

Two isomeric zeolite-like metal-organic frameworks with mechanically responsive luminescence emission and gas adsorption property

Shuang Peng,^{a‡} Yan-Jie Qi,^{a‡} Xin-Hao Li,^b Cai Sun,^a Ling-Yun Li,^{b*} Xin-Xiong Li,^{a*} Shou-Tian Zheng,^a Qichun Zhang ^{c*}

^a *State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China.*

^b *Key Laboratory of Eco-materials Advanced Technology, College of Materials Science and Engineering, Fuzhou University, Fuzhou, Fujian 350108, China.*

^c *School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore (Singapore).*

This file includes:

Section S1 Synthesis and Methods

Section S2 Additional Table

Section S3 Additional Figures

Section S4 References

Section S1 Synthesis and Methods

Materials and General methods: All the reagents and solvents were procured from commercial sources and were used without further purification. The H₃TPO ligands were prepared according to the previously described procedures. Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 1.54051 \text{ \AA}$). Elemental analyses (EA) of C, H and N were carried out based on a Vario MICRO elemental analyzer. Thermal stability were studied by using a Mettler Toledo TGA/SDTA 851e analyzer under an air-flow atmosphere at a heating rate of 10 °C/min with the temperatures ranging from 30 °C to 1000 °C. The IR was experimented on the Nicolet iS50 at room temperature. The solid-state luminescence emission/excitation spectra were recorded on an Edinburgh Instrument FLS920 fluorescence spectrophotometer equipped with a continuous Xe-900 xenon lamp and a F900 microsecond flash lamp. Single-component gas adsorption measurements were performed with an Accelerated Surface Area and Porosimetry 2020 (ASAP 2020) surface area analyzer. All gases were used in the adsorption experiment of 99.999% purity or higher. The crystal morphology analyses were performed using a Hirox SH-4000 M type desktop scanning electron microscope.

Synthesis of [(CH₃)₂NH₂][Cd(TPO)] (1- α): CdCl₂·2^{1/2}H₂O (47.3 mg), H₃TPO (20.4 mg) were added to 5 mL NMF and 1 mL CH₃CN in a 20 mL vial, and the mixture was stirred for 1 hour. Then, the reactants were sealed and heated at 100 °C for 5 days. After cooling to room temperature, colorless stick crystals were obtained after the solid products were washed with CH₃CN (5 mL) for three times. The yield is about 12% based on H₃TPO. Elemental analysis (%) calcd for C₂₃H₂₀CdNO₇P (565.79): C, 48.82; H, 3.56; N, 2.48; found: C, 49.16; H, 3.97; N, 2.23.

Synthesis of [(CH₃)₂NH₂][Cd(TPO)] (1- β): CdCl₂·2^{1/2}H₂O (46.8 mg), H₃TPO (20.9 mg) were added to 2 mL NMF, 3 mL CH₃CN, and 1 mL deionized water in a 20 mL vial, and the mixture was stirred for 1 hour. Then, the reactants were sealed and heated at 100 °C for 5 days. After cooling to room temperature, colorless stick crystals were obtained after the solid products were washed with CH₃CN (5 mL) for three times. The yield is about 12% based on H₃TPO. Elemental analysis (%) calcd for C₂₃H₂₀CdNO₇P (565.79): C, 48.82; H, 3.56; N, 2.48; found: C, 48.66; H, 3.27; N, 2.17.

Single-crystal structure analysis: Single-crystal X-ray diffraction data of **1- α** and **1- β** were collected on Bruker Apex Duo CCD diffractometer with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) operating at 175(2) K. The structures of **1- α** and **1- β** were solved through direct methods and refined by full-matrix least-squares refinements based on F^2 adopting the SHELX-2014 program package. The contribution of disordered solvent molecules to the overall intensity data of structures were treated using the SQUEEZE method in PLATON. All non-H atoms were located with successive difference Fourier syntheses and refined anisotropically. Crystallographic data and structure refinements for **1- α** and **1- β** are summarized in [Table S1](#). CCDC 2063858 and 2063859 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Section S2 Additional Table

Table S1 Crystal data and structure refinement for compounds **1- α** and **1- β** .

name code	1-α	1-β
formula	C ₂₁ H ₁₂ CdO ₇ P	C ₂₁ H ₁₂ CdO ₇ P
Fw (g/mol)	519.68	519.68
temperature (K)	175(2)	175(2)
λ , (Å)	1.54178	0.71073
cryst syst	Orthorhombic	Monoclinic
space group	<i>Pbca</i> (# 61)	<i>P2₁c</i> (# 14)
a, (Å)	23.728(3)	15.135(4)
b, (Å)	13.165(2)	22.7028(5)
c, (Å)	30.085(6)	18.370 (4)
β , (o)	90	101.248(4)
V, (Å ³)	9398(3)	6007(2)
Z	8	8
ρ_{calcd} (g/cm ³)	0.735	1.251
F(000)	2056	2272
crystal size (mm)	0.15 × 0.13 × 0.06	0.12 × 0.06 × 0.05
theta range (o)	1.894~25.061	1.654 ~ 25.089
limiting indices	-28 ≤ h ≤ 27, -15 ≤ k ≤ 15, -32 ≤ l ≤ 35	-13 ≤ h ≤ 18, -17 ≤ k ≤ 26, -21 ≤ l ≤ 14
R _{int}	0.0390	0.0443
Goof	0.997	1.004
R [$I > 2\sigma$]	R ₁ ^a = 0.0456, wR ₂ ^b = 0.1368	R ₁ ^a = 0.0440, wR ₂ ^b = 0.1110
R (all data)	R ₁ ^a = 0.0562, wR ₂ ^b = 0.1425	R ₁ ^a = 0.0850, wR ₂ ^b = 0.1190

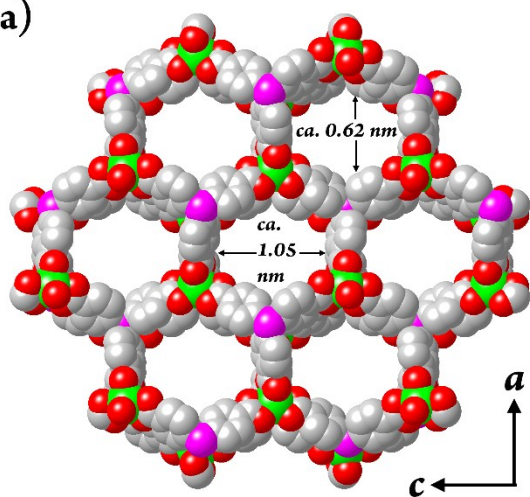
^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / w(F_o^2)]^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2) / 3$, where $x = 0.0883$, $y = 4.4049$ for **1- α** ; $x = 0.0704$, $y = 0$ for **1- β** .

Table S2 The angles of the tetrahedral nodes in compounds **1- α** and **1- β** .

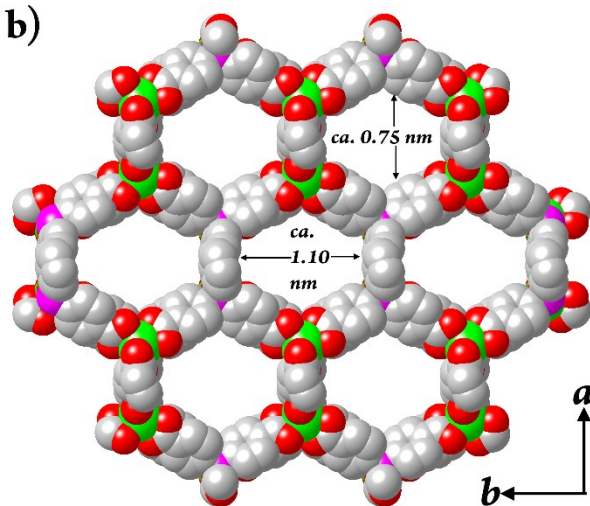
compound 1-α		compound 1-β	
The angles of the Cd ²⁺ node	The angles of the TPO ³⁻ node	The angles of the Cd ²⁺ node	The angles of the TPO ³⁻ node
76.919°	98.123°	74.857°	85.945°
99.694°	103.081°	94.130°	101.205°
103.005°	105.785°	109.680°	105.286°
121.243°	107.357°	119.084°	114.430°
123.764°	117.514°	123.750°	119.704°
129.087°	122.311°	129.003°	131.640°

Section S3 Additional Figures

a)



b)



c)

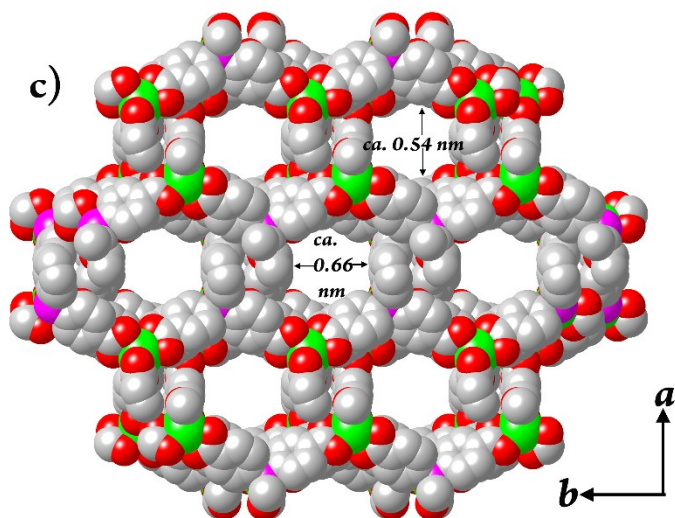


Fig. S1. The sizes of channels in **1- α** and **1- β** , a) the framework of **1- α** ; b-c) the framework of **1- β** before and after interpenetration.

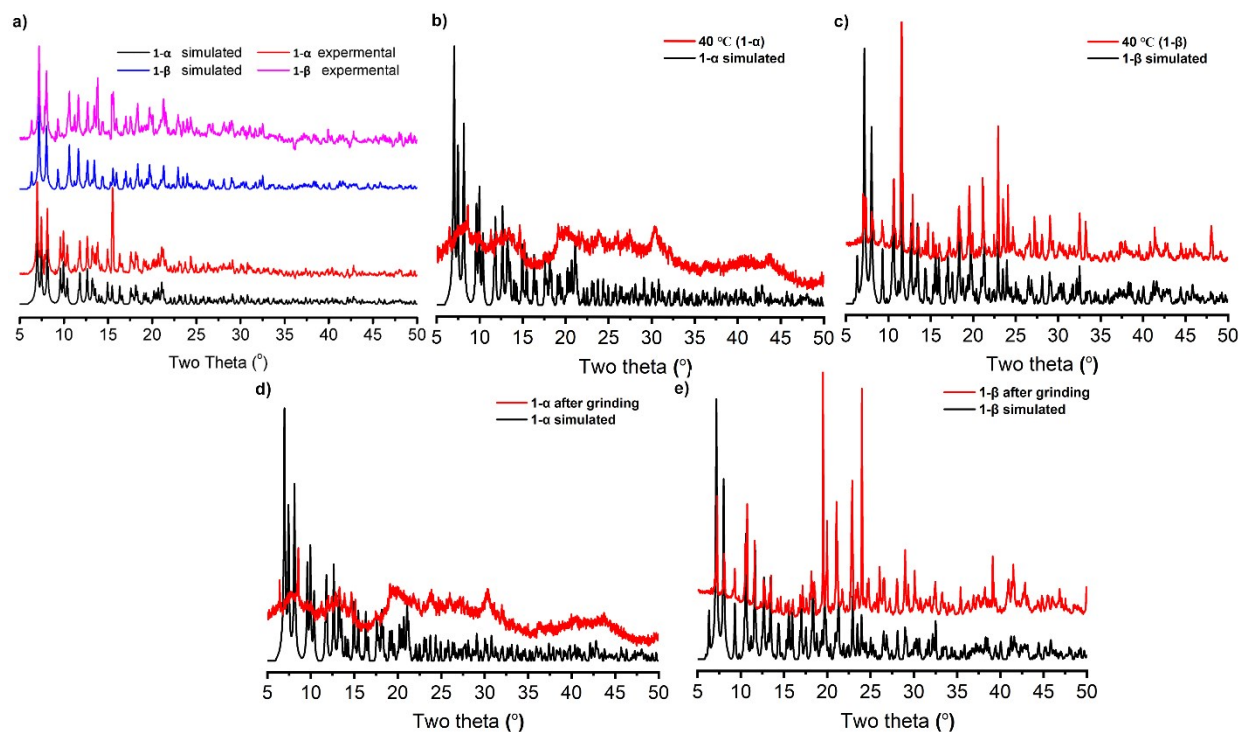


Fig. S2. (a) The theoretical simulated and experimental PXRD patterns of **1- α** and **1- β** at room temperature; (b) The theoretical simulated and PXRD patterns of **1- α** at 40°C; (c) The theoretical simulated and PXRD patterns of **1- β** at 40°C; (d) The theoretical simulated and PXRD patterns of **1- α** after grinding; (e) The theoretical simulated and PXRD patterns of **1- β** after grinding.

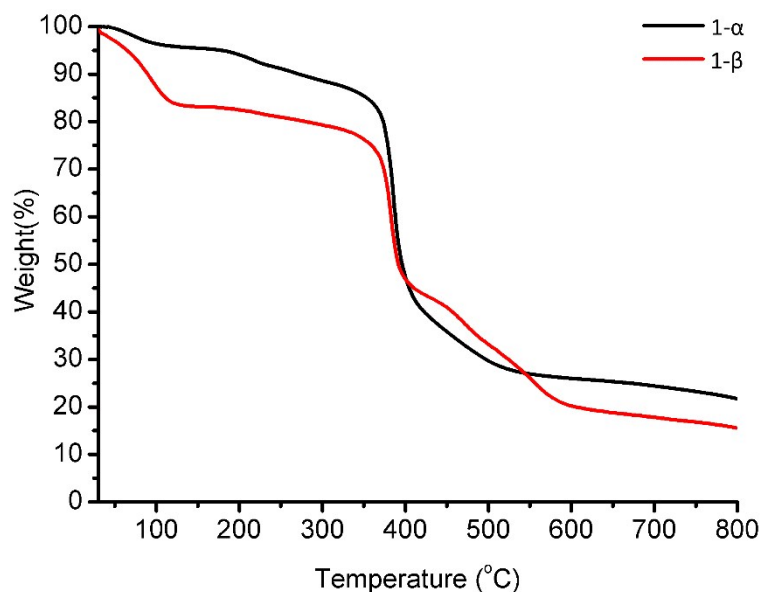


Fig. S3. The TG curves of **1- α** and **1- β** .

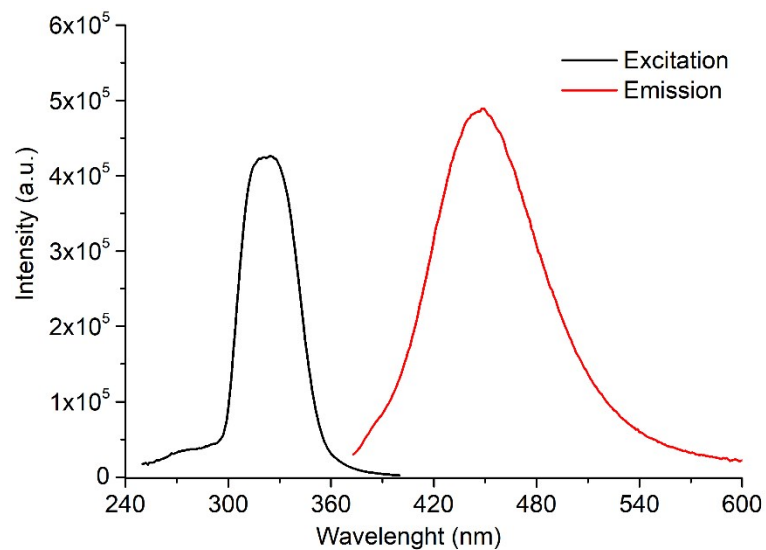


Fig. S4. The excitation and emission spectra of H_3TPO molecule.

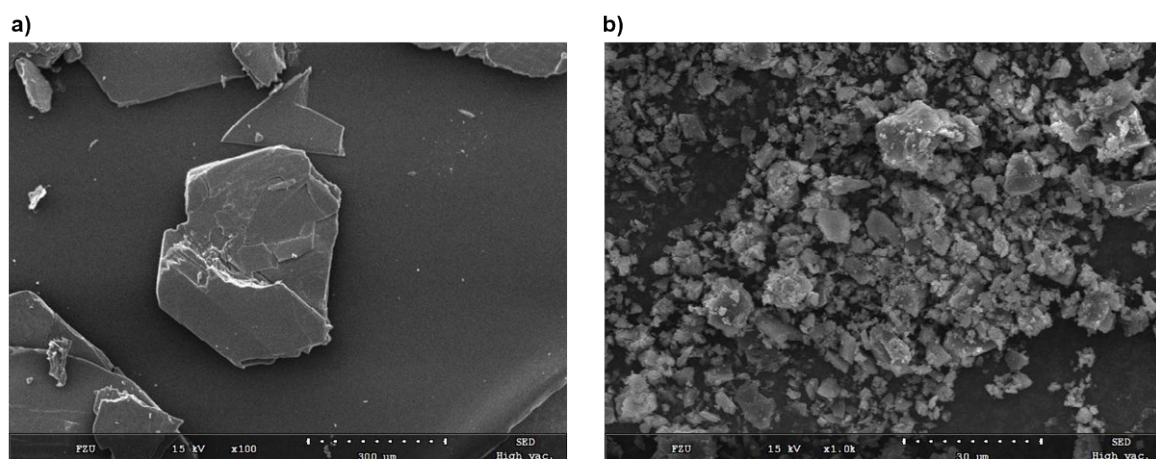


Fig. S5. The SEM images of compound $1-\beta$ before (a) and after (b) grinding.

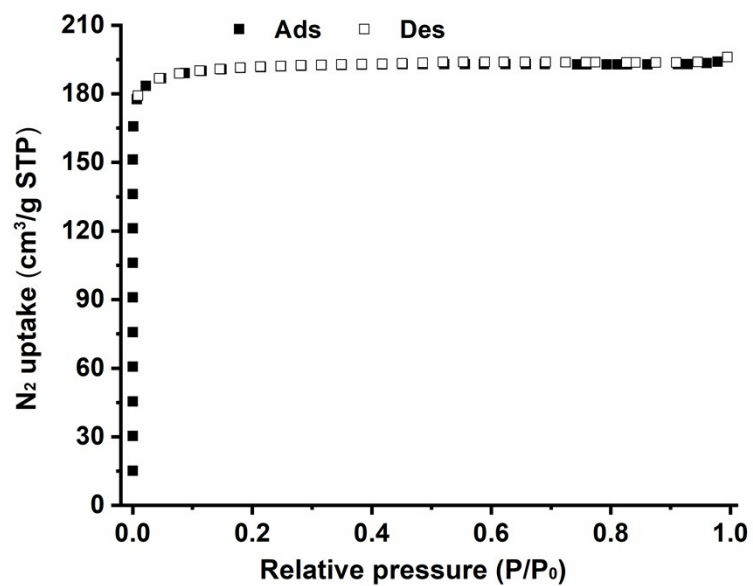


Fig. S6. The N₂ sorption isotherms of compound 1-β at 77 K after grinding.

Section S4 References

S1 A. Tézé, G. Hervé, R. G. Finke, D. K. Lyon, *Inorg. Synth.* **1990**, *27*, 85-135.