

Supporting Information for

Preferential CO₂ Adsorption by an Ultra-Microporous Zinc-Aminotriazolato-Acetate MOF

Piyush Singh,^{a,b} Himan Dev Singh,^{a,b} Abhijith Hari Menon,^{a,b} and Ramanathan Vaidhyanathan^{a,b*}

^a Department of Chemistry, Indian Institute of Science Education and Research, Dr. Homi Bhabha Rd. Pashan, Pune, 411008. E-mail: vaidhya@iiserpune.ac.in (R.V.).

^b Centre for Energy Science, Indian Institute of Science Education and Research, Dr. Homi Bhabha Rd. Pashan, Pune, 411008. E-mail: vaidhya@iiserpune.ac.in (R.V.).

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1. Materials and methods:

All reagents and solvents were purchased from commercial source and used without further purification.

Single-crystal X-ray diffraction was done on a Bruker SMART APEX four-circle diffractometer equipped with a CMOS photon 100 detector and Micro focus ($1\mu\text{S}$) using a $\text{Cu-K}\alpha$ radiation.

Powder XRDs were done using a Rigaku Miniflex-600 instrument and processed using PDXL software. The Variable temperature powder X-ray diffraction (VT-PXRD) were carried out on a full fledged Bruker instrument using the in-built furnace and in air.

The infrared (IR) spectrum was recorded on a Nicolet FT-170SX instrument using KBr discs in the $400\text{--}4000\text{ cm}^{-1}$ region.

Field Emission Scanning Electron Microscopic (FESEM) study was done using Ultra Plus Field Emission Scanning Electron Microscope with integral charge compensator and embedded EsB and AsB detectors.

Thermogravimetry analysis of as made MOF was performed on NETSZCH TGA-DSC instrument. The routine TGAs were done under N_2 gas flow (20 ml/min) (purge + protective) and samples were heated in the temperature range of 25 to $550\text{ }^\circ\text{C}$ with a heating rate of $5\text{ }^\circ\text{K min}^{-1}$

All the gas adsorption isotherms were collected from Micromeritics ASAP 2020HD surface area analyzer.

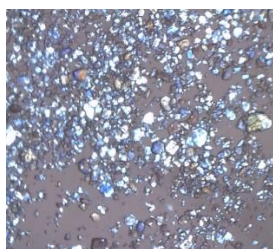
a. Synthesis of IISERP-MOF28

A solvothermal reaction between Zinc acetate dihydrate (0.5 mmol) and 3-Amino-1,2,4-Triazole (0.5 mmol) in a solution containing 3 ml DMF +3 ml water was carried out at 150°C for 48hrs. Block shaped colourless crystals were isolated by filtration and washed with plenty of methanol. The air-dried sample gave a yield of ~70% based on Zn. The PXRD pattern indicated this to be a pure phase of IISERP-MOF28. In a single synthesis up to 2g of the MOF was synthesized just by scaling up of the above synthesis.

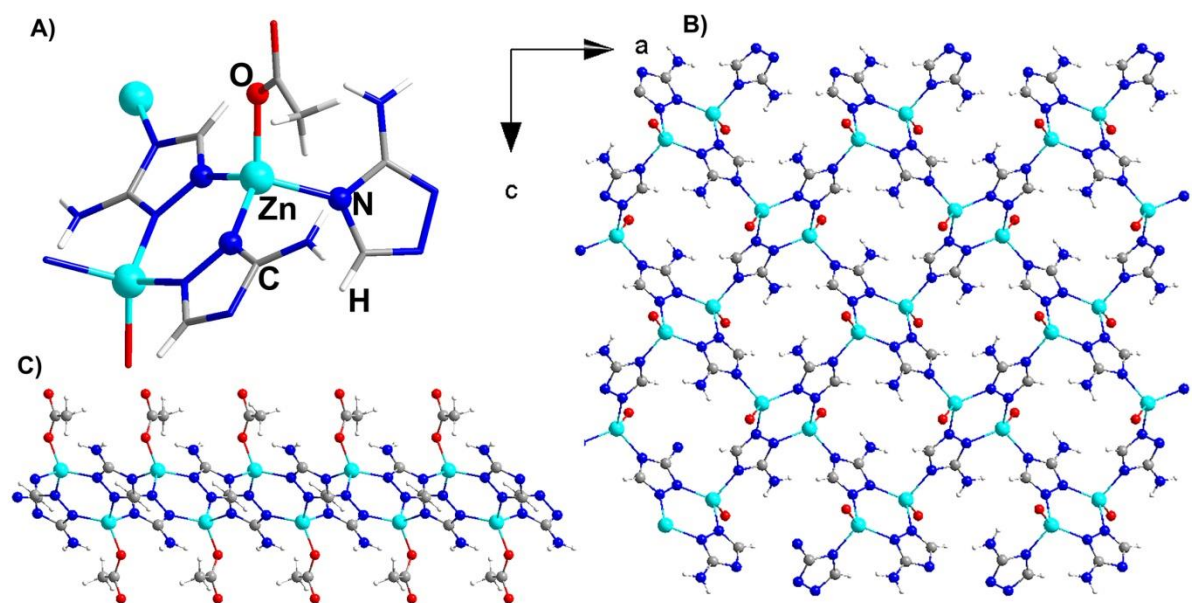
2. Analytical Characterizations:

(a) Single crystal structure determination:

Single-crystal X-ray diffraction was done on a Bruker SMART APEX four-circle diffractometer equipped with a CMOS photon 100 detector and Micro focus($1\mu\text{S}$) using a $\text{Cu-K}\alpha$ radiation. The crystal of IISERP-MOF28d was mounted on nylon Cryo loops using Paratone-N oil. Data was collected at 150 (2) K. Total data was integrated using Bruker SAINT Software and using SADABS it was corrected for absorption. Structure was solved using Intrinsic Phasing routine and was refined using the SHELXTL 6.3.1 (2004) software suite. All the non-hydrogen atoms were located from iterative examination of difference F-maps following which the structure was refined using least-squares method. Hydrogen atoms were fixed geometrically in a riding model.



Photograph S1. Images of the crystals under an optical microscope.



Angle Between adjacent zinc-triazolate planes

Zinc-triazolate MOFs	θ	References
Porous 3D ZnAtzOx	87.385	1
3D ZnAtzCO ₃	81.401	2
IISERP_MOF28, 3D ZnAtzAcetate	77.836	This work
2D ZnAtzAcetate	75.501	3
Porous 3D ZnAtzOx (dynamic fmwk)	70.849	4
CALF-20, Porous 3D ZntzOx	65.525	5
2D ZnAtzFormate	59.097	2

Note: Atz = 3-amino-1,2,4-triazole; tz = 1,2,4-triazole; CO₃ = carbonate; Ox = oxalate.

1. R. Vaidhyanathan, S. S. Iremonger, K. W. Dawson, G. K. Shimizu, *Chem. Commun.*, 2009, **35**, 5230–5232.
2. Y. Lin, Y. Zhang, J. Zhang and X. Chen, *Cryst. Growth Des.*, 2008, **8**, 3673.
3. Z. L. Chen, X. L. Li and F. P. Liang, *J. Solid State Chem.*, 2008, **181**, 2078.
4. A. Banerjee, S. Nandi, P. Nasa and R. Vaidhyanathan, *Chem. Commun.*, 2016, **52**, 1851-54.
5. J.-B. Lin, T. T. T. Nguyen, R. Vaidhyanathan, J. Burner, J. M. Taylor, H. Durekova, F. Akhtar, R. K. Mah, O. Ghaffari-Nik, S. Marx, N. Fylstra, S. S. Iremonger, K. W. Dawson, P. Sarkar, P. Hovington, A. Rajendran, T. K. Woo and G. K. H. Shimizu, *Science*, 2021, **374**, 1464.

Figure S1. A) Basic building unit of IISERP-MOF28. Showing the coordination sphere of Zinc, that adopts a tetrahedral geometry. B) Zinc-aminotriazolate layer lying on the ac-plane. Note the oxygens running up-down the layer. C) The layer viewed down the b-axis showing the acetate units running up-down the layer. Color code: Zn- cyan; O- red; C- grey; N- blue and H- white. Bottom: The angle between the planes defined by the Zn₂tz₂ dimers within the Zn-triazolate layers. This signifies the extent of buckling within the layer. Highly buckled layers enable short pillars to participate in creating a 3D structure.

Table S1: Crystallographic Information for IISERP-MOF28

a/Å	9.7110(9)
b/Å	16.1290(15)
c/Å	9.7091(9)
α/deg	90
β/deg	90
γ/deg	90
V/Å ³	1520.72(2)
Crystal System	Orthorhombic
Space Group	Pnma
Color	colourless
Expt. Crystal description	Block shape
Z	4
T/ K	150 K
Diffraction Source	CuKα
Diffraction radiation wavelength/ Å	1.54178
Diffraction reflection theta min	5.3
Diffraction reflection theta max	69.1
Diffraction reflection theta full	67.79
Reflection number total	1463
Reflection number gt	1341
R1,wR2 [<i>I</i> >2σ(<i>I</i>)]	0.058, 0.174
R1,wR2(all data)	0.062, 0.178
GoF	1.115

b. PLATON analysis:

Total Potential Solvent Accessible Void Vol (SOLV-Map Value) = 302 Å³

Unit cell volume, V = 1520.72 Å³

Now, Void volume = (302/1520.72) x 100 = ~ 19.85 % of the IISERP-MOF28.

Now, IISERP-MOF28 (1) has a cationic framework with one hydroxide ions per formula unit. So, formula unit present in the crystal structure of the IISERP-MOF28 is Zn₂(Atz)₂(Ac)(OH⁻)(H₂O)_x(DMF)_y, where, x,y = any integer represents no of water and dmf molecules.

Z for IISERP-MOF28 is 4.

Hence the unit cell formula is Zn₈(Atz)₈(Ac)₄(OH⁻)₄(H₂O)_{4x}(DMF)_{4y}

From the squeeze result, electrons found in solvent Accessible Void = 42.

Considering 40 electrons for one DMF molecule.

The final Unit Cell formula Zn₈(Atz)₈(Ac)₄(OH⁻)₄(DMF)₄

and formula of formula unit is Zn₂(Atz)₂(Ac)(OH⁻)(DMF)

DMF weight percentage is 15.7% and from TGA we have approximately 16% weight loss corresponding to DMF.

(b) Powder X-ray diffraction:

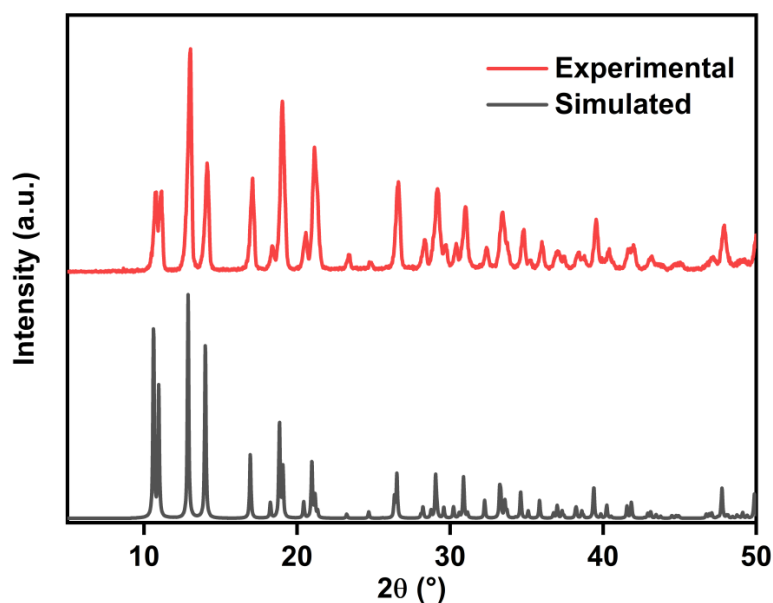


Figure S2. The PXRD profile of IISERP-MOF28 indicating the bulk purity of the MOF.

(c) TGA analysis:

There is a gradual mass loss up to 230 °C due to loss of solvent molecules trapped in the pore of IISERP-MOF28.

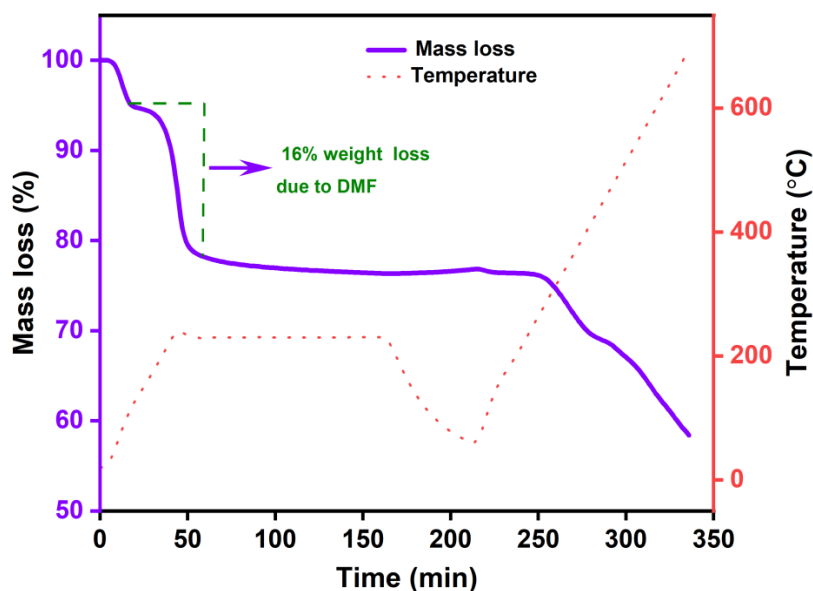


Figure S3. TGA of as made IISERP-MOF28 showing the thermal stability upto 260°C. The continuous mass loss upto 230 °C is due to the DMF and water molecules present in the pores of the MOF.

(d) IR analysis:

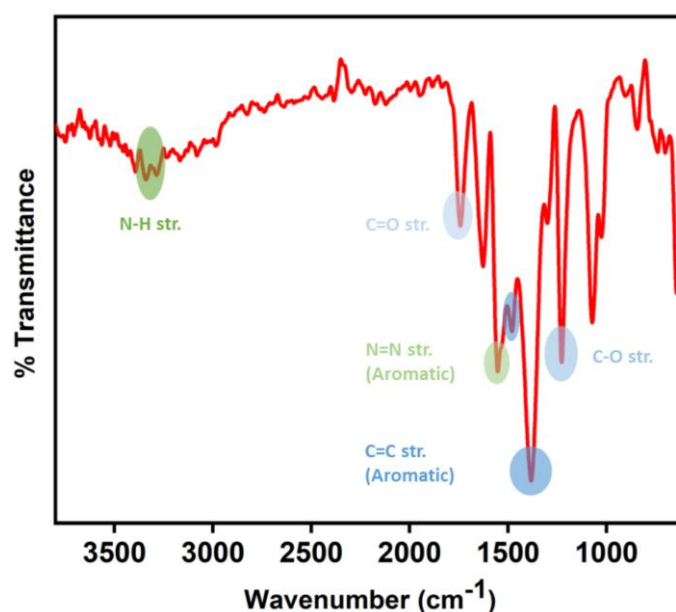


Figure S4. Infra-red spectra of IISERP-MOF28, showing the various stretching and bending modes present. Selected peaks: IR (cm^{-1}): $\nu(\text{N-H})$: 3230-3395; $\nu(\text{CO})$: 1740s; $\nu(\text{N=N})$: 1556s; $\nu(\text{C=C})$: 1475 and 1380; $\nu(\text{C-O})$: 1225.

3. Adsorption Analysis

All the gas adsorption analysis were carried out using ~ 100 mg of IISERP-MOF21d Sample was directly activated by evacuation at 150°C for 24 hrs (10-6 mbar) till an outgas rate was $\leq 2 \mu\text{bar}/\text{min}$ was achieved. Then the activated MOF was transferred to the analysis port of Micromeritics ASAP 2020HD or 3-FLEX instrument for the gas sorption analysis. Gas analyses were carried out with ultrahigh purity gases (≥ 4.8 grade).

Langmuir Fits:

In all cases the isotherms were fit to the Single-Site Langmuir (SSL) equation. The isotherms were fit by solving the Langmuir isotherm equation using the solver function in Microsoft Excel following a similar protocol to Keller *et al.*^{S1} Utilizing this routine circumvents some of the problems associated with favouring either high or low pressure regions when linearizing the Langmuir equation^{S2} and offers a balanced approach.

Single-Site Langmuir (SSL):

$$q_i = q_m \frac{k_i}{1 + k_i P}$$

Dual-Site Langmuir (DSL):

$$q_i = q_{m,1} \frac{K_1}{1 + K_1 P} + q_{m,2} \frac{K_2}{1 + K_2 P}$$

Ideal Adsorbed Solution Theory (IAST):

IAST calculations were undertaken as described by Prausnitz et al.⁵³ The selectivity equation involved in calculation is provided below.

Selectivity:

$$S_{1,2} = \frac{q_1/q_2}{p_1/p_2}$$

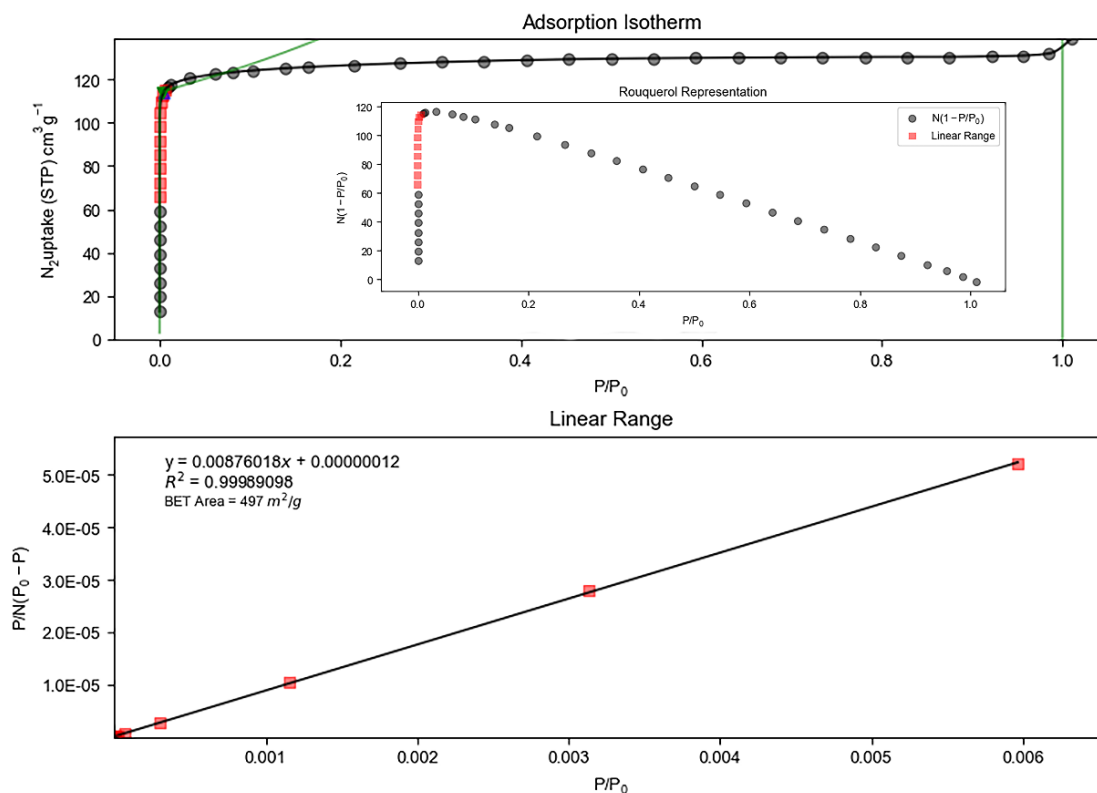


Figure S5. BET fit for the IISERP-MOF28 calculated from the 77K N₂ isotherm.

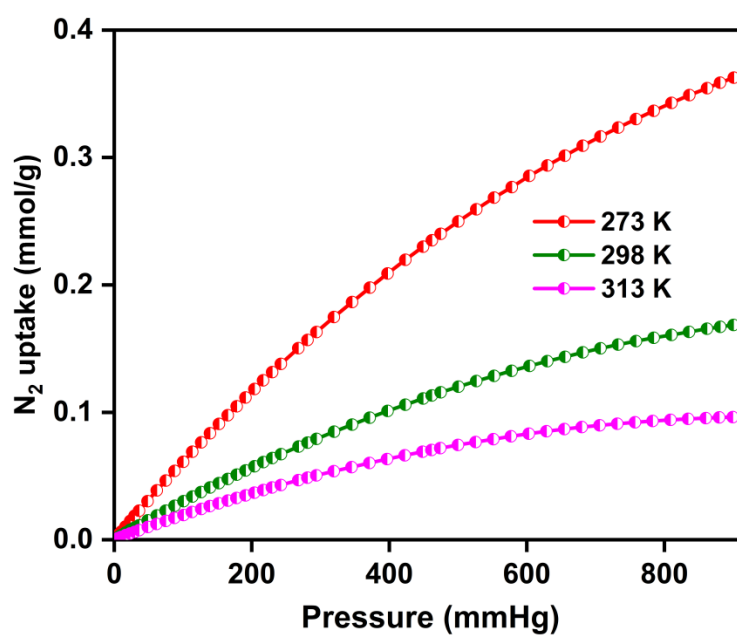


Figure S6. N₂ sorption isotherm of IISERP-MOF28 at different temperatures.

Virial analysis:

The CO₂ adsorption data were collected from 0-1 bar at 313,298, 283, 273 and 195 K. For virial fitting the 273, 298 and 313 K isotherms were taken and fitted by the virial equation (1).

$$\ln(P) = \ln(V_a) + (A_0 + A_1 \cdot V_a + A_2 \cdot V_a^2 + \dots + A_6 \cdot V_a^6) / T + (B_0 + B_1 \cdot V_a) \dots \dots \dots (1)$$

Where, P is the pressure during experiment, V_a is amount of gas adsorbed, T is temperature, and A₀, A₁, A₂..., A₄ and B₀, B₁ are temperature independent empirical parameters.

Table S2: Summary of the fitted Virial parameters for IISERP-MOF28.

A ₀	-3866.518441	B ₀	16.25885602
A ₁	-167.0322344	B ₁	0.129610206
A ₂	120.203798	B ₂	0
A ₃	-0.006573956	B ₃	0
A ₄	0.017728823	B ₄	0

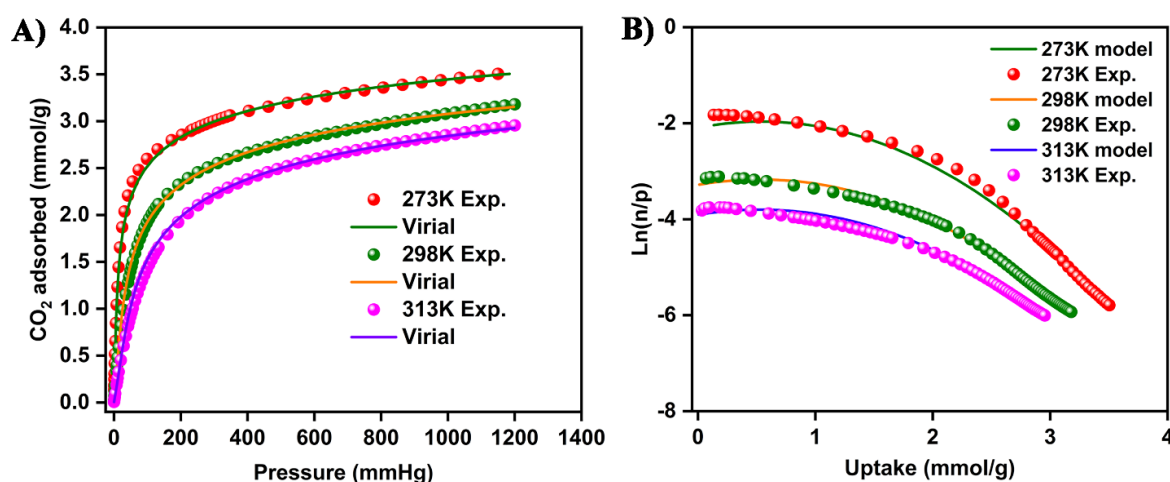


Figure S7. (A) Comparison of experimental isotherms of IISERP-MOF28 to the ones obtained from virial modelling carried out using CO₂ isotherms collected at 273, 298 and 313K. (B) Virial plots of IISERP-MOF28 carried out using CO₂ isotherms collected at 273, 298 and 313K.

IAST selectivities:

CO₂/N₂ selectivity was calculated for IISERP-MOF28 using the experimental single component CO₂ and N₂ isotherms and ideal adsorbed solution theory (IAST) with a nominal composition of 15CO₂:85N₂. At 1 bar total pressure, and 298K & 313K, conditions of relevance to post combustion CO₂ capture.

IAST fitting parameters for IISERP-MOF28 (CO₂/ N₂):

At 298 K

Gas A = CO₂

Gas B = N₂

Table S3: Fitted IAST parameters for CO₂/N₂ (15CO₂:85 N₂ composition) selectivity at 298 K for IISERP-MOF28

Gas A Constants		Gas B Constants	
q _{s1} (mmol g ⁻¹) =	3.413531176	q _{s1} (mmol g ⁻¹) =	4.924949522
q _{s2} (mmol g ⁻¹) =	0	q _{s2} (mmol g ⁻¹) =	0
K ₁ (mbar ⁻¹) =	0.022334194	K ₁ (mbar ⁻¹) =	7.44E-05
K ₂ (mbar ⁻¹) =	0	K ₂ (mbar ⁻¹) =	0
n ₁ =	0.880228916	n ₁ =	0.906103856
n ₂ =	0	n ₂ =	0
H ₁ (mmol mbar ⁻¹ g ⁻¹)=	0.076238467	H ₁ (mmol mbar ⁻¹ g ⁻¹)=	0.000366619
H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0	H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0

At 313 K

Gas A = CO₂

Gas B = N₂

Table S4: Fitted IAST parameters for CO₂/ N₂ (15CO₂:85 N₂ composition) selectivity at 313K for IISERP-MOF28 .

Gas A Constants		Gas B Constants	
q _{s1} (mmol g ⁻¹) =	3.240186165	q _{s1} (mmol g ⁻¹) =	2.000428068
q _{s2} (mmol g ⁻¹) =	0	q _{s2} (mmol g ⁻¹) =	0
K ₁ (mbar ⁻¹) =	0.007958866	K ₁ (mbar ⁻¹) =	6.89E-05
K ₂ (mbar ⁻¹) =	0	K ₂ (mbar ⁻¹) =	0
n ₁ =	0.939317452	n ₁ =	0.903488549
n ₂ =	0	n ₂ =	0
H ₁ (mmol mbar ⁻¹ g ⁻¹)=	0.025788208	H ₁ (mmol mbar ⁻¹ g ⁻¹)=	0.000137783
H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0	H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0

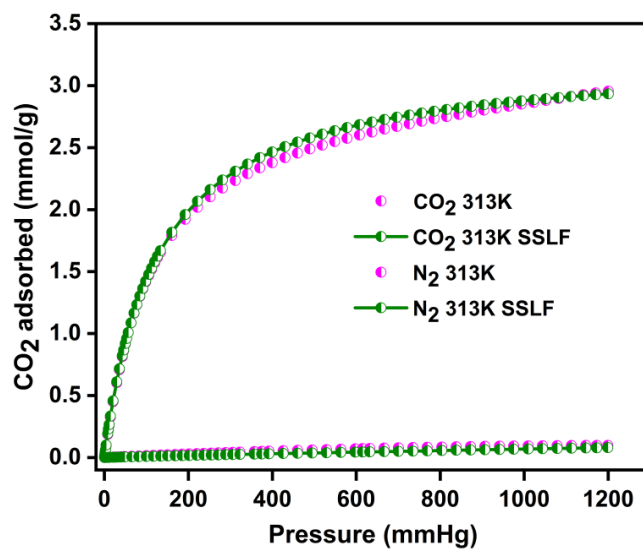
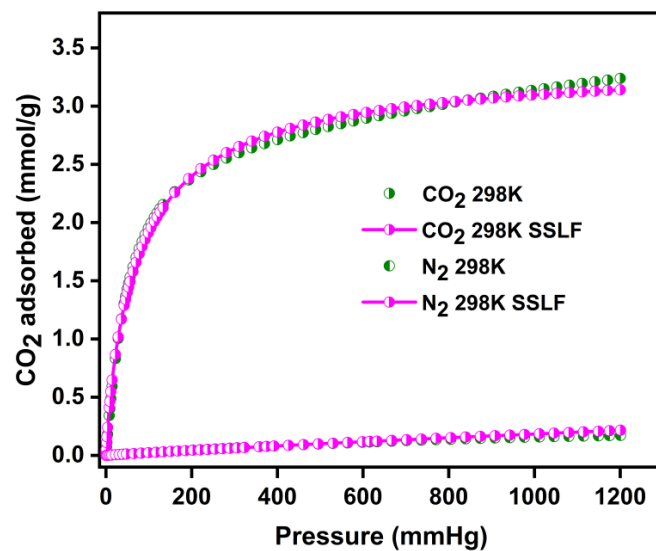


Figure S8. IAST fitting of CO₂ and N₂ isotherms for IISERP-MOF28 collected at 298 and 313 K.

4. Stability Studies

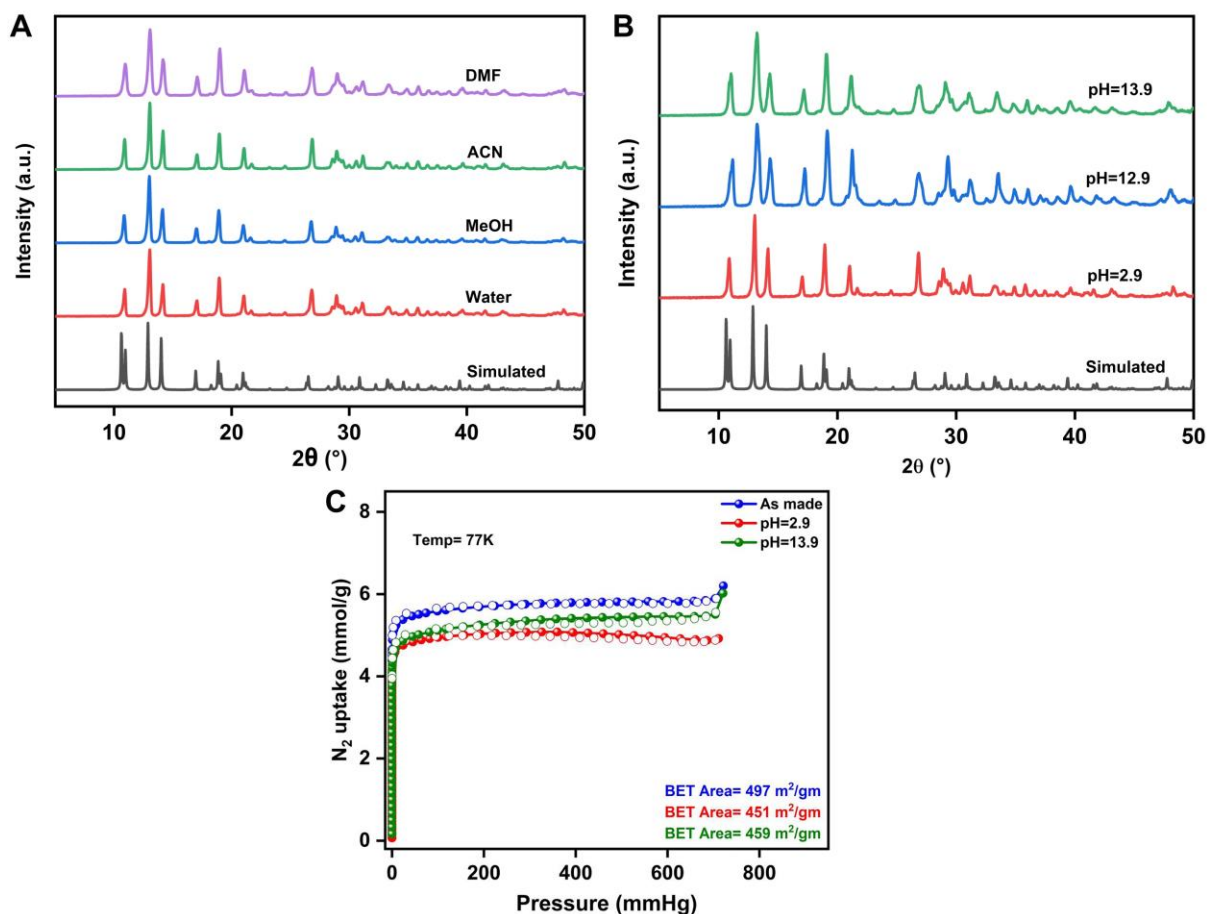


Figure S9. (A) After soaking for 20 days, PXRD profiles demonstrate the stability of IISERP-MOF28 in various solvents. (B) PXRD patterns of post acid-base treatment of the MOF. (C) 77K liquid N_2 adsorption isotherms of the MOF after treating with acid and base for 15 days.

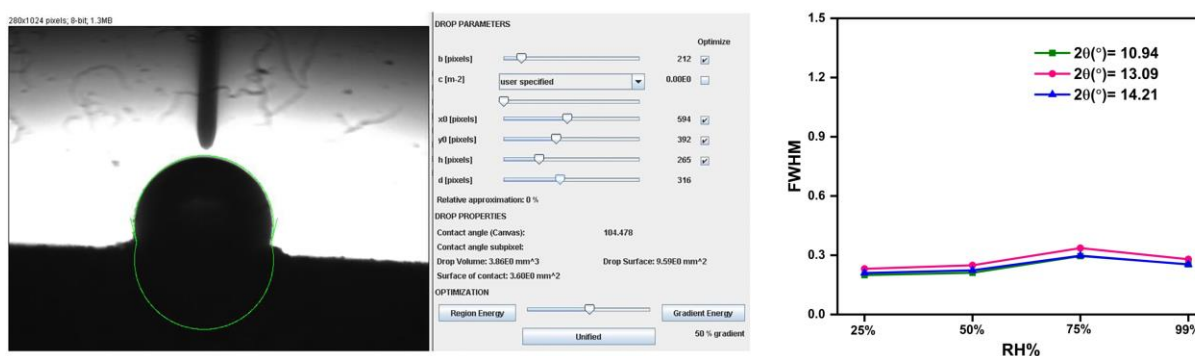


Figure S10. Left: Contact angle measurement for water on IISERP-MOF28. Right: FWHM plot of IISERP-MOF28 at different relative humidity condition at constant temperature.

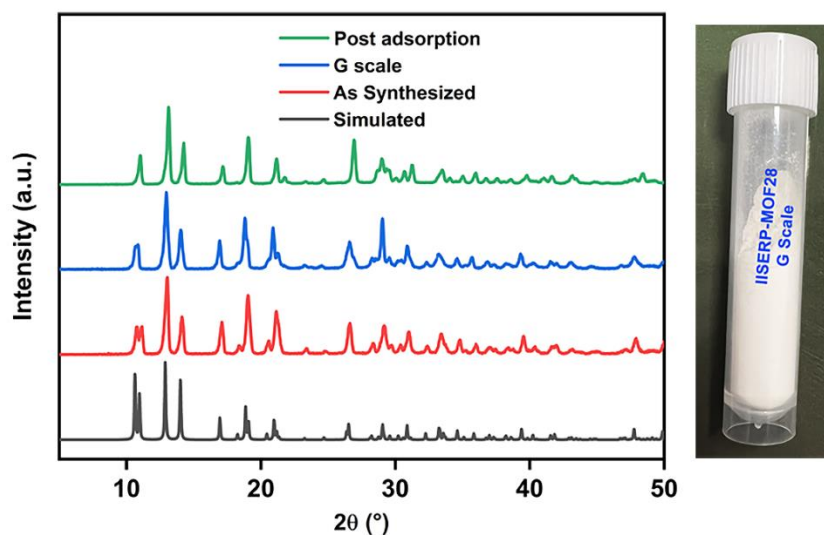


Figure S11. A comparative PXRD plot showing the bulk purity of the gram scale synthesis and the stability of the MOF to the repeated adsorption-desorption and evacuation cycles. Note: This material can be scaled up to 4 gram in a single synthesis.

Table S5: Comparison of the adsorption characteristics of **1** with some of the leading CO₂ capturing MOFs.

MOF	CO ₂ capacity at 298 K (mmol/g)		HOA (kJ/mol)	ref
	0.15 bar	1.0 bar		
IISERP-MOF28	2.2	3.1	32	<i>This work</i>
Calf-20 (303 K)	2.5	3.54	39	<i>Science 2021, 374, 1464–1469</i>
ALF	2.7	3.98	47.9	<i>Sci. Adv., 2022, 1473</i>
Zn-Atz_Ox (293 K)	2.1	3.65	40	<i>Science 2010, 330, 650.</i>
IISERP-MOF2 (303 K)	1.6	4.1	33	<i>J. Am. Chem. Soc. 2017, 139, 1734–1737</i>
ZnF(daTZ)	0.96	3.3	33	<i>J. Am. Chem. Soc. 2020, 142, 2750–2754</i>
mmen-Mg ₂ (dobpdc)	3.2	3.9	75	<i>J. Am. Chem. Soc. 2012, 134, 7056.</i>
Zn ₃ (Atz) ₃ (PO ₄) (273K)	1.76	3.16	30	<i>Angew. Chem. 2012, 124, 1862.</i>
UTSA-16	2.54	4.4	37	<i>ACS-AMI 2017, 9, 455.</i>
MAF66	1.29	4.41	26	<i>Inorg. Chem. 2012, 51, 9950–9955</i>

Zn ₂ (TRZ) ₂ (Fuma)	1.32	3.92	27	<i>Fuel</i> , 2022
SIFSIX-3-Zn	2.38	2.55	46	<i>Nat. Commun.</i> 2014, 5, 4228.
SIFSIX-3-Cu	2.45	2.6	53	<i>Nat. Commun.</i> 2014, 5, 4228.
MIL-101(Cr)	0.6	2.25	32	<i>Chem. Eng. Sci.</i> 2016, 147, 109.
NH ₂ -MIL-53(Al)	0.9	1.5	38.4	<i>J. Am. Chem. Soc.</i> 2009, 131, 6326.
MIL-91(Ti)	1.5	3.5	44	<i>J. Mater. Chem. A</i> 2016, 4, 1383
CAU-1	1.1	4.0	48	<i>Energy Environ. Sci.</i> 2011, 4, 4522.
bio-MOF-13	1.0	2.0	41	<i>Chem. Sci.</i> 2013, 4, 1746.
bio-MOF-12	1.34	3.15	39	<i>Chem. Sci.</i> 2013, 4, 1746.
JUC-132-Cd	0.65	1.71	30.3	<i>Chem. Commun.</i> 2015, 51, 9463.

5. Computational details:

All computational calculations and simulations were performed using the Accelrys (Materials Studio V 8.0) software. An adsorption isotherm was simulated using the GCMC routine embedded in the sorption algorithm of the Materials Studio software.(S4-S7) For these 1000000, equilibration steps were calculated and the Metropolis algorithm with Drieding forcefield was used. The Lennard–Jones equation, with a cut-off radius of 18.5 Å, was used to calculate the van der Waals interactions. The long-range electrostatic interactions and Coulomb interactions were both obtained by three-dimensional Ewald & Group methods, with the accuracy of 1.0 e-5 kcal/mol. The calculations were repeated three times to establish the error-bar (see Figure 4B of the main text). Following this, the favorable positions for the CO₂ within the MOF were identified using the Simulated Annealing routines embedded in the Materials Studio. A Smart algorithm was employed. A total of 10 cycles with 100000 steps/cycle were used to achieve the low-energy configurations. Charges were calculated using the Qeq charge equilibration method. The above simulations all conducted by the Sorption of the Materials Studio package.

Separately, the binding energy for the various zinc-triazolate MOFs were calculated using the DMOL³ module of the Accelrys. In all cases large super cells ~ 3 x 3 x3 were employed. A high tolerance of 1x10⁻⁶ for the SCF convergence and high electrostatic, van der waal and hydrogen-bond cut offs were used.(S8,S9) UFF-based Lennard-Jones dispersion corrections were included in Energy, Force and Displacement calculations. All calculations are at 0 K and were spin-unrestricted, adopting the formal spin as the initial spin. Core elements were treated with all-electron pseudopotentials and

the DNP basis set with a basis cut-off of 3.7 Å. For our dispersion corrections, we used Generalized Gradient Approximation (GGA) for calculating the exchange and the correlation energies and employed the Perdew-Wang 91 (PW91) functional.(S10) Density mixing was done using the Pulay scheme. The final configuration considered in the analysis converged well. We used this final optimized structure for the molecular dynamics simulations.

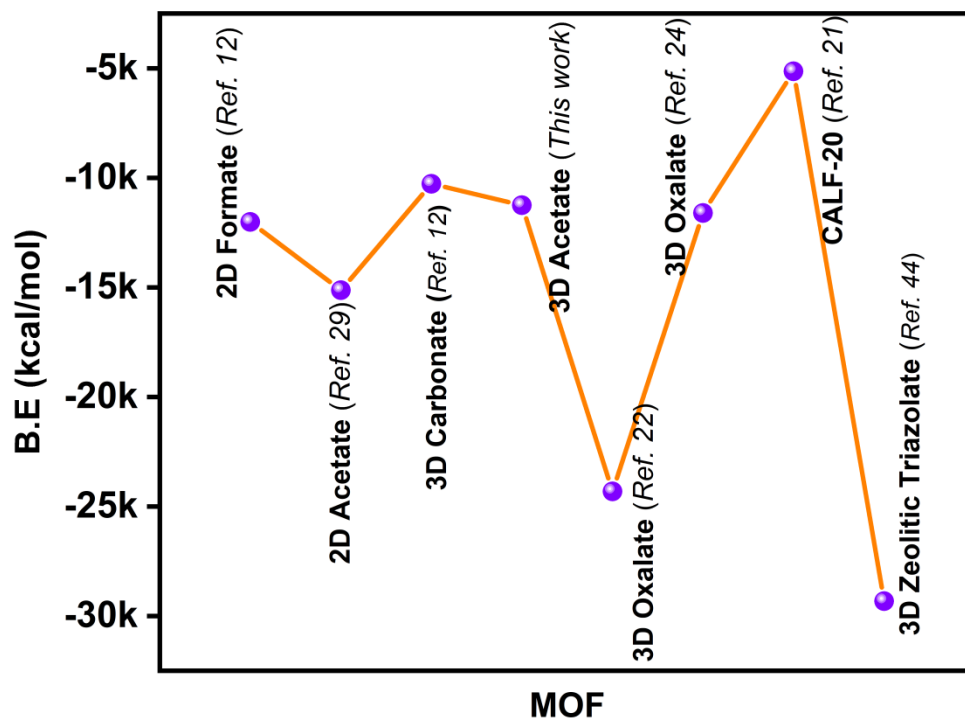


Figure S12. Calculated binding energies for different zinc-triazolate MOFs. Note: The references correspond to the references in the maintext.

To analyze the adsorption sites of CO₂ on the MOF, we used radial distribution functions (RDFs) extracted from detailed MD simulations carried out using the Forcite Dynamics. The lowest energy configuration from the simulated annealing routine was applied as the input for the MD. A 10 ns NPT MD simulation (1.0 fs time step; T = 298K; P = 1bar for CO₂) was used to reach the equilibrium state; the framework was allowed to relax. Then a 10 ns NVE MD simulation (1.0 fs time step) was used to obtain the final configuration at the lowest energy state. This was used to calculate the RDF.(S11, S12)

References:

- (S1) Kemmer, G.; Keller, S. Nat. Protoc. 2010, 5, 267–81.
- (S2) Richter, E.; Schuetz, W.; Myers, A. L. Chem. Eng. Sci. 1989, 44, 1609–1616.
- (S3) Myers, A. L.; Prausnitz, J. M. AIChE J. 1965, 11, 121–127.
- (S4) Cerný, V. "A thermodynamical approach to the travelling salesman problem: an efficient simulation algorithm", J. Optim. Theor. Appl., 45, 41-51 (1985).
- (S5) Frenkel, D.; Smit, B. Understanding Molecular Simulation: From Algorithms to Applications, 2nd Edition, Academic Press: San Diego (2002).
- (S6) Kirkpatrick, S.; Gelatt, C. D.; Vecchi, M. P. "Optimization by Simulated Annealing", Science, 220, no. 4598, 671-680 (1983).
- (S7) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. "Equation of State Calculations by Fast Computing Machines", J. Chem. Phys., 21, 1087 (1953).
- (S8) B. Delley, J. Chem. Phys. 92, 508 (1990).
- (S9) Delley: J. Phys. Chem. 100, 6107 (1996).

- (S10) P91 exchange: Perdew, Physica B 172, 1 (1991).
(S11) Rappé, A. K.; Goddard, W. A., J. Phys. Chem., 95, 3358 (1991).
(S12) Ray, J. R. Comput. Phys. Rep., 8, 109 (1988) and references therein.