Supporting Information

Reticular Chemistry Guided Single-Linker Constructed Pillar-Layered Metal-Organic Frameworks Via *In Situ* "One-Pot" Strategy

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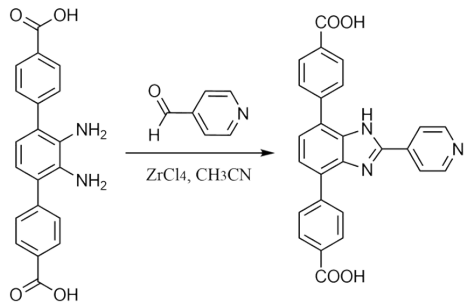
Chemicals

Isonicotinaldehyde and 4-(pyridin-4-yl)benzaldehyde were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 2',3'-diamino-[1,1':4',1"-terphenyl]-4,4"-dicarboxylic acid (H_2DATC) was synthesized according to our previous work.[1] All the other chemicals were obtained from the chemical supplies and used without further purification.

Characterization

Powder X-ray diffraction (PXRD) patterns were recorded using Bruker D8 Advance X-ray diffractometer. Single crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer. Nuclear magnetic resonance (NMR) data was collected using 400 MHz JEOL JNM-ECZ400S. The photoluminescent spectra were measured on FLS1000 spectrofluorometer (Edinburgh Instruments). The UV-vis spectra were recorded on Shimadzu UV-3600 spectrophotometer. The TGA data was collected using TGA 550 (TA Instruments) analyzer and the samples were heated from room temperature to 600°C at a ramp rate of 10°C / min.

Synthesis of 4,4'-(2-(pyridin-4-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoic acid (H_2PBIA)



2',3'-diamino-[1,1':4',1"-terphenyl]-4,4"-dicarboxylic acid (2.0 mmol, 0.70 g), isonicotinaldehyde (2.1 mmol, 0.22 g) and $ZrCl_4$ (0.20 mmol, 46.6 mg) were added into a flask containing 30 mL CH_3CN. The mixture was stirred at room temperature for 24 h under N_2 atmosphere. Then 4,4'-(2-(pyridin-4-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoic acids (H_2PBIA) was obtained after filtration (0.79 g, yield: 90.8%). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 8.84 (2H), 8.47 (2H), 7.09 (8H), 7.62 (2H).

Synthesis of HIAM-3016-op

$Zn(NO_3)_2 \cdot 6H_2O$ (0.17 mmol, 49.4 mg), H_2DATC (0.075 mmol, 26.1 mg) and isonicotinaldehyde (0.077 mmol, 8.2 mg) were added into a 5 mL vial containing 3 mL DMF. After sonicating for 5 minutes, the capped vial was put in a pre-heated oven to react at 100 °C for 3 days. The obtained single crystals were washed with DMF (1 mL) several times to remove unreacted organic linkers.

Synthesis of HIAM-3016

$Zn(NO_3)_2 \cdot 6H_2O$ (0.2 mmol, 59.4 mg) and H_2PBIA (0.075 mmol, 33.0 mg) were added into a 5 mL vial containing 3 mL DMF. After sonicating for 5 minutes, the capped vial was put in a pre-heated oven to react at 100 °C for 3 days. The obtained single crystals were washed with DMF (1 mL) several times to remove unreacted ligand.

Synthesis of HIAM-3017-op

$Zn(NO_3)_2 \cdot 6H_2O$ (0.17 mmol, 49.4 mg) and H_2DATC (0.075 mmol, 26.1 mg) and 4-(pyridin-4-yl)benzaldehyde (0.077 mmol, 14 mg) were added into a 5 mL vial containing 3 mL DMF. After sonicating for 5 minutes, the capped vial was put in a pre-heated oven to react at 100 °C for 3 days. The obtained single crystals were washed with DMF (1 mL) several times to remove unreacted organic linkers.

Digestion Procedure of Zn-MOFs for ^{1}H NMR measurement

10 mg as-synthesized HIAM-3016-op were washed several times using DMF, then the collected solid samples in 5 mL vials were put into one 150 ℃ oven overnight. After cooling down to room temperature, 500 uL 10 M NaOH/D_2O solution was added into the vial by sonication for 5 mins and standing for 5 h. The D_2O layer was used for ^{1}H NMR measurement. 10 mg as-synthesized HIAM-3017-op were washed several times using DMF, then the collected solid samples in 5 mL vials were put into one 150 ℃ oven overnight. After cooling down to room temperature, 100 uL 10 M NaOH solution was added into the vial, which were put into one 100 ℃ oven for 4 hours. Then 100 uL concentrated HCl was added, which were put into one 100 ℃ oven for 4 hours. Then 800 uL DMSO-d_6 was added to dissolve the digested sample. After filtering, the solution of DMSO-d_6 containing linkers was used for the ^{1}H NMR measurement.

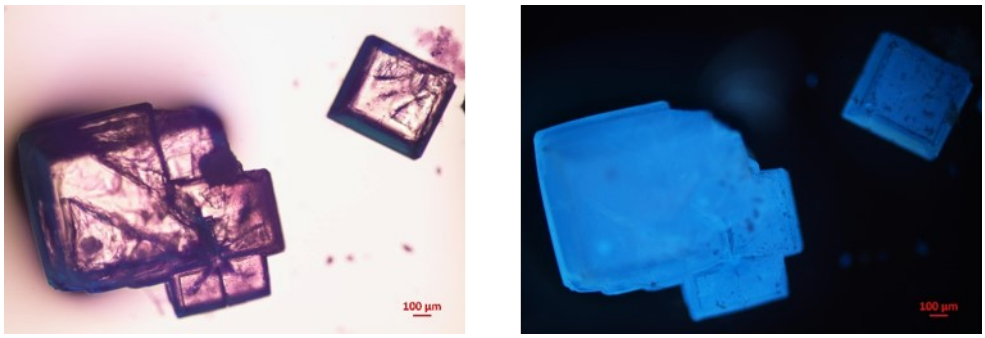


Figure S1. The single-crystal images of HIAM-3016-op under daylight (left) and 365 nm excitation (right).

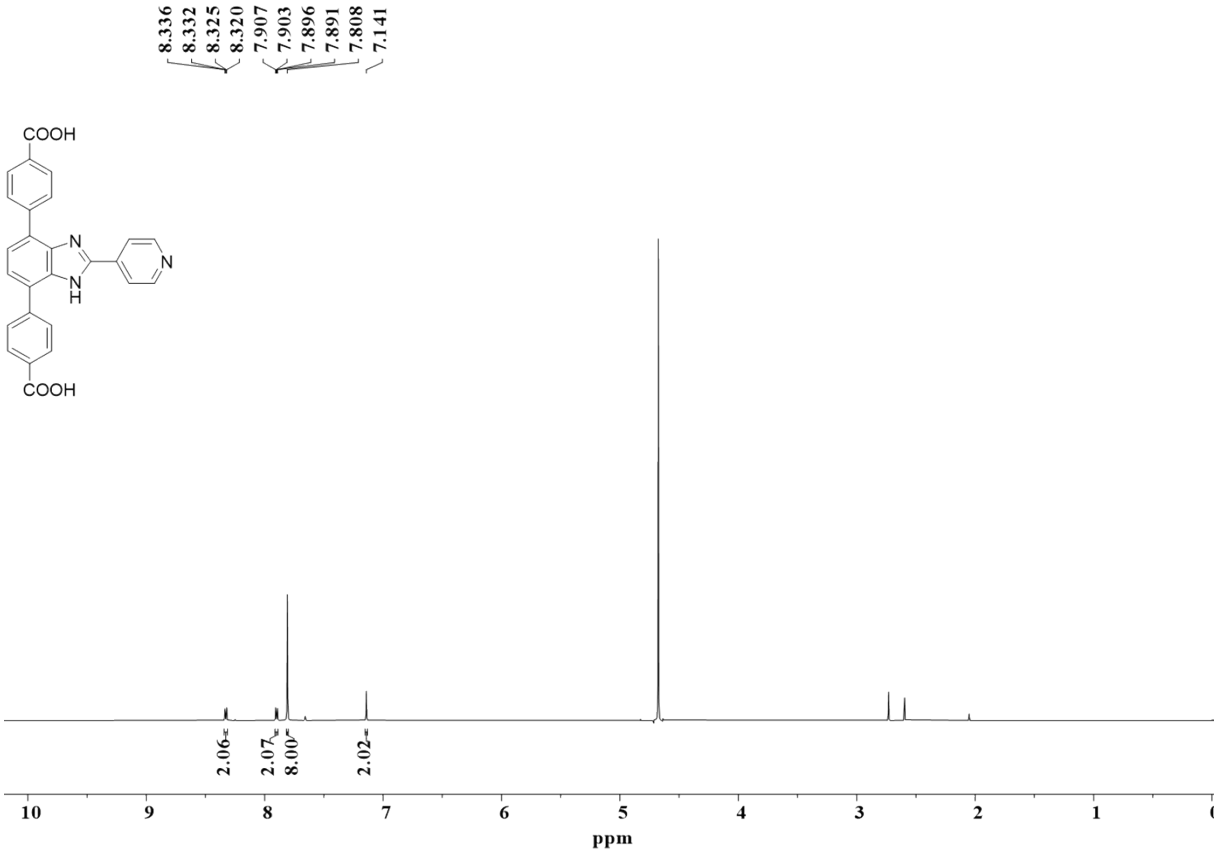


Figure S2. The ^{1}H NMR spectrum of digested HIAM-3016-op in D_2O and the molecular structure of H_2PBIA.

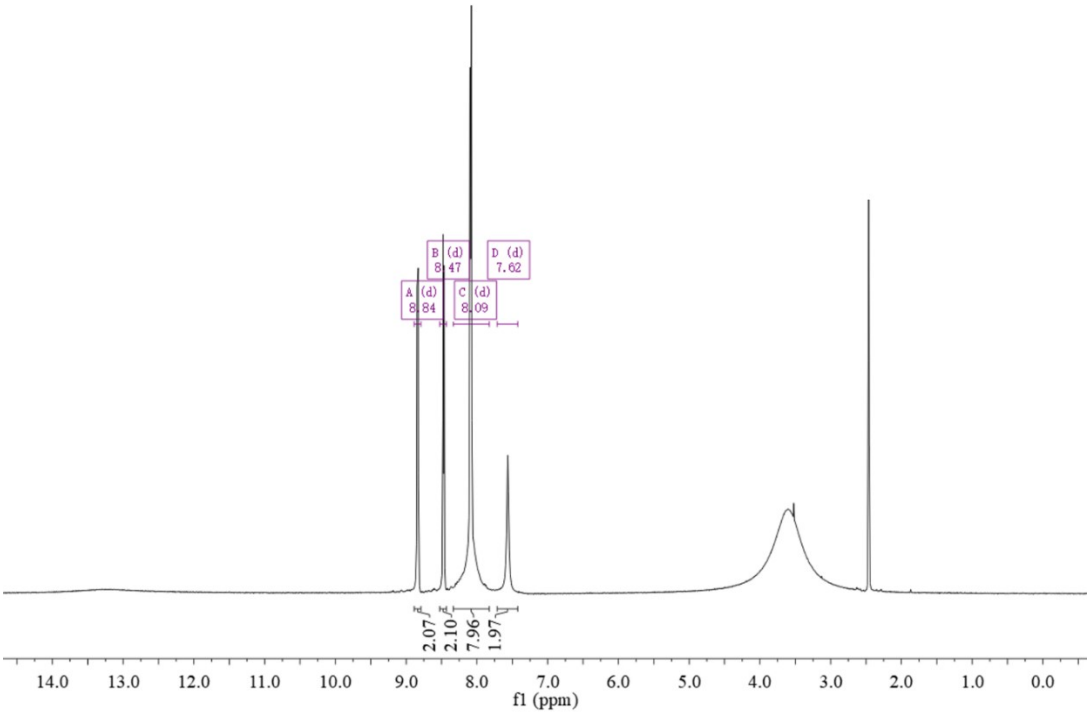


Figure S3. ^{1}H NMR spectrum of directly synthesized H_2PBIA in DMSO-d_6.

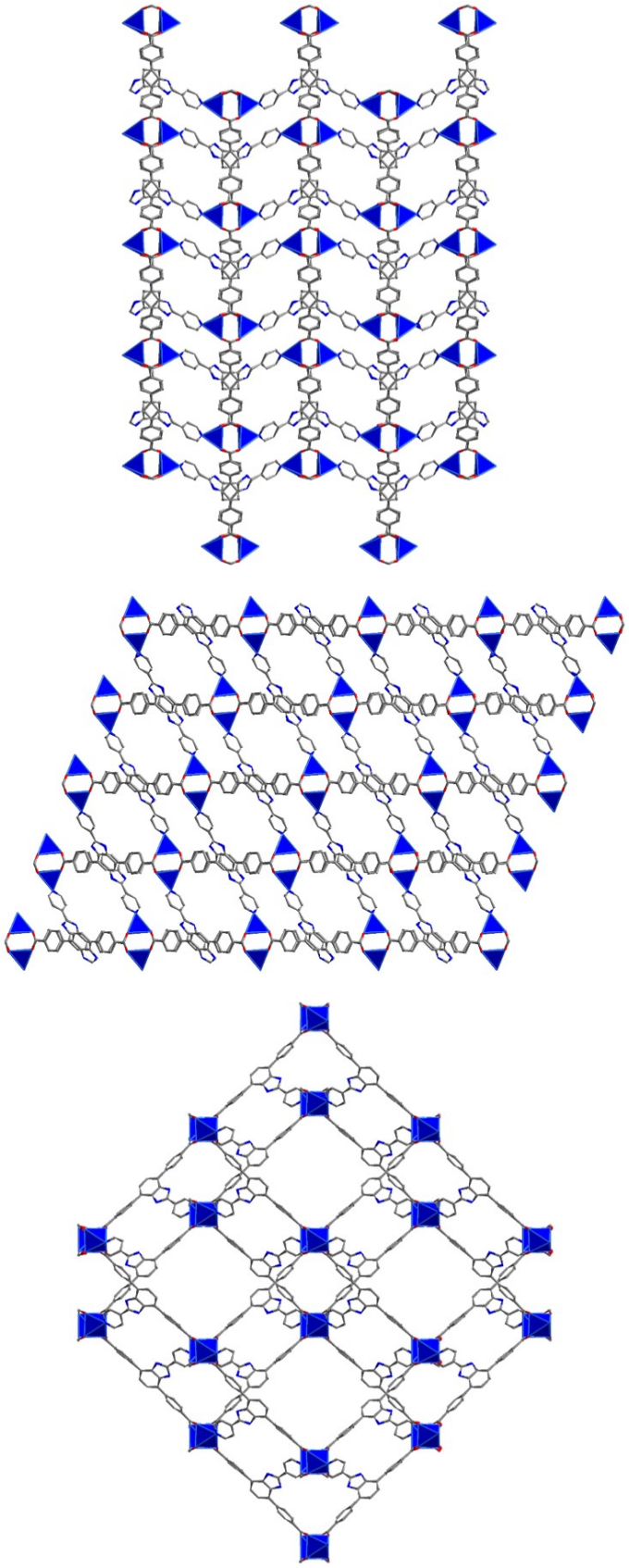


Figure S4. The single crystal structure of HIAM-3016-op viewed along a (above), b (middle) and c (below) axis.

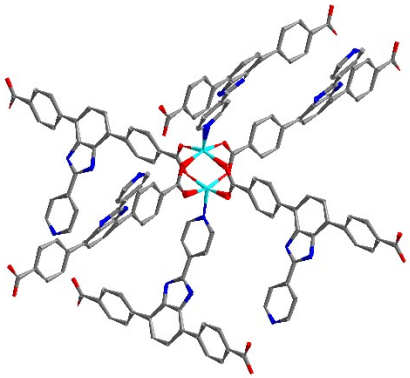


Figure S5. The coordination condition of paddle-wheel $Zn_2(COO)_4$ in HIAM-3016-op.

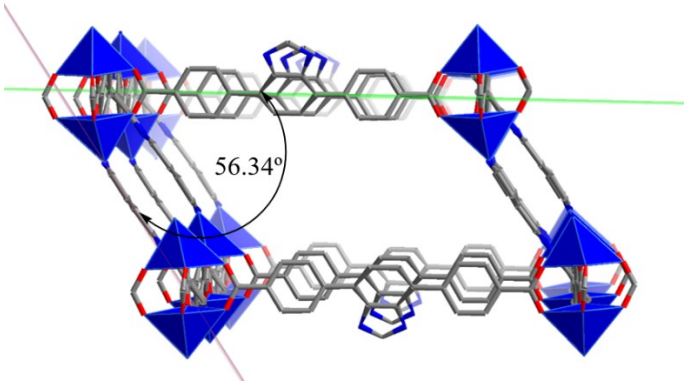


Figure S6. The angle between the 2D layer and the pillar in HIAM-3016-op.

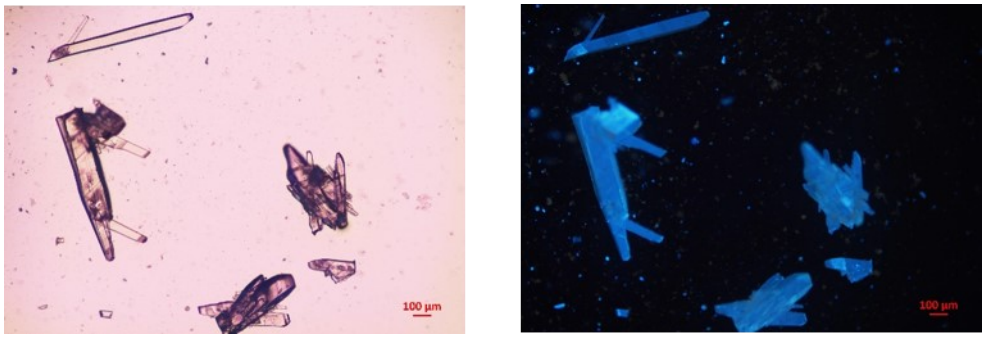


Figure S7. The single-crystal images of HIAM-3017-op under daylight (left) and 365 nm excitation (right).

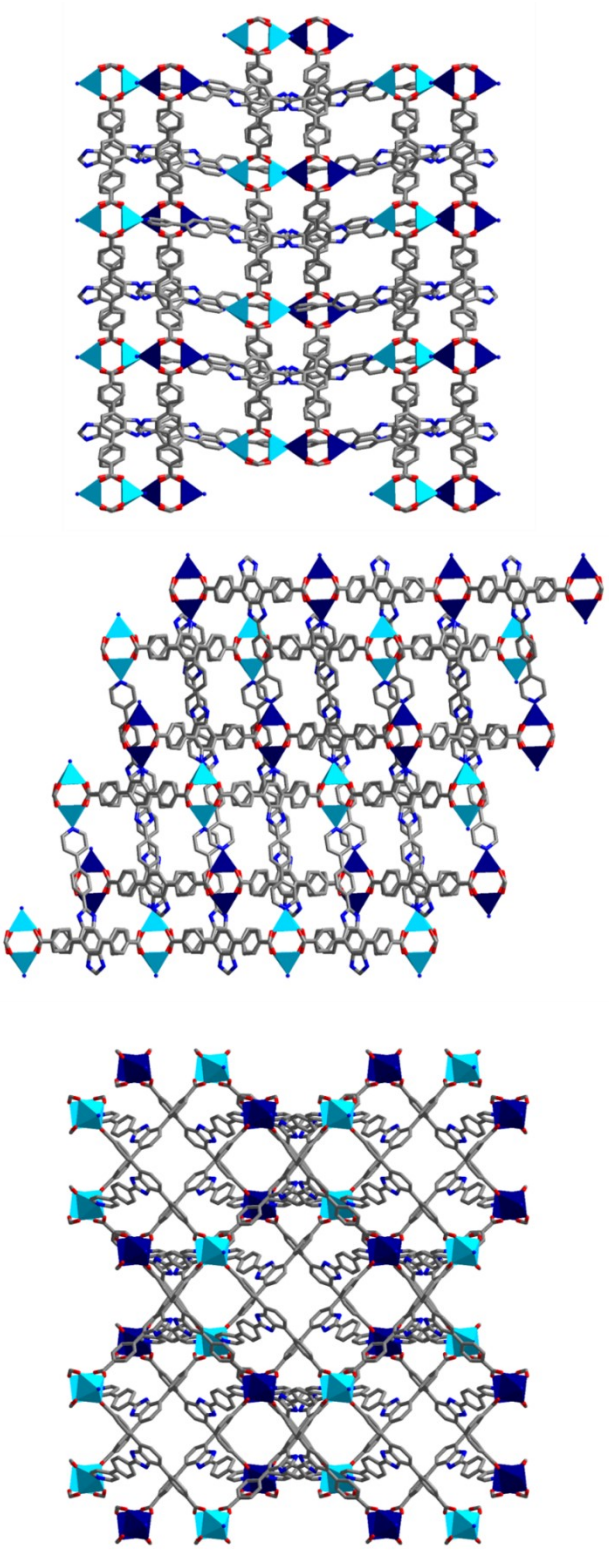


Figure S8. The single crystal structure of HIAM-3017-op viewed along a (above), b (middle) and c (below) axis.

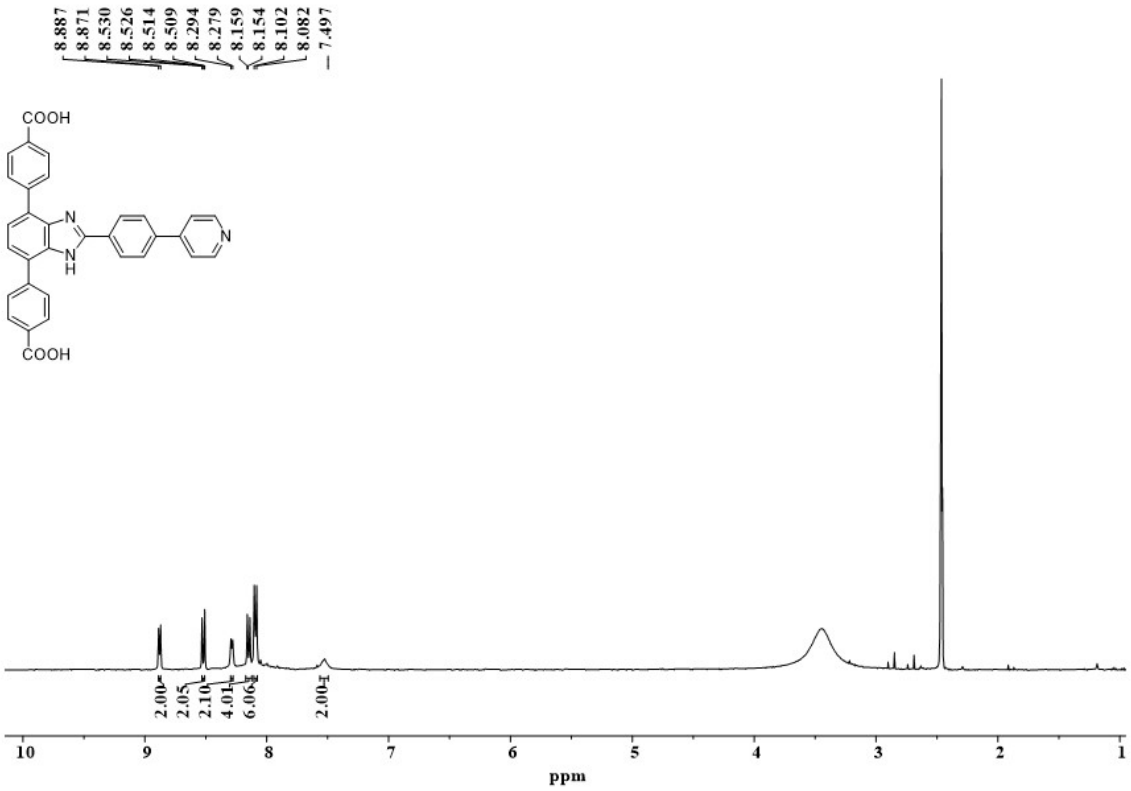


Figure S9. The ^{1}H NMR spectrum of digested HIAM-3017-op in D_2O and the molecular structure of H_2PPBIA.

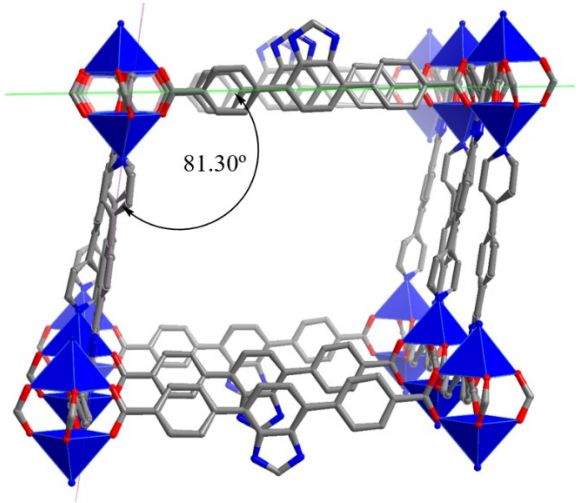


Figure S10. The angle between the 2D layer and the pillar in HIAM-3017-op.

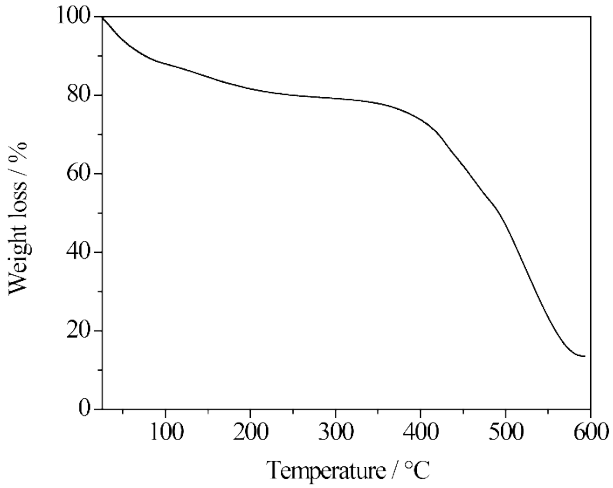


Figure S11. TGA curve of HIAM-3016-op.

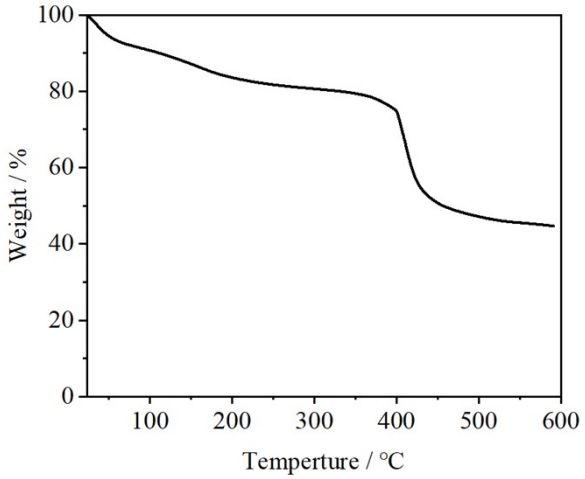


Figure S12. TGA curve of HIAM-3017-op.

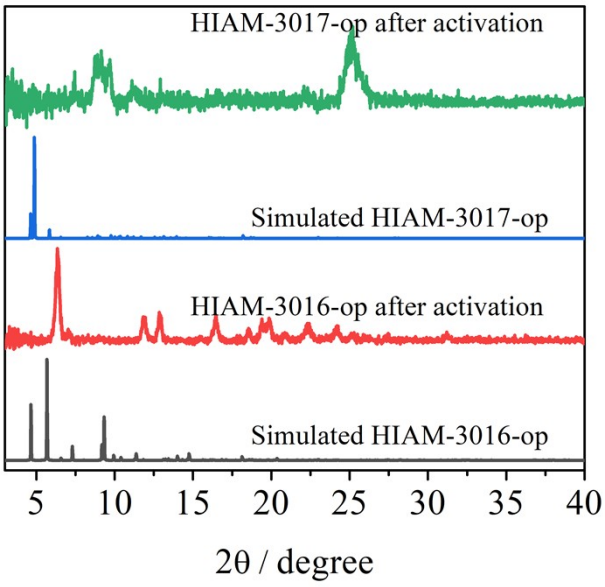


Figure S13. The PXRD patterns of HIAM-3016-op and HIAM-3017-op after activated using supercritical CO_2.

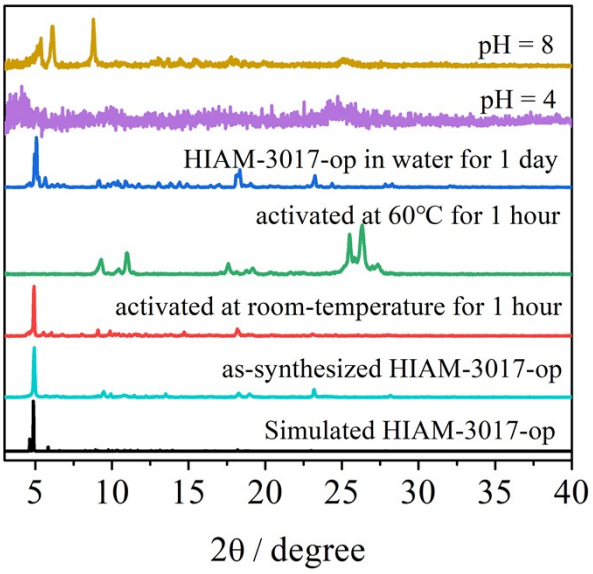


Figure S14. The PXRD patterns of HIAM-3017-op after treated under various conditions.

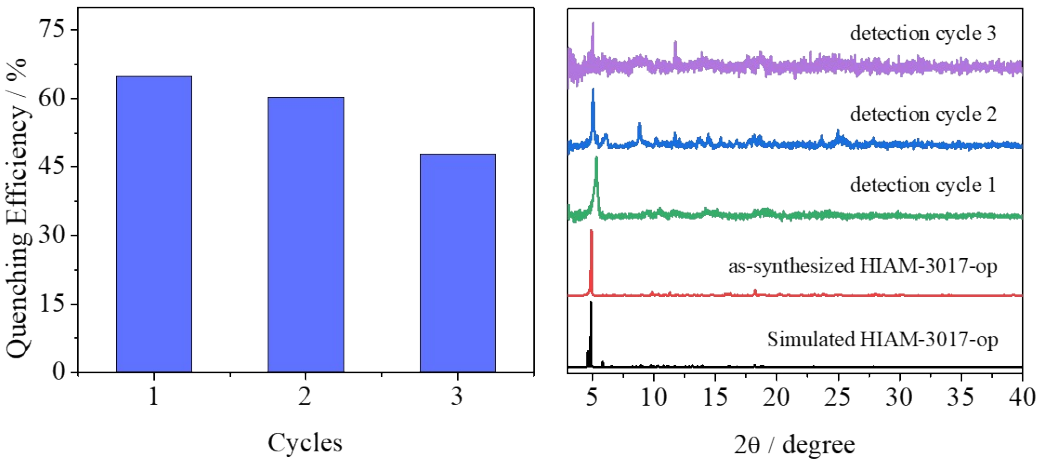


Figure S15. The quenching efficiencies of HIAM-3017-op for three cycles (left) and corresponding PXRD patterns of HIAM-3017-op after each cycle (right).

Table S1. Crystal data and structure refinement parameters for HIAM-3016-op.

CCDC No.	2354184	
Empirical formula	C26 H15N3O4Zn	
Formula weight	498.78	
Temperature	193 K	
Wavelength	1.34139 Å	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 28.486(6) Å	α = 90°
	b = 26.892(6) Å	β = 110.239(12)°
	c = 20.509(5) Å	γ = 90°
Volume	14741 (6) $Å^3$	
Z	8	
Density (calculated)	0.449 g/cm^3	
Absorption coefficient	0.368 mm^{-1}	
F(000)	2031	
Crystal size	0.2 x 0.1 x 0.1 mm^3	
Theta range for data collection	4.06 to 105.91°	
Index ranges	-33<=h<=31, -31<=k<=31, 0<=l<=24	
Reflections collected	24396	
Independent reflections	24396[R(int) = 0.1055, R(sigma) = 0.0966]	
Data / restraints / parameters	24396/3/311	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.1010, wR2 = 0.2403	
R indices (all data)	R1 = 0.1699, wR2 = 0.2871	
Largest diff. peak and hole	0.44 and -0.90 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement parameters for HIAM-3016.

CCDC No.	2368472	
Empirical formula	$C_{32}H_{29}N_5O_6Zn$	
Formula weight	644.97	
Temperature	193 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 28.630(2) Å	α = 90°
	b = 26.8008(19) Å	β = 109.961(2)°
	c = 20.3644(16) Å	γ = 90°
Volume	14686.9(19) $Å^3$	
Z	8	
Density (calculated)	0.583 g/m^3	
Absorption coefficient	0.356 mm^{-1}	
F(000)	2672.0	
Crystal size	0.13 x 0.12 x 0.1 mm^3	
Theta range for data collection	3.71 to 54.988°	
Index ranges	-37<=h<=37, -30<=k<=34, -26<=l<=23	
Reflections collected	67204	
Independent reflections	16814[R(int) = 0.0835, R(sigma) = 0.0850]	
Data / restraints / parameters	16814/48/449	
Goodness-of-fit on F^2	0.961	
Final R indices [I>2sigma(I)]	R1 = 0.0557, wR2 = 0.1498	
R indices (all data)	R1 = 0.0869, wR2 = 0.1642	
Largest diff. peak and hole	0.50 and -0.46 e.$Å^{-3}$	

Table S3. Crystal data and structure refinement parameters for HIAM-3017-op.

CCDC No.	2354185	
Empirical formula	C67H45N7O9Zn2	
Formula weight	1222.84	
Temperature	193 K	
Wavelength	1.34139 Å	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 27.145(7) Å	α = 90°
	b = 28.184(7) Å	β = 108.221(12)°
	c = 31.874(8) Å	γ = 90°
Volume	23162(10) $Å^3$	
Z	8	
Density (calculated)	0.701 g/cm^3	
Absorption coefficient	0.509 mm^{-1}	
F(000)	5024	
Crystal size	0.15 x 0.1 x 0.1 mm^3	
Theta range for data collection	4.04 to 106.98°	
Index ranges	-28<=h<=32, -33<=k<=33, -37<=l<=37	
Reflections collected	119774	
Independent reflections	20547[R(int) = 0.0675, R(sigma) = 0.0476]	
Data / restraints / parameters	20547/687/793	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.1406, wR2 = 0.3180	
R indices (all data)	R1 = 0.1549, wR2 = 0.3252	
Largest diff. peak and hole	1.74 and -1.60 $e.Å^{-3}$	

References

1. Han, C.-Q.; Wang, L.; Si, J.; Zhou, K.; Liu, X.-Y., Reticular Chemistry Directed “One-Pot” Strategy to in situ Construct Organic Linkers and Zirconium-Organic Frameworks. Small 2024, 20, 2402263.