

Supplementary Materials
for
**A Highly Stable Zn₉-Pyrazolate Metal-Organic Framework with
Metallosalen Ligands as Carbon Dioxide Cycloaddition Catalyst**

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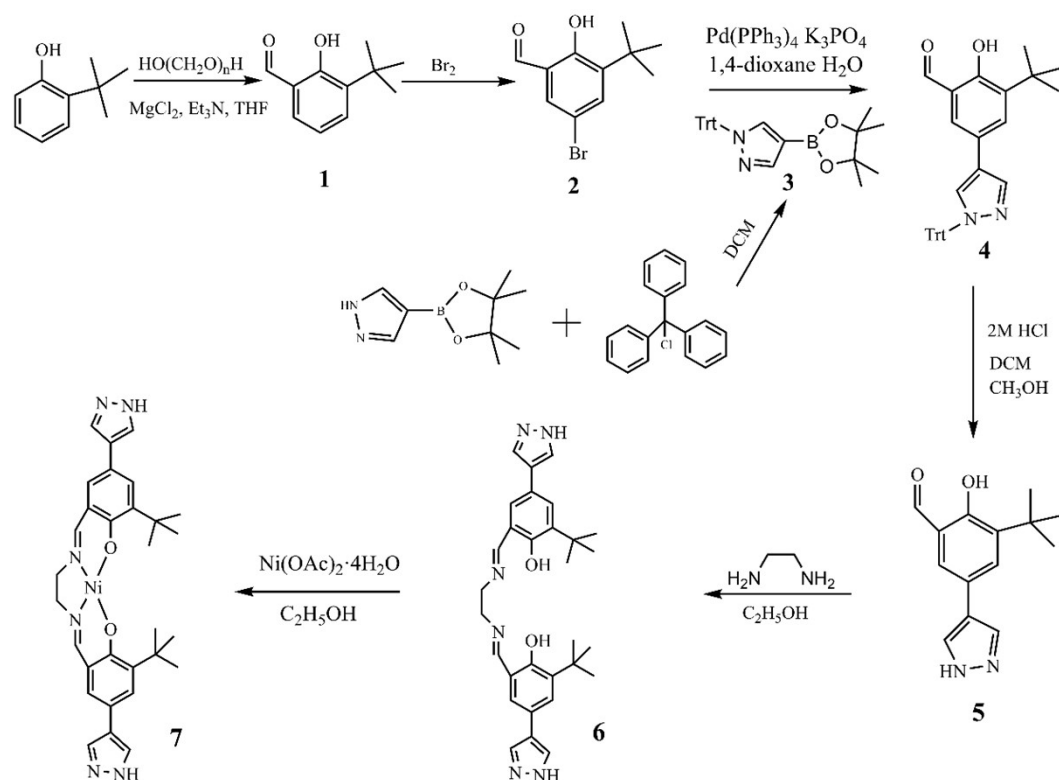
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1. Reagents and Apparatus

All chemicals and reagents were used as received from commercial sources without further purification. Powder X-ray diffraction (PXRD) patterns were recorded on a Miniflex 600 diffractometer using Cu K α radiation ($\lambda = 0.154$ nm). SEM images were taken with an SU-8010 field emission scanning electron microscope with the secondary electron imaging resolution ≤ 1 nm (15 kV, XWD ≥ 4 mm) or ≤ 1.3 nm (1 kV). N₂ sorption isotherms were measured by a Micromeritics ASAP 2460 instrument. CO₂ sorption isotherms were measured by a Micromeritics ASAP 2020 instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al K α source (15 kV, 10 mA). The static contact angle (CA) was measured with a contact angle measuring instrument JC2000D. Inductively Coupled Plasma Optical Emission spectrometric (ICP-OES) measurements for quantification of Zn and Ni contents were conducted with a HORIBA Jobin Yvon Ultima2. Thermogravimetric analyses (TG) was conducted with a Netzsch STA449F3 instrument with an Al₂O₃ crucible at a heating rate of 10 °C/min under nitrogen atmosphere. The enantiomeric excess test of styrene carbonate was determined by chiral HPLC analysis using an Agilent 1150 HPLC.

2. Synthesis of the ligand and MOF.

The H₂L ligand was synthesized following the route in Scheme S1.



Scheme S1. Synthesis of H₂L (**7**) Ligand.

3-(tert-butyl)-2-hydroxybenzaldehyde (1). Anhydrous magnesium dichloride (4.76 g, 50 mmol), 2-tert-butylphenol (3.76 g, 25 mmol), paraformaldehyde (2.25 g, 75 mmol) and anhydrous tetrahydrofuran (120 mL) were added subsequently to a dry, nitrogen-protected, 250 mL three-neck round-bottom flask with a slight positive pressure maintained over the addition process. Triethylamine (5.06 g, 50 mmol) was added dropwise by syringe when the mixture was stirred vigorously. After addition, the mixture was heated to 75 °C for 4 h, which turned bright light-yellow color. After cooling down, 100 mL of ether was added to the reaction mixture, which was subsequently washed with 1N HCl (aq) (3 × 50 mL) and water (3 × 50 mL). The organic layer was dried over anhydrous MgSO₄ and the solvent removed on rotavapor. The resulting crude product was purified by column chromatography (10% EtOAc/PE) to give **1** as a yellow oil (3.78 g, 85%). ¹H NMR (400 MHz, CDCl₃) δ 11.79 (s, 1H), 9.88 (s, 1H), 7.53 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.40 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.95 (dd, *J* = 9.5, 5.9 Hz, 1H), 1.43 (s, 9H).

5-Bromo-3-tert-butyl-2-hydroxybenzaldehyde (2). Compound **2** was synthesized according to literature procedure.¹ To a solution of compound **1** (5.0 g, 28.0 mmol) in 20 mL dichloromethane (DCM) at 0 °C was added dropwise a solution of Br₂ (1.45 mL, 28.0 mmol) in DCM (15 mL) over a period of 30 min. After the addition was complete,

the mixture was stirred for an additional 1 h before the organic volatiles were removed under reduced pressure. The crude product was purified by column chromatography (5% EtOAc/PE) to yield **2** as yellowish solid (7.00 g, 97 %). ¹H NMR (400 MHz, CDCl₃) δ 11.73 (s, 1H), 9.81 (s, 1H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 2.5 Hz, 1H), 1.40 (s, 9H).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-trityl-pyrazole (3). Compound **3** was synthesized according to literature procedure.² 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (8.0 g, 41.2 mmol) was dissolved in 80 mL of DCM and the mixture was added to a dried 200 mL three-neck round bottom flask equipped with a stirring bar and a reflux condenser. Et₃N (8.0 mL) was then added dropwise to the reaction mixture. The mixture was heated to reflux, and cautiously stirred for 30 min to give a clear colorless solution. Tritylchloride (11.2 g, 40.4 mmol) was added to the solution and the reaction was proceeded for another 2 h. The reaction mixture was then cooled to room temperature, poured over 100 mL of ice water and extracted with DCM (3 × 100 mL). The organic layer was collected and dried over anhydrous MgSO₄. The solvents were removed by rotary evaporation to give compound **3** (16.18 g, 90.0%). ¹H NMR (400 MHz, CDCl₃): δ 7.69 (s, 1H), 7.43 (s, 1H), 7.32 (m, 9H), 7.14 (m, 6H), 1.20 (s, 12H).

3-(tert-butyl)-2-hydroxy-5-(1-trityl-1H-pyrazol-4-yl)benzaldehyde (4). Compound **2** (7.2 g, 28 mmol) and compound **3** (15.3 g, 35 mmol) were dissolved in 200 mL of 1,4-dioxane and 20 ml H₂O, and the solution was degassed with nitrogen for 15 min. PPh₃ (0.33 g, 1.25 mmol), Pd(PPh₃)₄ (1.45 g, 1.25 mmol) and K₃PO₄ (5.84 g, 27.5 mmol) were then added to the solution with a slight positive pressure of nitrogen maintained. The mixture was heated to reflux for 3 days under nitrogen atmosphere. After that, the reaction mixture was cooled to room temperature. The resulting mixture was extracted with DCM (5 × 100 mL), and the organic layer was collected, dried over anhydrous MgSO₄ and concentrated on a rotavapor. The crude product was purified by column chromatography (15% EtOAc/PE) to yield **4** (9.13g, 67%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 11.70 (s, 1H), 9.85 (s, 1H), 7.89 (s, 1H), 7.59 – 7.55 (m, 2H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.36 – 7.31 (m, 9H), 7.21 (dt, *J* = 6.7, 3.9 Hz, 6H), 1.42 (s, 9H).

3-(tert-butyl)-2-hydroxy-5-(1H-pyrazol-4-yl)benzaldehyde (5). Compound **4** (486.62 mg, 1 mmol) was suspended in 15 mL of DCM/MeOH (1:1) mixed solvent. 5 ml of 2 N HCl (aq) was slowly added to the suspension, and the resulting mixture was

stirred at 45 °C for 6 h. The reaction mixture was then cooled down, neutralized by NH_4OH to $\text{pH} = 7$, and extracted with DCM ($3 \times 50 \text{ mL}$). The organic layer was collected and dried with anhydrous MgSO_4 , then concentrated in vacuo. The solid residue was dissolved in a small amount of DCM and purified by column chromatography (DCM to DCM/MeOH 10:1) to yield **5** (219.9 mg, 90%) as a yellow solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 11.73 (br s, 1H), 9.92 (s, 1H), 7.85 (s, 2H), 7.65 (d, $J = 2.0 \text{ Hz}$, 1H), 7.50 (d, $J = 2.0 \text{ Hz}$, 1H), 1.46 (s, 9H).

6,6'-((1E,1'E)-(ethane-1,2-diylbis(azaneylylidene))bis(methaneylylidene))bis(2-(tert-butyl)-4-(1H-pyrazol-4-yl)phenol) (6). Compound **5** (0.489 g, 2 mmol) was dissolved in 125 mL of ethanol and heated to reflux with stirring for an hour. Ethylenediamine (140 μL , 1 mmol) was added to the solution in a dropwise fashion, and the resulting mixture was heated for another 4 h. After reaction, the solvent was removed by filtrating and the product **6** (487 mg, 0.95 mmol, 95%) was obtained as yellow solid. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 14.16 (s, 1H), 12.84 (s, 1H), 8.61 (s, 1H), 8.03 (s, 1H), 7.79 (s, 1H), 7.48 (d, $J = 2.0 \text{ Hz}$, 1H), 7.44 (d, $J = 2.0 \text{ Hz}$, 1H), 3.96 (s, 2H), 1.39 (s, 9H).

H₂L (7). A solution of compound **6** (512.66 mg, 1 mmol) in 100 ml ethanol was heated to reflux for an hour. $\text{Ni}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ (290 mg, 1 mmol) was added to the solution and the reaction mixture was refluxed for another 4 h. After reaction, the mixture was cooled to room temperature and filtrated to give **7** (518 mg, 0.91 mmol, 91%) as dark yellow solid. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 12.77 (s, 1H), 7.88 (s, 2H), 7.75 (br s, 1H), 7.32 (d, $J = 4.0 \text{ Hz}$, 2H), 3.42 (s, 2H), 1.36 (s, 9H).

Zn₉O₂(OH)₂(L)₆. Compound **H₂L** (15 mg) and $\text{Zn}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ (90 mg) were dissolved in 15 mL $\text{DMF}/\text{H}_2\text{O}$ ($v:v = 3:2$) mix solvent and sealed in a 20 ml glass bottle and then heated at 110°C for 72 h in an oven. The dark red octahedral crystals of **Zn₉O₂(OH)₂(L)₆** were collected by filtration after cooling down, washed with DMF, H_2O , and EtOH subsequently, and dried in air (yield: 70% based on **H₂L**).

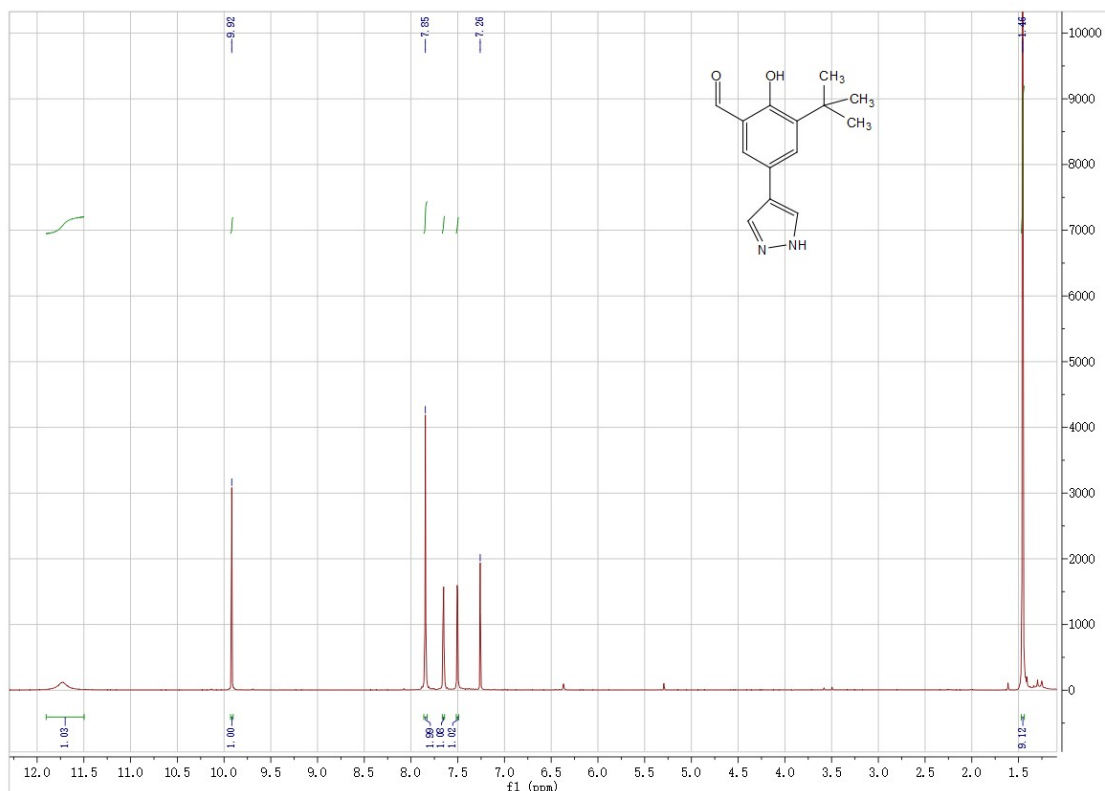


Figure S1. ^1H NMR (400 MHz, CDCl_3) of compound 5.

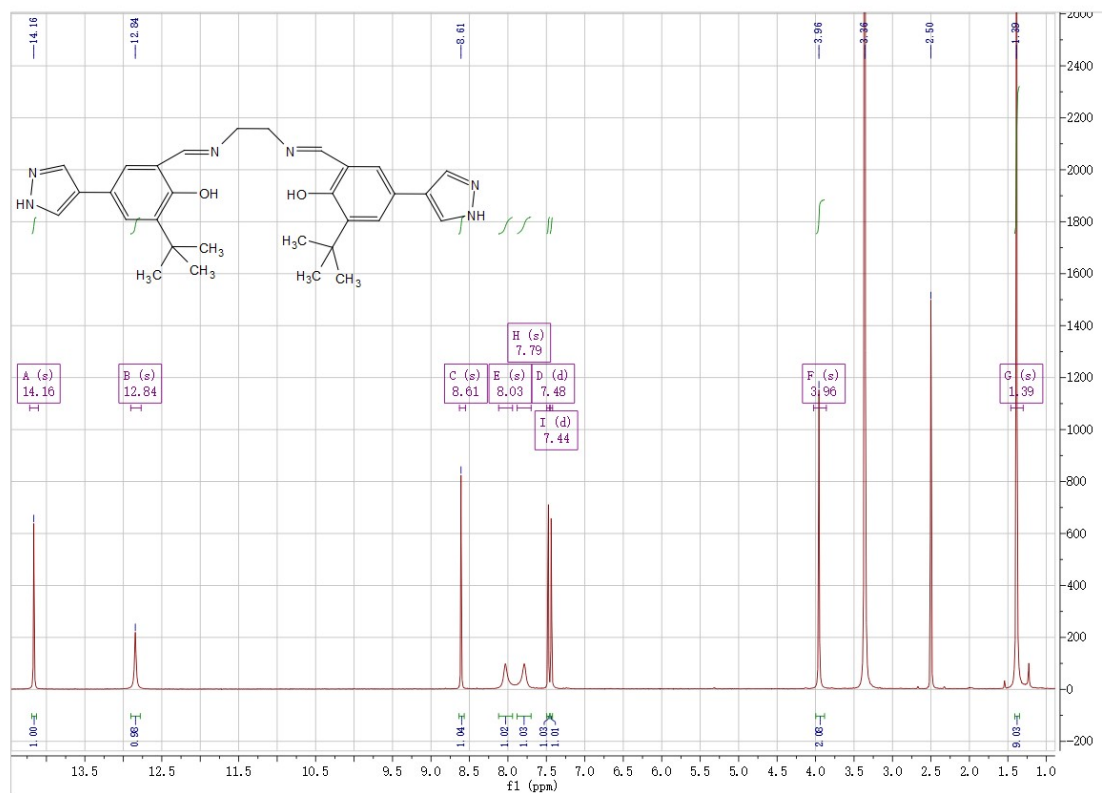


Figure S2. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) of compound 6.

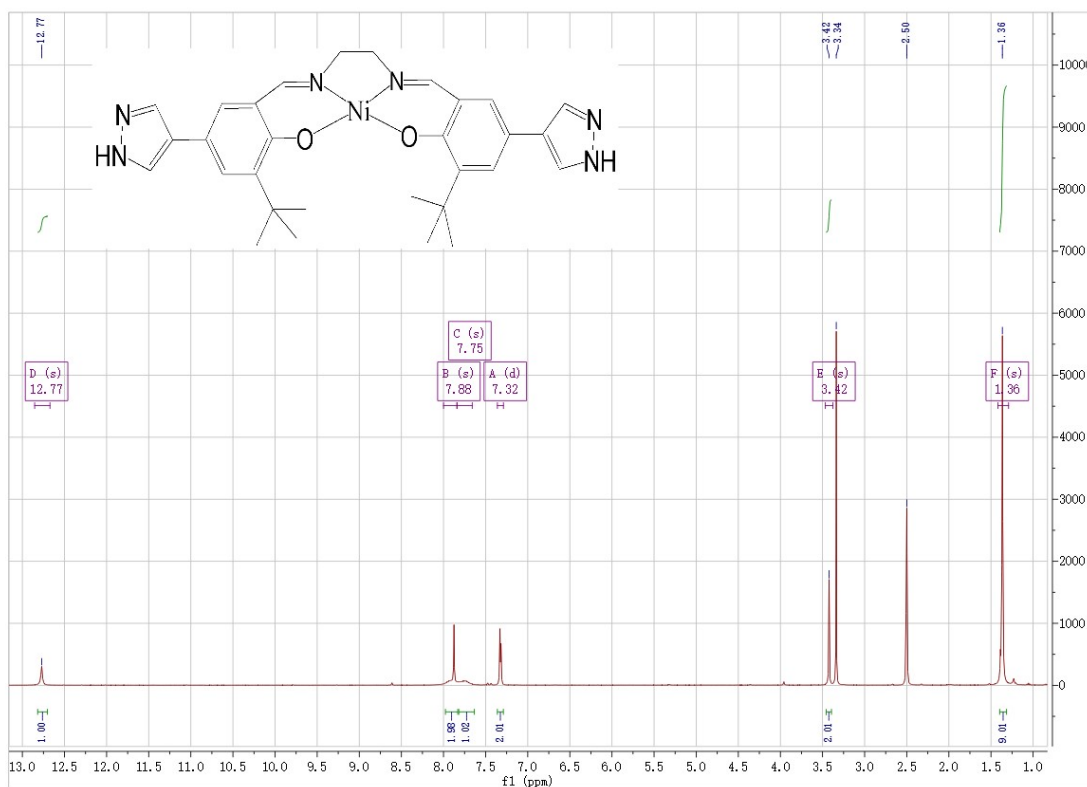


Figure S3. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) of compound **7** (H_2L).

3. Single crystal X-ray crystallography.

Single crystal X-ray diffraction of MOF was performed with a BRUKER D8 VENTURE equipped with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at room temperature. The frames were integrated with the Bruker SAINT© build in APEX III software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS. Structures were solved by intrinsic phasing and refined to convergence by least squares method on F^2 using the SHELX-2019 software suite. Scattering from the highly disorder guest molecules was modelled by the SQUEEZE program in PLATON software suite.^{3,4} All non-hydrogen atoms are refined anisotropically.

Table S1. Crystallographic data of $\text{Zn}_9\text{O}_2(\text{OH})_2(\text{L})_6$

Name	$\text{Zn}_9\text{O}_2(\text{OH})_2(\text{L})_6$
Empirical Formula	$\text{C}_{180}\text{H}_{192}\text{N}_{36}\text{Ni}_6\text{O}_{16}\text{Zn}_9$
Formula weight	4056.27
Temperature (K)	293(2)
Crystal system	cubic
Space group	$F\bar{4}32$
a (Å)	37.2420(3)

b (Å)	37.2420(3)
c (Å)	37.2420(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å ³)	51653.4(12)
Z	8
Density (calcd. g/cm ³)	1.043
Wavelength (Å)	1.54178
Absorption coeff. (mm ⁻¹)	1.74
F(000)	16720
θ range data collection	3.937–72.506°
Limiting indices	-46 ≤ h ≤ 43, -42 ≤ k ≤ 41, -45 ≤ l ≤ 36
Reflection collected	32411
Independent reflections	4271
R(int)	0.0798
Data/restraints/parameters	4271/0/196
Goodness-of-fit on F^2	1.555
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1324$, $wR_2 = 0.3696$
R indices (all data)	$R_1 = 0.1609$, $wR_2 = 0.4030$

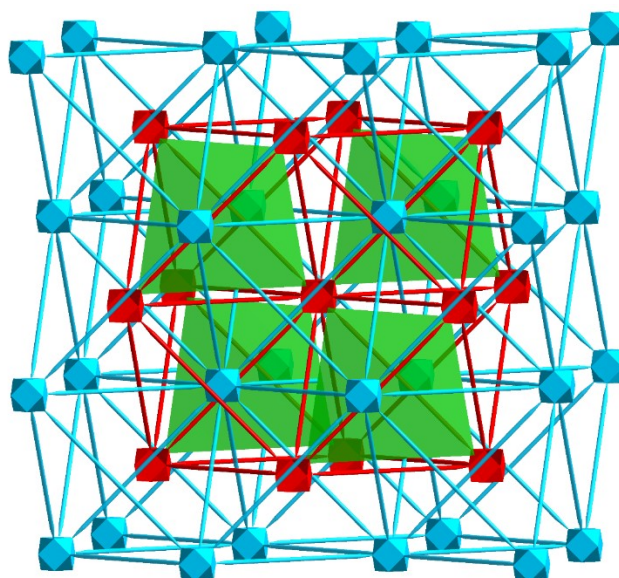


Figure S4. The Zn_9 cluster of one network locates in the tetrahedral cavity formed by the other network with 50% occupancy.

4. Characterization of the MOF.

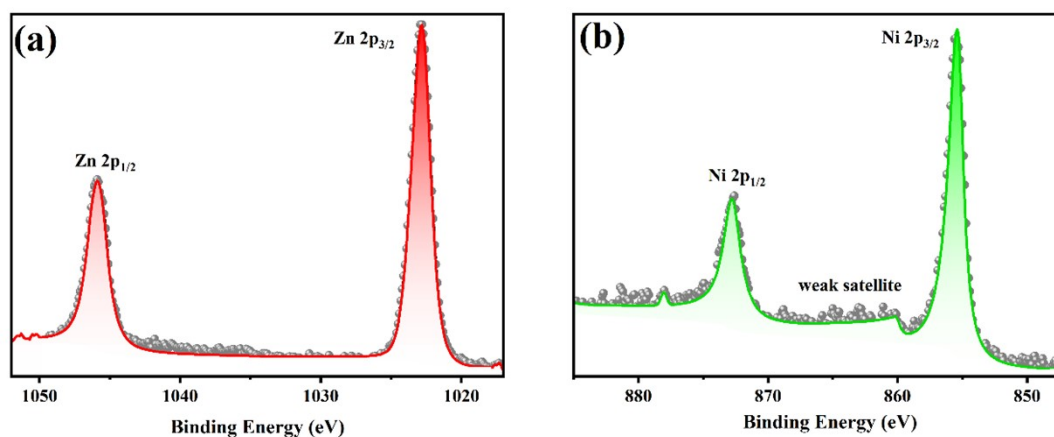


Figure S5. (a) Zn 2p and (b) Ni 2p XPS spectra of the MOF.

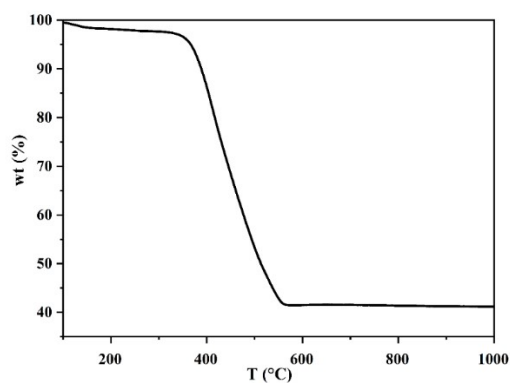


Figure S6. Thermogravimetric curves of Zn₉O₂(OH)₂(L)₆

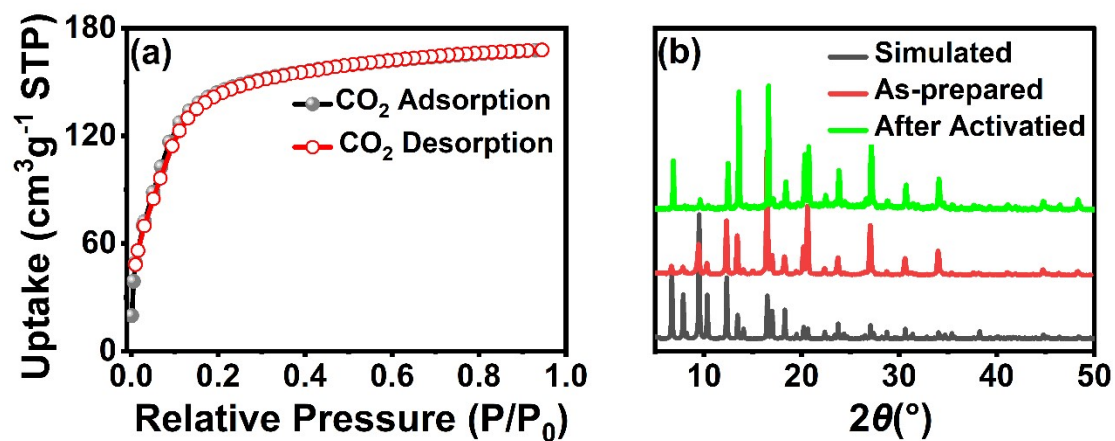


Figure S7. (a) CO₂ sorption isotherms of Zn₉O₂(OH)₂(L)₆ at 195 K; (b) PXRD patterns before and after N₂ and CO₂ adsorption/desorption test of Zn₉O₂(OH)₂(L)₆.

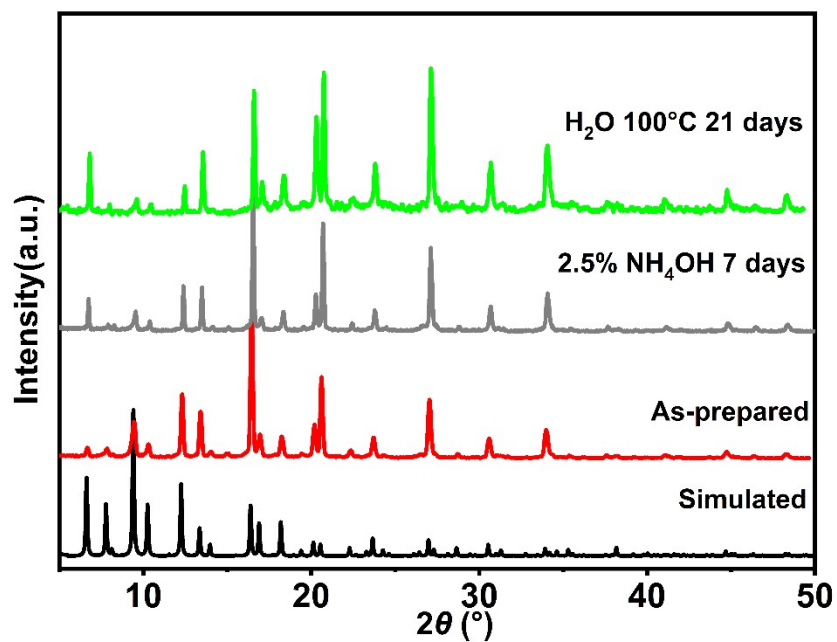


Figure S8. PXRD patterns of $\text{Zn}_9\text{O}_2(\text{OH})_2(\text{L})_6$ after ammonia and boiling water treatments.

CA-113.95

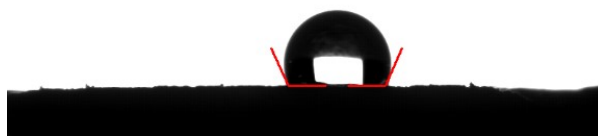


Figure S9. Test of the water contact angle of $\text{Zn}_9\text{O}_2(\text{OH})_2(\text{L})_6$ (CA=113.95°).

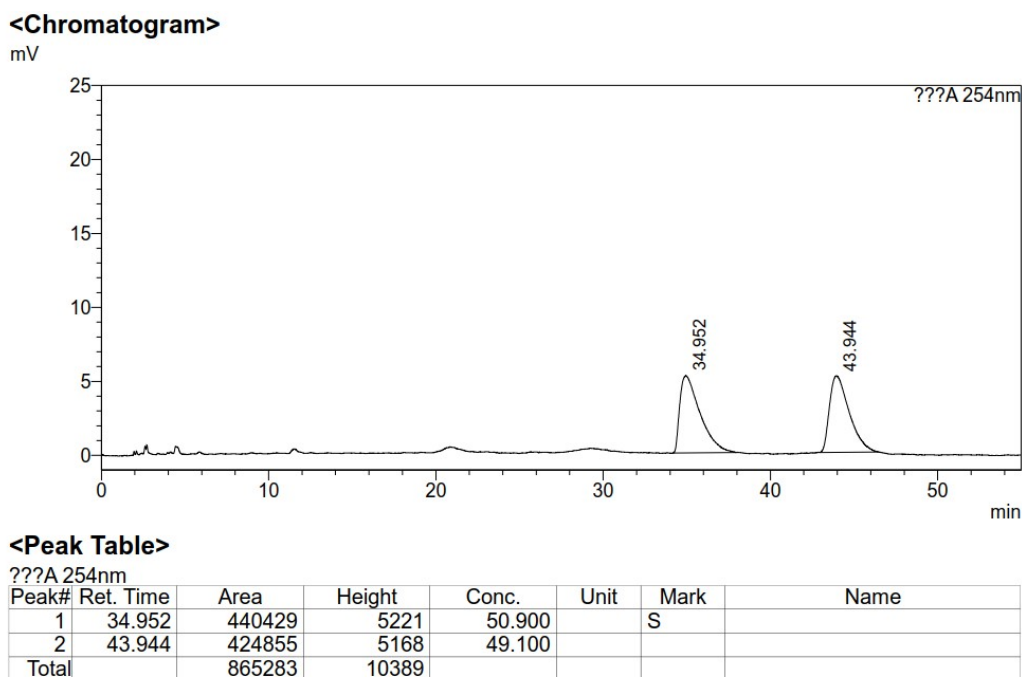


Figure S10. The ee test of styrene carbonate. HPLC analysis:0 ee. (Chiralcel OD-H, 2:98 *i*PrOH/Hexane, 1.0 ml/min, 40 °C, 254 nm)

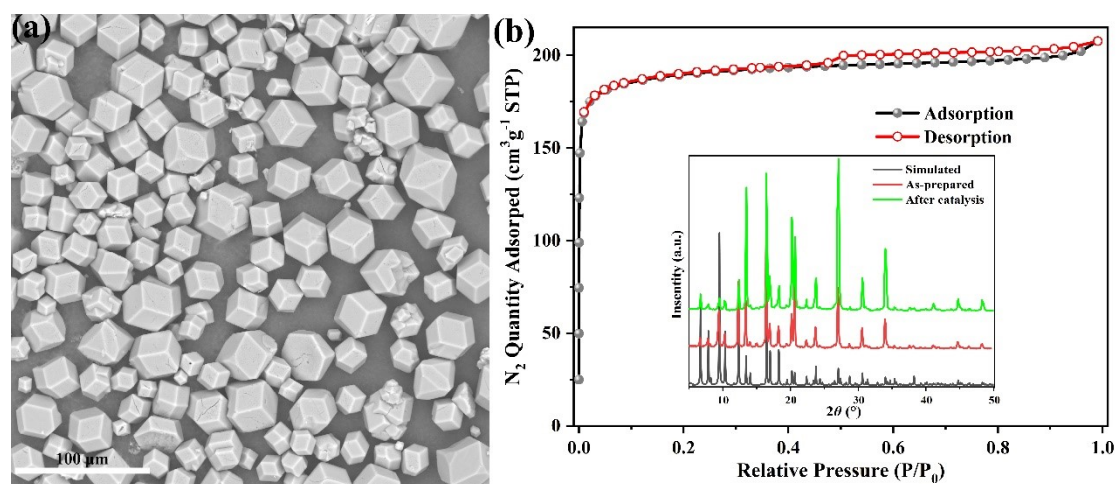


Figure S11. (a) SEM of MOF after catalysis; (b) N₂ adsorption/desorption test for MOF after catalysis (inset: PXRD patterns of MOF after catalysis)

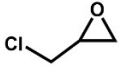
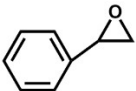
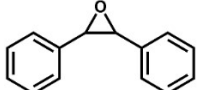
Table S2. The content of Zn and Ni in different solutions after 210 days chemical stability experiments of $Zn_9O_2(OH)_2(L)_6$.

$Zn_9O_2(OH)_2(L)_6$	solution	Zn (mg/L)	Ni (mg/L)
10 mg	2 M NaOH 1.5 ml	42.7	6.13
10 mg	pH 2 HCl 1.5 ml	0.56	14.66
10 mg	2.5% NH ₄ OH 1.5 ml	27.8	1.42

Table S3. The chemical stability of pyrazolate-based MOFs in literature reports.

MOF	Chemical stability test	Reference
α -[Zn(BPEB)]	pH 6-8 (8 h)	5
BUT-31	BUT-31 is not stable in acidic conditions.	6
$Zn_3(BTP)_2 \cdot 4CH_3OH \cdot 2H_2O$	pH 14 (0.5 h)	7
NiBDP-NH ₂	pH = 13	8
NiBDP-AgS	pH = 2-13	
PCF-9	pH = 3-12 (24 h)	9
NiL1	pH 3 HCl, 10 M NaOH (24 h)	10
$[Ni_8(OH)_4(OH)_2(4,4'-(buta-1,3-diyne-1,4-diyl)bispyrazolato)_6]_n$	pH = 2.3-12.80 (7 days)	11
PCN-601	0.1 mM HCl s-NaOH (24 h)	12
PCN-602	pH 4-14 (24 h)	2
PCN-624	1 M HCl (24 h)	13
BUT-32		
BUT-33	pH 3 HCl, 4 M NaOH (24 h)	14
BUT-48		
BUT-49	pH 5 HCl, 1 M NaOH (24 h)	15
BUT-123		
$Co_3(PCBA)_2(H_2O)_2$	pH 3-12 (24 h)	16
$Zn_9O_2(OH)_2(L)_6$	pH 2-14 (210 days)	this work

Table S4. CO₂ cycloaddition reactions with epoxide substrates of different sizes.

Entry	Substrate	Conversion (%)	Yield (%)
1		92	89
2		31	30
3		15	9

Reaction conditions: 1 mmol epoxides, 0.5 mol% $Zn_9O_2(OH)_2(L)_6$ MOF, 0.5 mol% TBAB, 5 ml THF, 24 h, 80 °C, 7 atm. Yields were determined by ¹H NMR.

Table S5. Catalytic performances of $\text{Zn}_9\text{O}_2(\text{OH})_2(\text{L})_6$ and other catalysts for the cycloaddition reaction of CO_2 with cyclohexene oxide

Catalysts	co-catalysts	Time (h)	T (°C)	P (atm)	Yield (%)	References
$\text{Zn}_4\text{Tb}_3\text{L}_4$ 50 mol%	TBAB 0.75 mmol%	8	120	10	37	17
Ni(Salen)-MOF 0.5 mol%	TBAB 0.5 mol%	12	80	10	68	18
SH4-Al(Cl) 0.25 mol%	$[\text{ClC}_6\text{Im}][\text{HCO}_3]$ 0.25 mol%	24	80	10	73	19
$\text{C}_{64}\text{H}_{52}\text{Ba}_3\text{N}_2\text{O}_{16}$ 1 mol%	TBAB 10 mol%	4	80	1	68.1	20
JLU-MOF58 0.1 mol%	TBAB 5 mol%	24	80	1	92	21
Al complex 0.1 mol%	TBAB 1 mol%	18	70	10	61	22
Zn-MOF-184 1.2 mol%	TBAB 1.5 mol%	6	80	1	59	23
Zn-MOF-74 1.2 mol%	TBAB 1.5 mol%	6	80	1	38	23
[Gd60] 7.5 mol%	TBAB 2.5 mol%	12	60	1	38	24
$\text{C}_{117}\text{H}_{160}\text{Zn}_2\text{Dy}_2\text{N}_9\text{O}_{28}$ 0.01 mol%	TBAB 0.75 mol%	8	120	10	90	25
$\text{Zn}_9\text{O}_2(\text{OH})_2(\text{L})_6$ 1.5 mol%	TBAB 1.5 mol%	24	80	7	82	this work

Reference

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