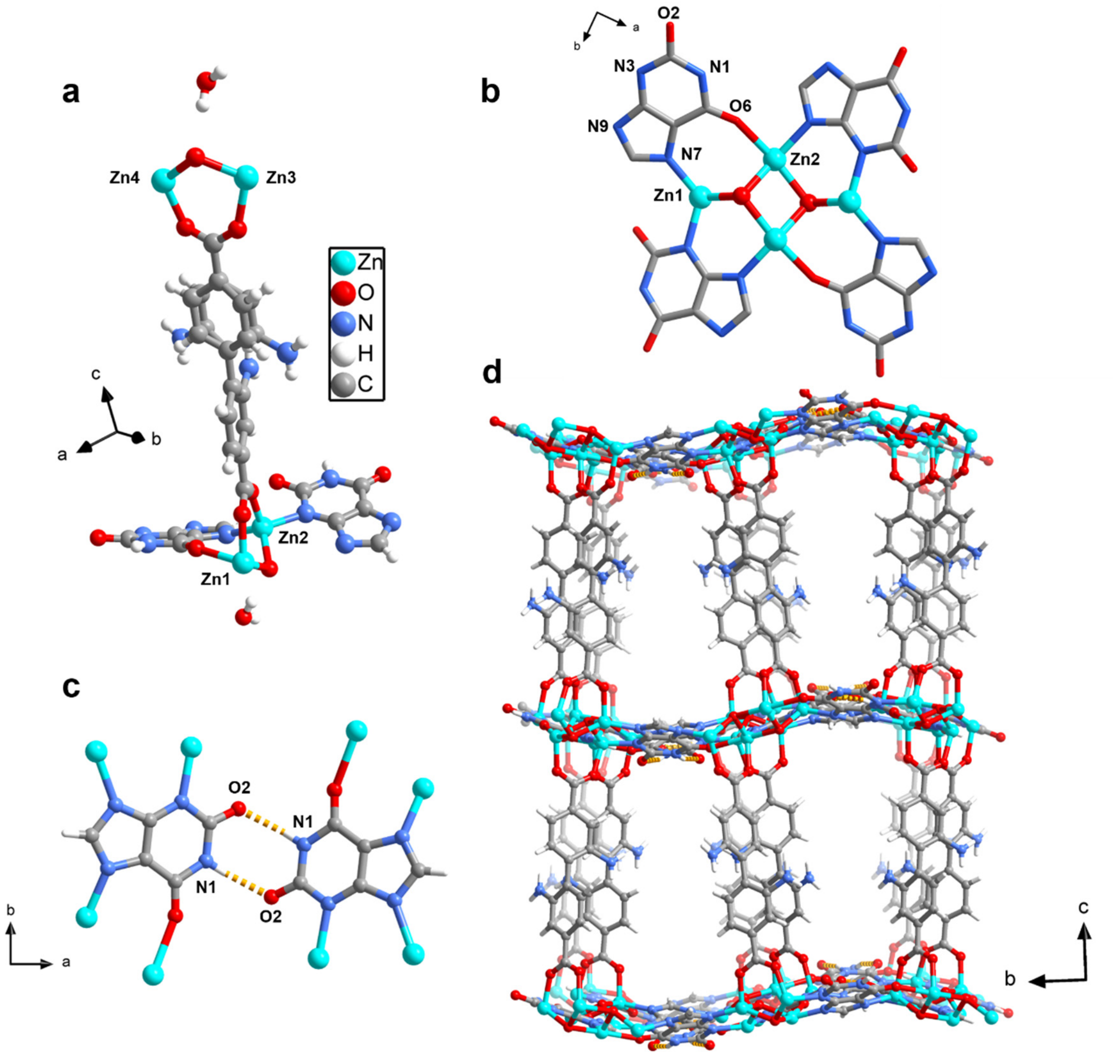

Fig. S2. (a) Asymmetric unit of **JNU-105-(NH$_2$)$_2$**. (b) Coordination modes of two kinds of Zn ions. (c) Hydrogen bonds between two xanthine linkers. (d) 3D framework looking through *a* axis.

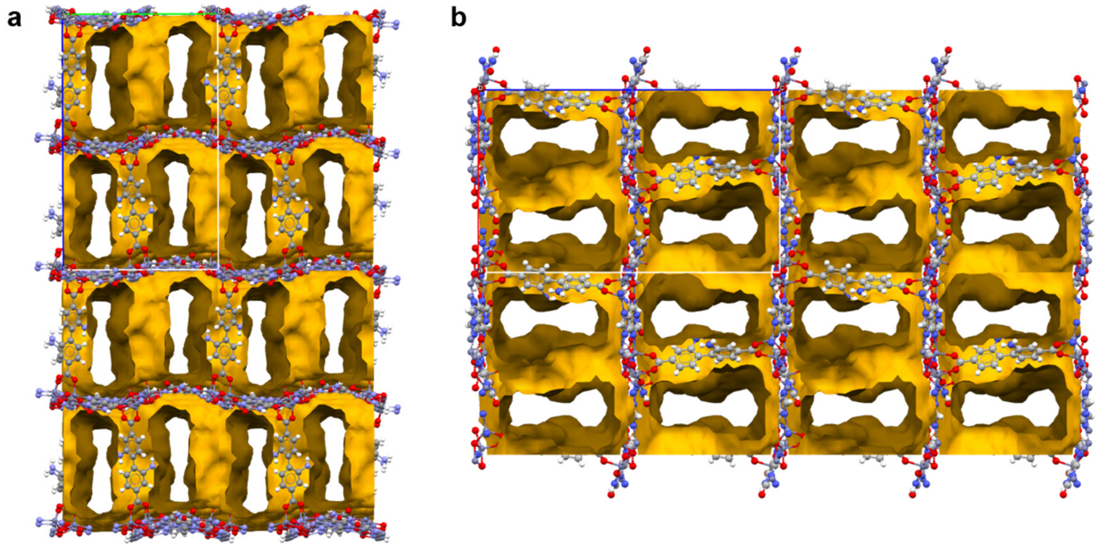

Fig. S3. 2D channels going through *a* axis (a) and *b* axis (b).

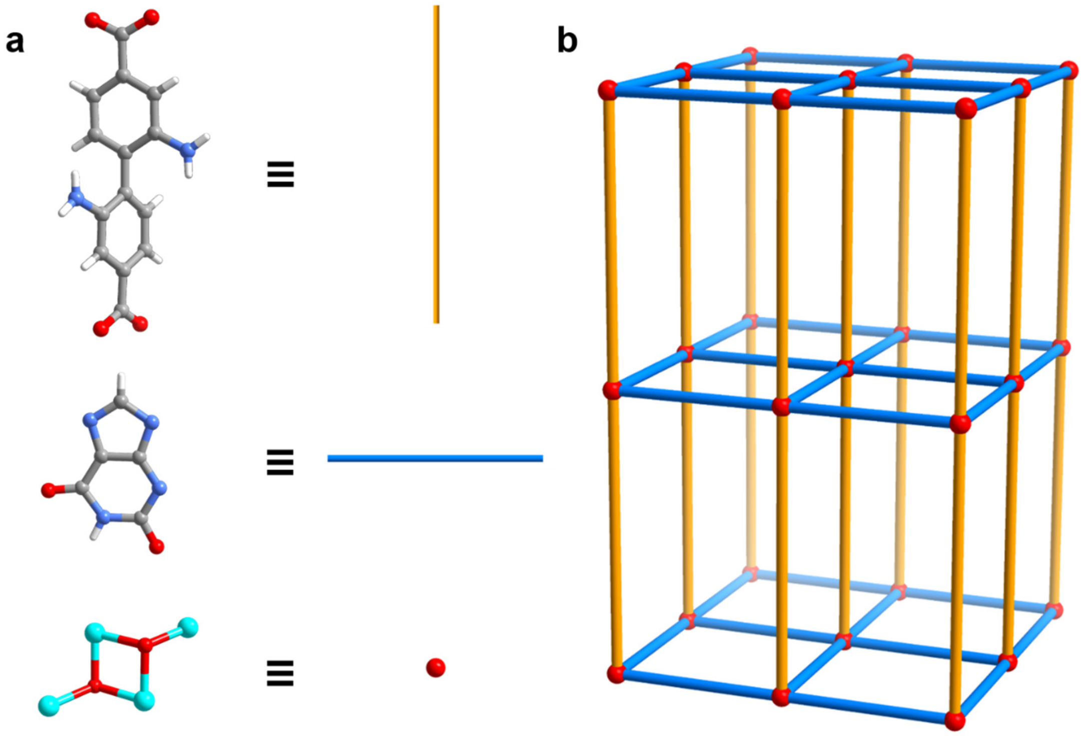

Fig. S4. (a) Schematic of building block in **JNU-105-(NH$_2$)$_2$**. (b) **pcu** topological structure of **JNU-105-(NH$_2$)$_2$**.

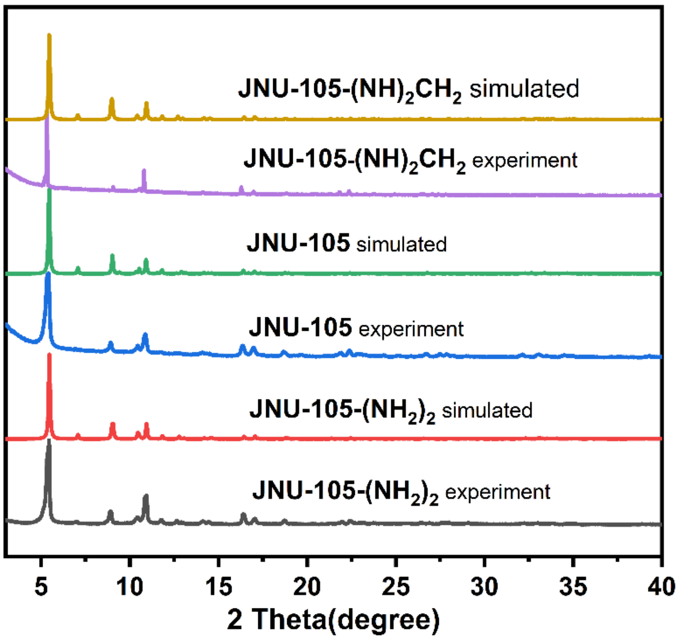

Fig. S5. The simulated and experiment PXRD pattern of **JNU-105**, **JNU-105-(NH$_2$)$_2$** and **JNU-105-(NH)$_2$CH$_2$**.

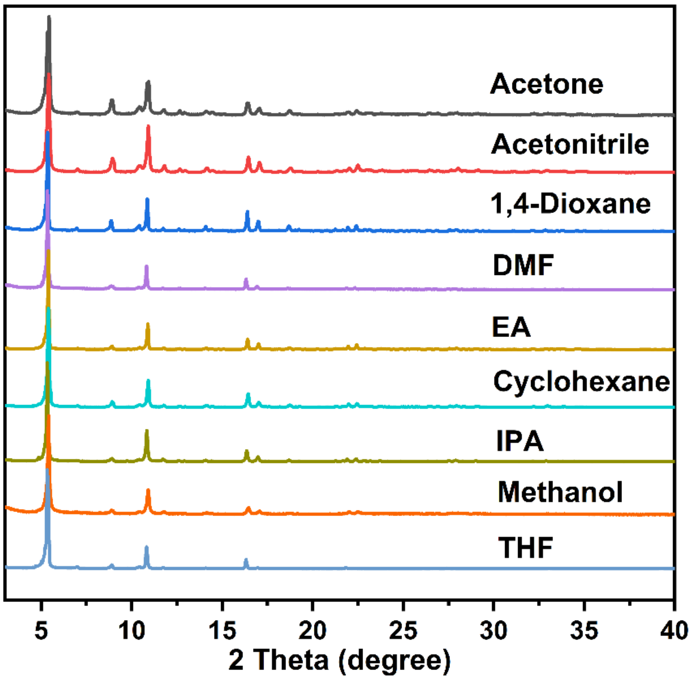

Fig. S6. PXRD pattern of **JNU-105-(NH$_2$)$_2$** after soaking in organic solvent.

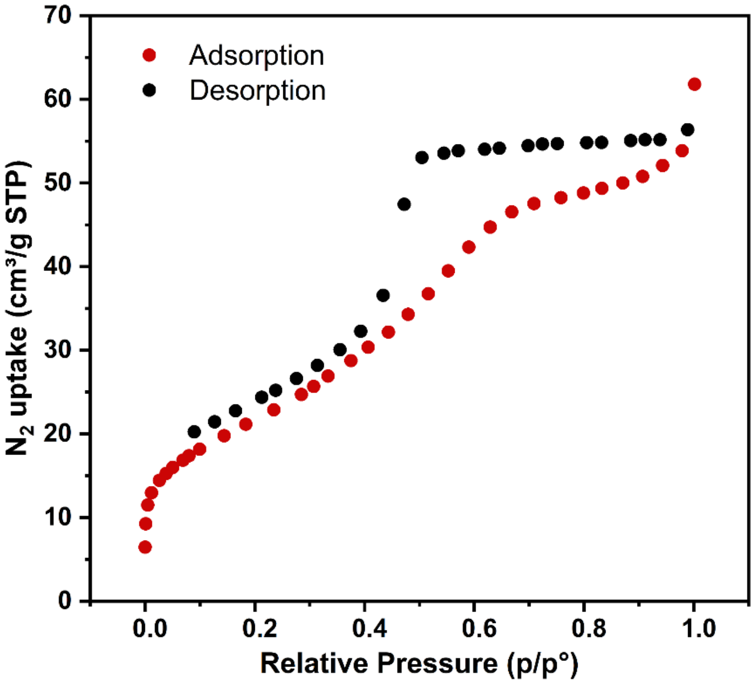

Fig. S7. N$_2$ adsorption isotherm of **JNU-105-(NH$_2$)$_2$** at 77 K.

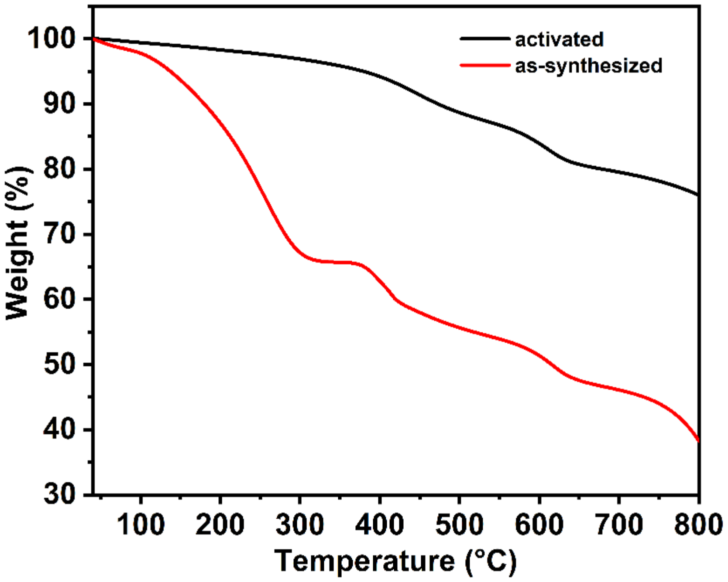

Fig. S8. The thermogravimetric analysis curve of **JNU-105-(NH_2)$_2$**.

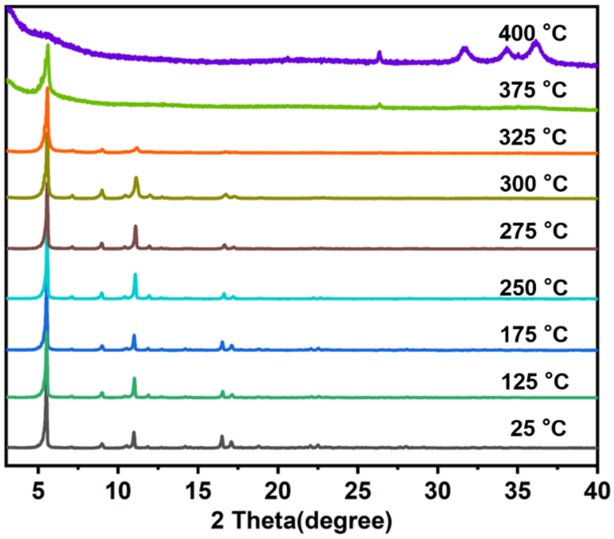

Fig. S9. The variable-temperature *in situ* PXRD pattern of **JNU-105-(NH_2)$_2$** (in air).

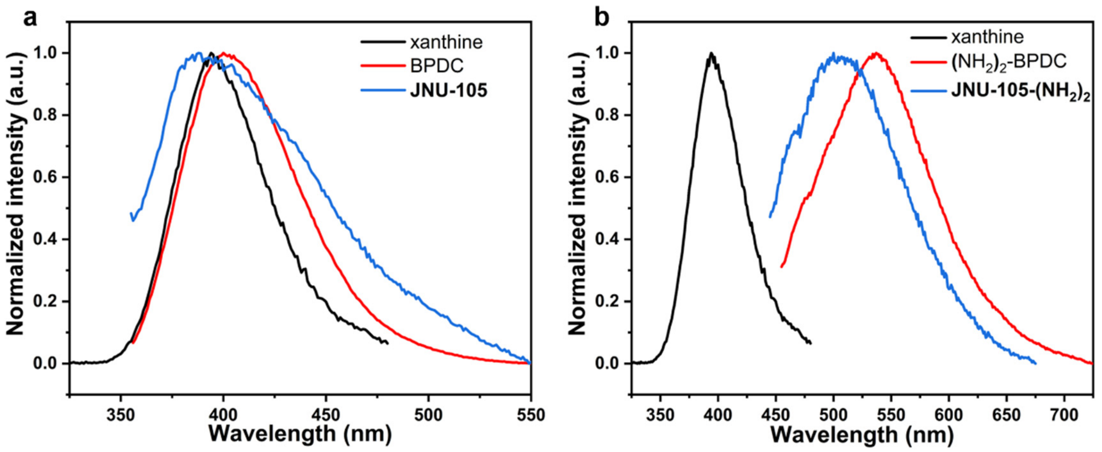

Fig. S10. (a) The emission spectra of **JNU-105**, xanthine and BPDC. (b) The emission spectra of **JNU-105-$(NH_2)_2$**, xanthine and $(NH_2)_2$-BPDC.

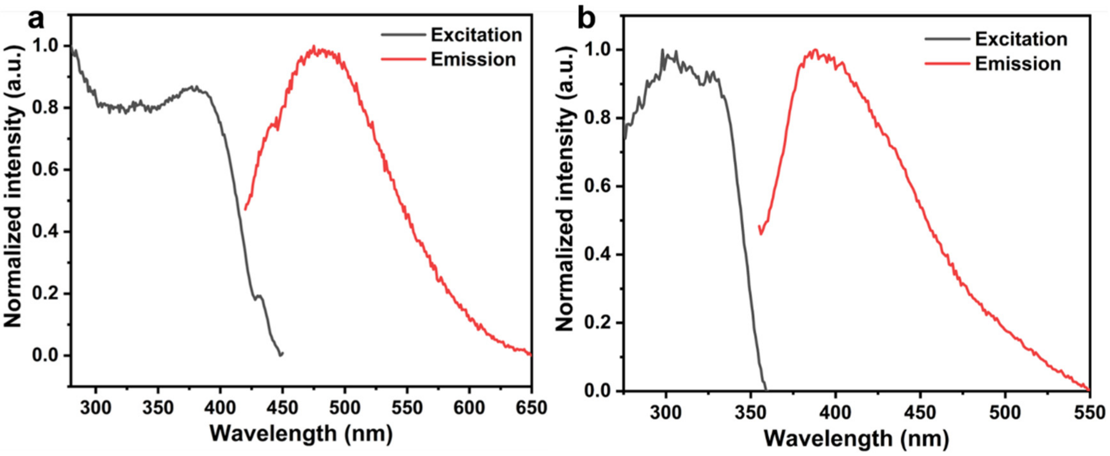

Fig. S11. The excitation and emission spectra of **JNU-105-$(NH_2)_2$** (a) and **JNU-105** (b).

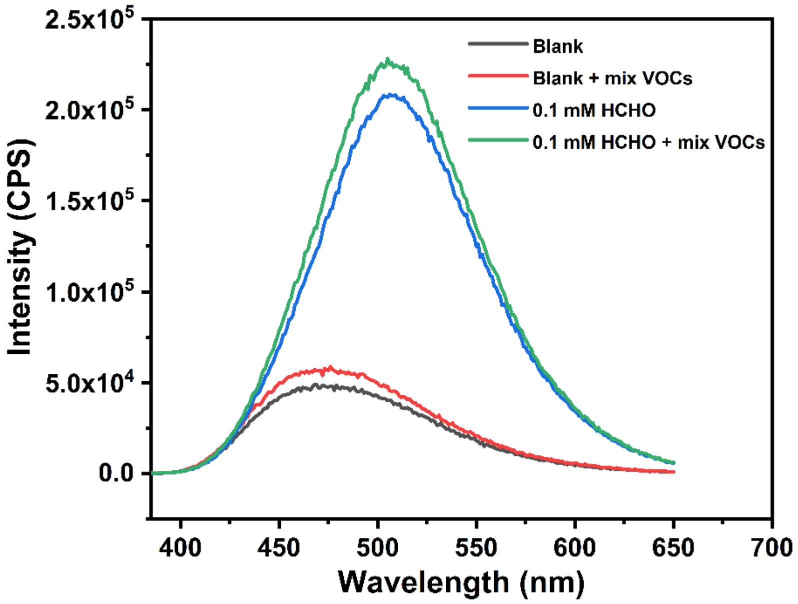

Fig. S12. The emission spectra of **JNU-105-(NH$_2$)$_2$** suspension with no addition, **JNU-105-(NH$_2$)$_2$** suspension with mix 10 kinds of VOCs, 0.1 mM HCHO aqueous suspension of **JNU-105-(NH$_2$)$_2$**, 0.1 mM HCHO aqueous suspension of **JNU-105-(NH$_2$)$_2$** with 10 kinds of VOCs.

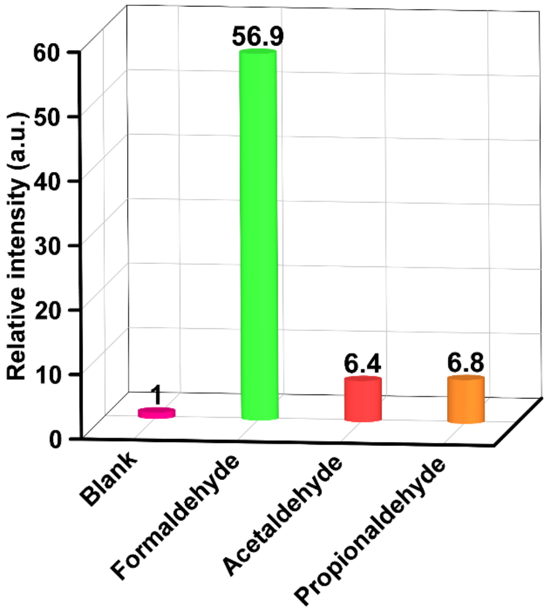

Fig. S13. The relative luminescence intensity of 0.1 M formaldehyde, acetaldehyde and propionaldehyde aqueous suspension of **JNU-105-(NH$_2$)$_2$**.

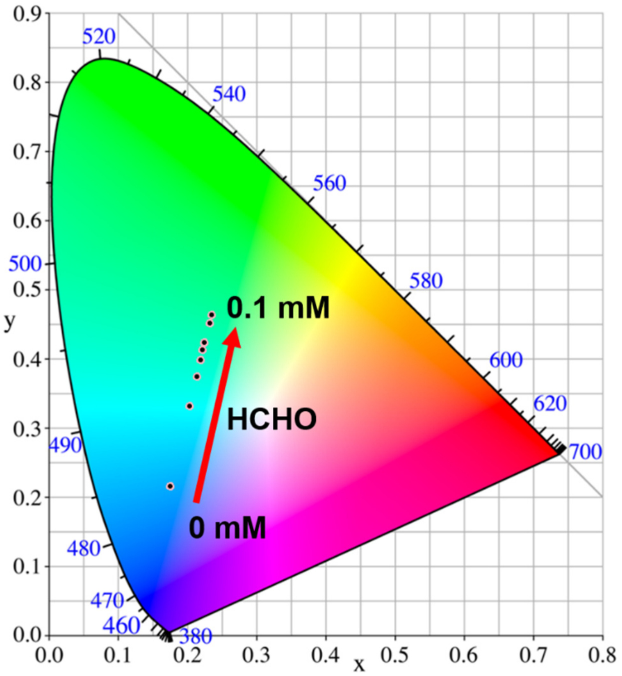

Fig. S14. CIE changes of **JNU-105-(NH_2)$_2$** in HCHO solutions from 0.0 to 0.1 mM.

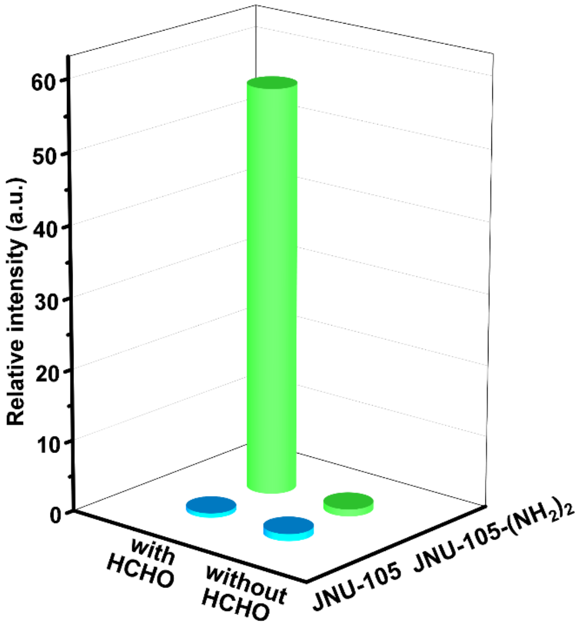

Fig. S15. The relative luminescence intensity of **JNU-105-(NH_2)$_2$** and **JNU-105** before and after the addition of HCHO.

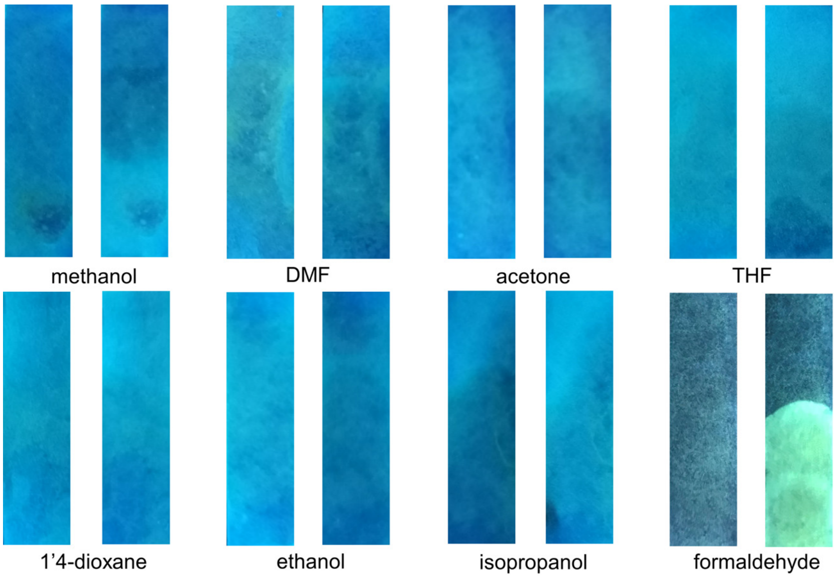

Fig. S16. Under the irradiation of 365 nm UV light, the optical pictures of the original and half-immersed **JNU-105-(NH_2)$_2$** MOF - based test paper in 0.05 M VOCs aqueous solution.

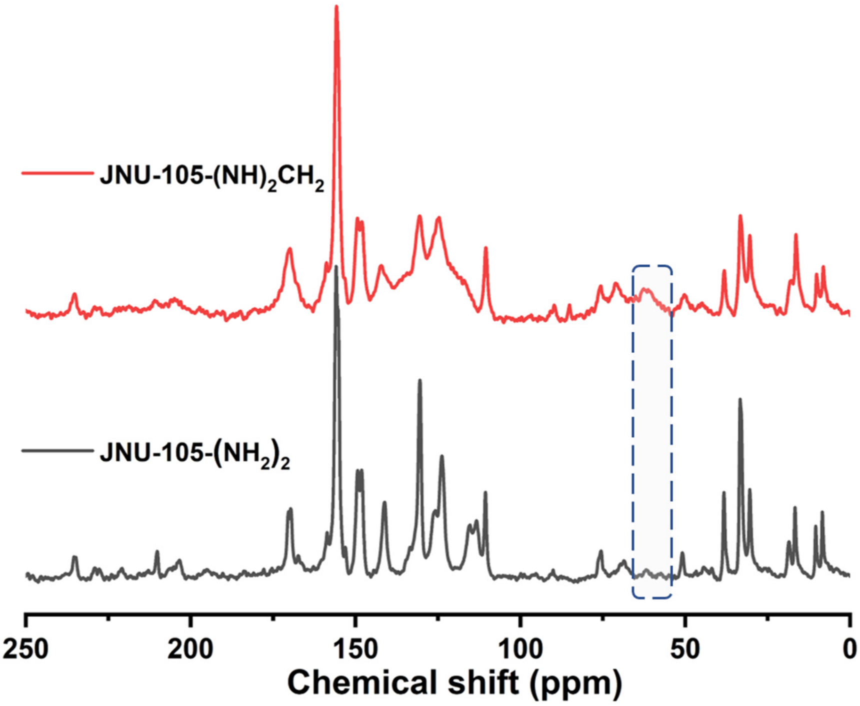

Fig. S17. The ^{13}C-solid state NMR spectrum of **JNU-105-(NH$_2$)$_2$** and **JNU-105-(NH)$_2$CH$_2$**.

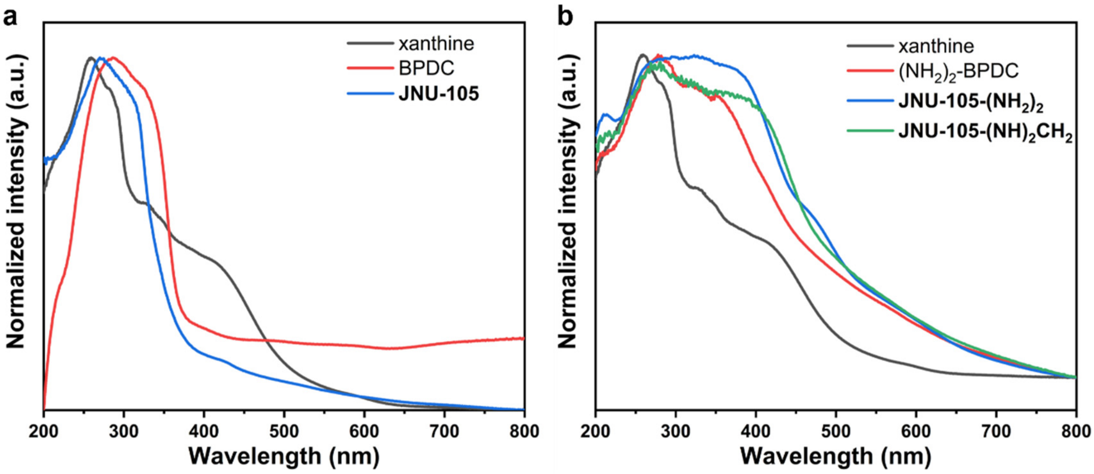

Fig. S18. Solid-state UV-Vis spectra of MOFs **JNU-105**, **JNU-105-(NH$_2$)$_2$**, **JNU-105-(NH)$_2$CH$_2$** and the linkers.

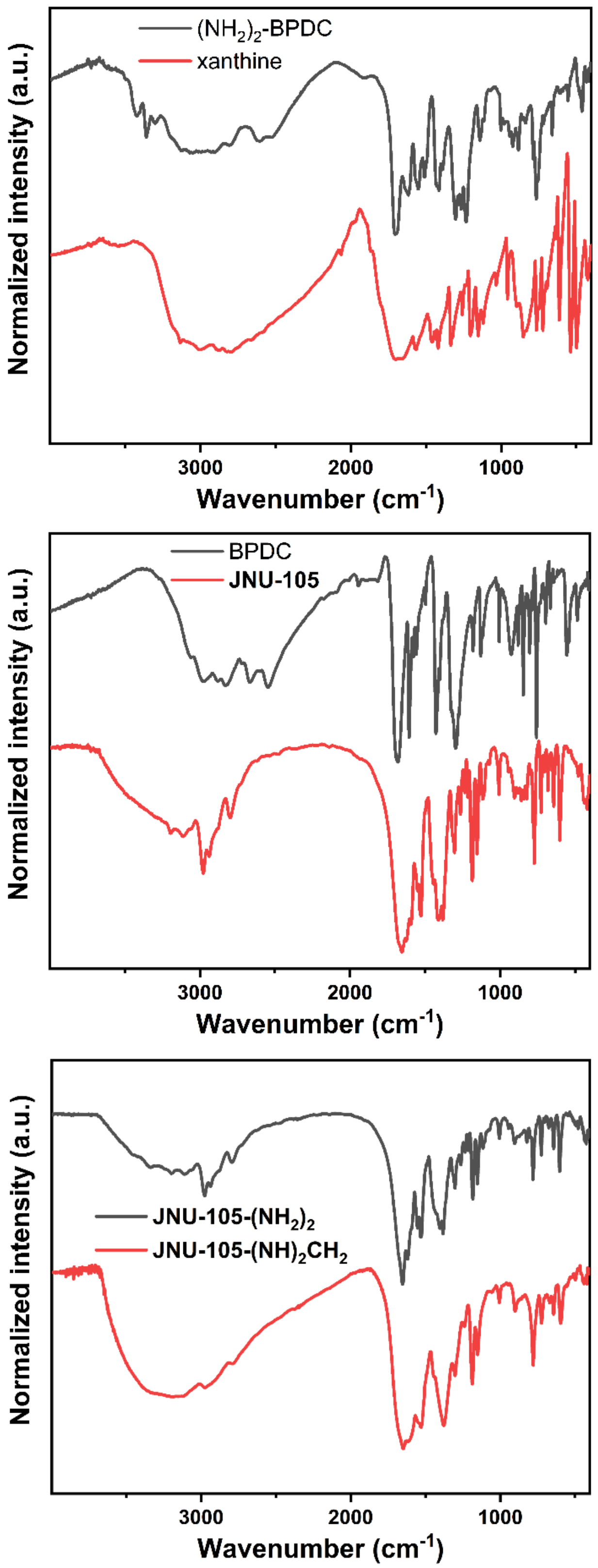

Fig. S19. FTIR spectra of linkers and **JNU-105**, **JNU-105-$(NH_2)_2$**, **JNU-105-$(NH)_2CH_2$**.

Table S1. Crystallographic data for JNU-105-$(NH_2)_2$, JNU-105, JNU-105-$(NH)_2CH_2$.

Compound	**JNU-105-$(NH_2)_2$**	**JNU-105**	**JNU-105-$(NH)_2CH_2$**
Empirical formula	$C_{24}H_{18}N_{10}O_{12}Zn_4$	$C_{48}H_{24}N_{16}O_{20}Zn_8$	$C_{25}H_{18}N_{10}O_{12}Zn_4$
M_r	899.96	1667.79	911.97
Temperature(K)	99.99(17)	293(2)	293(2)
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pccn*	*Aea*2	*Pccn*
a/Å	19.49970(10)	32.3895(2)	19.6175(6)
b/Å	19.64560(10)	27.4040(2)	19.741(2)
c/Å	32.3093(2)	28.0141(2)	32.3260(19)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	12377.15(12)	24865.4(3)	12519.1(17)
Z	8	8	8
F(000)	3584.0	6584.0	3632.0
Reflection collected	123274	73414	40469
Independent reflections	13122 [R_{int} = 0.0491, R_{sigma} = 0.0248]	19263 [R_{int} = 0.0318, R_{sigma} = 0.0271]	12424 [R_{int} = 0.0679, R_{sigma} = 0.0632]
GOF on F^2	1.058	1.568	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0514, wR_2 = 0.1478	R_1 = 0.1133, wR_2 = 0.3069	R_1 = 0.0627, wR_2 = 0.1870
Final R indexes [all data]	R_1 = 0.0578, wR_2 = 0.1529	R_1 = 0.1145, wR_2 = 0.3105	R_1 = 0.0703, wR_2 = 0.1942

Table S2. LOD comparison of formaldehyde luminescence probes in water environment.

Material	**LOD (ppb)**	**Reference**
HUN-44	27.41	4
CMERI-1	19	5
CMERI-2	41	5
UiO-66-NH_2	4000	6
MOF-1	370	7
Eu^{3+}@Bio-MOF-1	5500	8
Al-MIL-53	250	9
JNU-105-$(NH_2)_2$	1.87	This work

Reference

1. Y.-B. Wei, M.-J. Wang, D. Luo, Y.-L. Huang, M. Xie, W. Lu, X. Shu and D. Li, *Mater. Chem. Front.*, 2021, **5**, 2416-2424.
2. N. Ko, J. Hong, S. Sung, K. E. Cordova, H. J. Park, J. K. Yang and J. Kim, *Dalton Trans.*, 2015, **44**, 2047-2051.
3. R. Gil-San-Millan, E. Lopez-Maya, M. Hall, N. M. Padial, G. W. Peterson, J. B. DeCoste, L. M. Rodriguez-Albelo, J. E. Oltra, E. Barea and J. A. R. Navarro, *ACS Appl. Mater. Interfaces*, 2017, **9**, 23967-23973.
4. Y. Fang, G. J. Ren, M. L. Li, Y. H. Yang, D. Y. Guo and Q. H. Pan, *Sensor. Actuat. B-Chem.*, 2021, **349**.
5. S. Bej, S. Mandal, A. Mondal, T. K. Pal and P. Banerjee, *ACS Appl. Mater. Interfaces*, 2021, **13**, 25153-25163.
6. K. Vellingiri, A. Deep, K. H. Kim, D. W. Boukhvalov, P. Kumar and Q. Yao, *Sensor. Actuat. B-Chem.*, 2017, **241**, 938-948.
7. X. B. Yin, Y. Q. Sun, H. Yu, Y. Cheng and C. Wen, *Anal. Chem.*, 2022, **94**, 4938-4947.
8. Y. Zhang and B. Yan, *J. Mater. Chem. C*, 2019, **7**, 5652-5657.
9. S. Nandi, E. Sharma, V. Trivedi and S. Biswas, *Inorg. Chem.*, 2018, **57**, 15149-15157.