

Supporting Information for

A Microporous Mixed Metal-Mixed Ligand Metal Organic Framework for Selective CO₂ Capture

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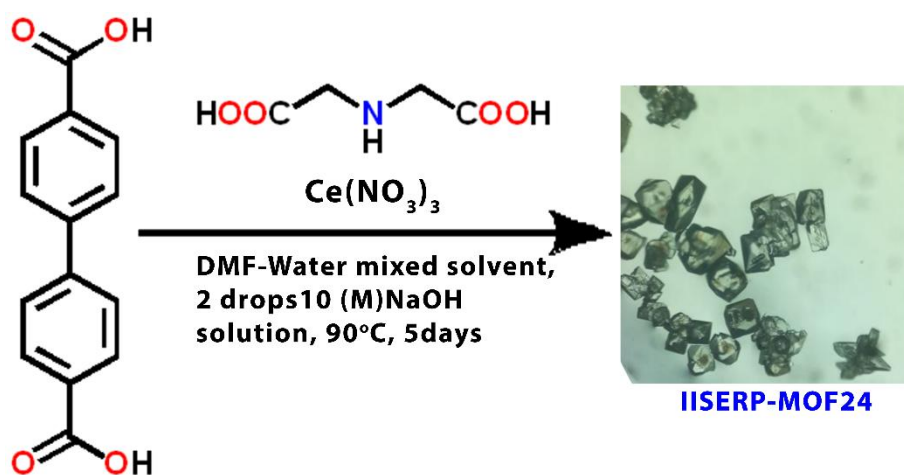
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1. Materials and methods

All the reagents were bought from Sigma Aldrich. For the synthesis all reagents and solvents were used without any further purification.

Synthesis of IISERP-MOF24:

A mixture of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (95.0 mg, 0.219 mmol), iminodiacetic acid (H_3IMDA , 69.0 mg, 0.519 mmol), and 4,4'-biphenyldicarboxylic acid (H_2BPDC , 65 mg, 0.269 mmol) was dissolved into a mixed solvent of *N,N'*-dimethyl formamide (DMF) and H_2O (9 mL; v/v = 8:1) in a screw-capped vial (20 mL), to which 50 μL of 10 M NaOH was added. The vial was capped and heated in an oven at 90 °C for 5 days. Colourless prismatic crystals were obtained by filtration and washed several times with DMF to afford IISERP-MOF24 in 75% yield based on metal salt. The experimental powder X-ray diffraction (XRD) profile of IISERP-MOF24 matches well with the simulated one based on the single-crystal X-ray data, indicating that the sample forms as a pure phase. (CHN: Calc. C- 37.70; H- 3.74; N- 3.66: Obsd. 37.79; 3.64, 5.35) calculated using the formula: $\text{Ce}_3\text{Na}_3(\text{C}_{14}\text{H}_8\text{O}_4)_3(\text{C}_4\text{H}_5\text{NO}_4)_3 \cdot (\text{C}_3\text{H}_7\text{NO})_2(\text{H}_2\text{O})_9$. The discrepancies in the observed values could be attributed to the partial loss of the solvent molecules when exposed to air.



Scheme S1. Schematic representation of the synthesis of IISERP-MOF24.

Solvent composition of IISERP-MOF24 using SQUEEZE and analytical data

Asymmetric unit present in IISERP-MOF24 is $\text{Ce}_{0.5}\text{Na}_{0.5}(\text{BPDC})_{0.5}(\text{IMDA})_{0.5}$

Formula unit present in IISERP-MOF24 is $\text{Ce}_3\text{Na}_3(\text{BPDC})_3(\text{IMDA})_3$.

So, Formula unit is just six times of the asymmetric unit.

Again, Z for IISERP-MOF24 is 3.

So, 3 units of $\text{Ce}_3\text{Na}_3(\text{BPDC})_3(\text{IMDA})_3$ and $(6 \times 3) = 18$ units of $\text{Ce}_{0.5}\text{Na}_{0.5}(\text{BPDC})_{0.5}(\text{IMDA})_{0.5}$ are present in unit Cell.

Again, squeeze results suggest that 507 electrons are present from solvent molecules in the unit cell.

So, per asymmetric unit $507 / (6 \times 3) = 28.6$ electrons are present &

Per formula unit $507/3 = 169$ electrons are present.

Number of Solvent molecules determination:

CHN analysis:

No. of DMF	No. of water	Electron counts	CHN analysis
2	9	$(2 \times 40) + (9 \times 10) = 170$	Calc: C = 37.7, H = 3.74, N = 3.66 (Obsd. 37.79, H = 3.64, N = 5.35)

So, actually from CHN analysis it is understandable that 2 DMF and 9 water molecules present in the formula unit, $\text{Ce}_3\text{Na}_3(\text{C}_{14}\text{H}_8\text{O}_4)_3(\text{C}_4\text{H}_5\text{NO}_4)_3 \cdot (\text{C}_3\text{H}_7\text{NO})_2(\text{H}_2\text{O})_9$.

TGA analysis: (For TGA plot see figure S3)

Molecular mass of formula unit **without** solvent $\text{Ce}_3\text{Na}_3(\text{BPDC})_3(\text{IMDA})_3$ is 1603.2.

Now, molecular mass of formula unit **with** solvent $\text{Ce}_3\text{Na}_3(\text{BPDC})_3(\text{IMDA})_3(\text{DMF})_2(\text{H}_2\text{O})_9$ is $1603.2 + (9 \times 18) + (2 \times 40) = 1911.533$.

% mass of DMF = $(160/1911) \times 100 = 8.4$

% mass of water = $(162/1911) \times 100 = 8.5$

Total calculated % mass loss = $(8.4 + 8.5) = 16.9$

Note that there are solvent losses at low temperatures from the surface adsorbed methanol molecules used during the washing of the sample. This most likely is the origin of the discrepancy in the calculated and the observed CHN values.

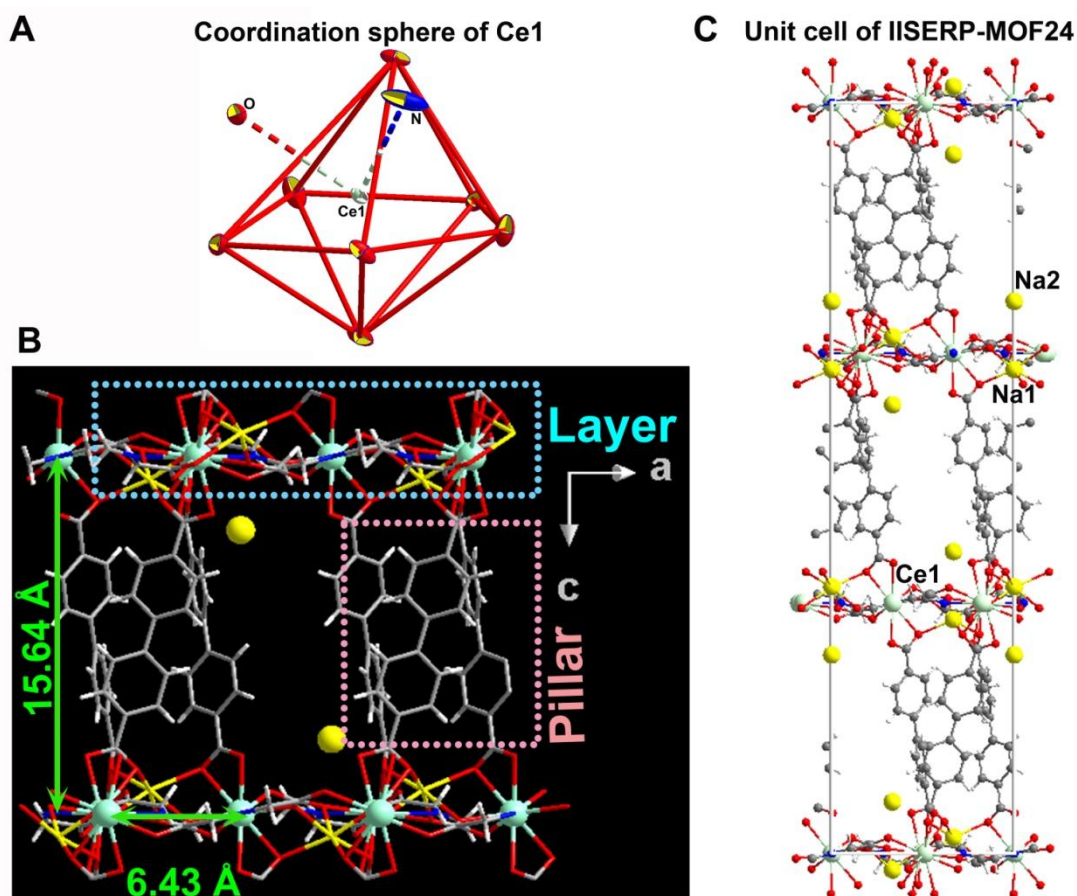
Table S1. Crystal structure information for the solvated and squeezed structure of IISERP-MOF24 obtained from SCXRD and PLATON analysis.

Parameters	Non-squeezed IISERP-MOF24	Squeezed IISERP-MOF24
Chemical formula	*Ce ₃ Na ₃ (C ₁₄ H ₈ O ₄) ₃ (C ₄ H ₅ NO ₄) ₃ •(solvent) _x .	Ce ₃ Na ₃ (C ₁₄ H ₈ O ₄) ₃ (C ₄ H ₅ NO ₄) ₃
Formula weight	1911.5	1603.19
Crystal system	Trigonal	Trigonal
Space group	R32	R32
Unit-cell parameter	a(Å) =12.8523(4), b(Å) =12.8523(4), c(Å) =45.7558(17), α = 90°, β = 90°, γ = 120°, V(Å ³) = 6545.43(4)	a(Å) =12.8523(4), b(Å) =12.8523(4), c(Å) =45.7558(17), α = 90°, β = 90°, γ = 120°, V(Å ³) = 6545.43(4)
Crystal color	Colorless prismatic crystal	Colorless prismatic crystal
Temperature	100(2)	100(2)
No. of formula units in unit cell (Z)	3	3
Density (g cm ⁻³)	1.27	1.22
Abs. Coeff. (mm ⁻¹)	12.578	12.522
F(000)	2436.0	2340.0
Flack	0.007 (5)	-0.087(7)
Reflection Data		
No. of reflections meas.	17802	5365
No. of uniq. reflections	2862	2862
No. of obs. reflections	2834	2821
λ (Å)	1.54178	1.54178
R _{merge}	0.041	0.027
Av. I/sig(I)	31.35	24.88
θ _{max}	72.3	72.3
θ _{min}	4.4	4.4
Refinement Data		

R _{all}	0.036	0.028
R _{obs}	0.036	0.027
wR _{2(all)}	0.120	0.080
wR _{2(obs)}	0.120	0.080
Ext. Coeff.	0.0002	0.0003
Goodness-of-fit (GOOF)	1.193	1.132
Largest diff. peak and hole: Delta-rho (eÅ ⁻³) _{max}	1.276	1.044
Largest diff. peak and hole: Delta-rho (eÅ ⁻³) _{min}	-0.906	-0.623

***Note.** PLATON analysis suggests the presence of substantial amount of solvent accessible voids in the structure of IISERP-MOF24 (Ce₃Na₃(C₁₄H₈O₄)₃(C₄H₅NO₄)₃•(solvent)_x). The solvents could not be modelled satisfactorily. From the *SQUEEZE* analysis was carried out to determine the number of DMF & H₂O molecules. From squeezed electron counts and with the aid of feasible analytical methods like TGA & elemental (CHN) analysis the solvent content was estimated. It was found that 2 DMF and 9 water molecules present in the each formula unit of IISERP-MOF24 (Ce₃Na₃(C₁₄H₈O₄)₃(C₄H₅NO₄)₃). So, actual formula of IISERP-MOF24 is Ce₃Na₃(C₁₄H₈O₄)₃(C₄H₅NO₄)₃•(C₃H₇NO)₂(H₂O)₉.

The structure of IISERP-MOF24:



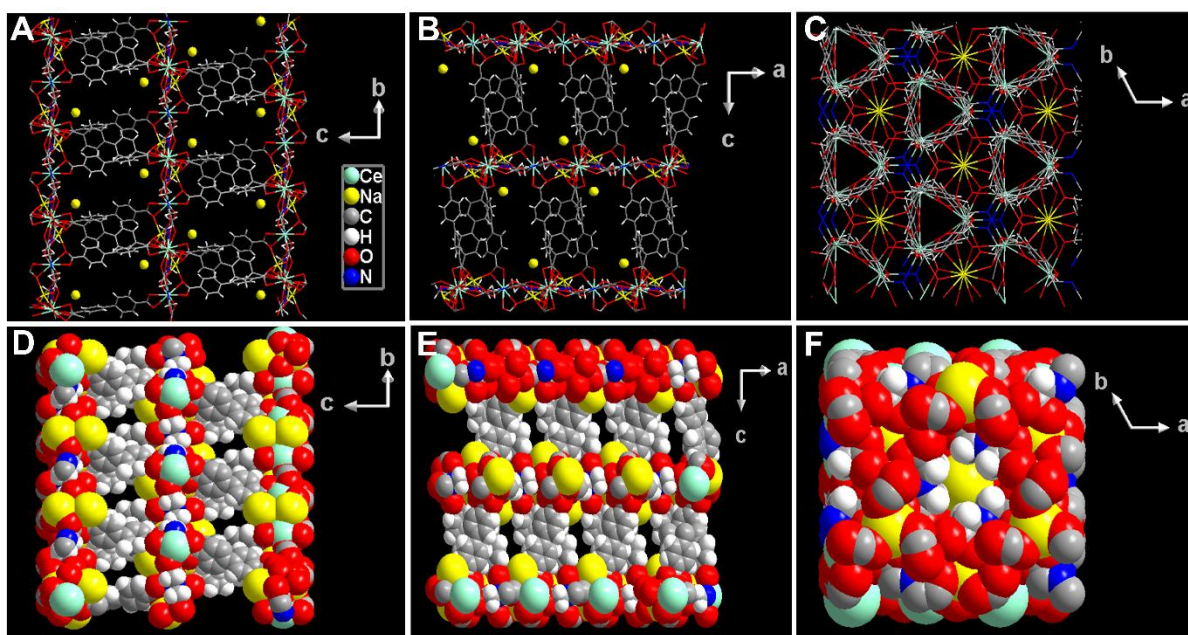


Figure S1. Top: (A) Shows the coordination sphere of Cerium ions, which adopts a bicapped pentagonal bipyramidal geometry. (B) The 3D layered-pillared topology of IISERP-MOF24. (C) The unit cell of IISERP-MOF24 showing selected atomic labels. The thermal ellipsoids are plotted at 50% probability. **Bottom:** (A) View along a-axis, (B) View along b-axis (a layered pillared structure), (C) View along c- axis, (D) Space-fill model along a-axis (without pore DMF and water molecules), (E) Space-fill model along b- axis and (F) Space fill model along c- axis.

2. Analytical characterizations

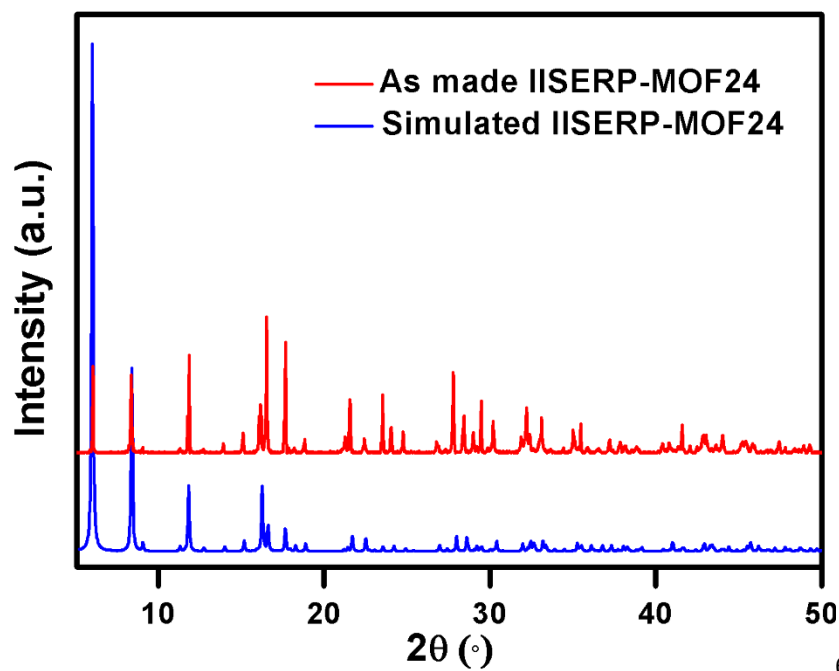


Figure S2. Comparison between the powder X-ray diffraction patterns simulated from the single crystal data and the experimentally obtained one.

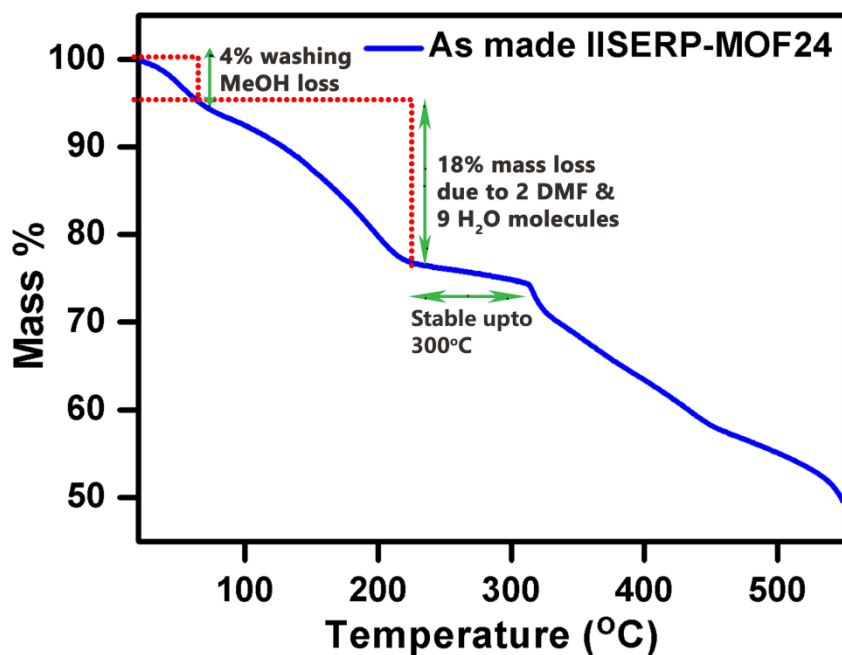


Figure S3. TGA carried out on the as made IISERP-MOF24. A two step weight loss is observed from room temperature to 220 °C. The first weight loss up to 100 °C is due to the evaporation of pore water molecules, while the second weight loss observed from 100 °C to 220 °C is due to the loss of DMF molecules trapped inside the pore (total Wt. loss calc.: 23.9%; obsd: 24.0%). The weight loss have been calculated using the formula $\text{Ce}_3\text{Na}_3(\text{C}_{14}\text{H}_8\text{O}_4)_3(\text{C}_4\text{H}_5\text{NO}_4)_3 \cdot (\text{C}_3\text{H}_7\text{NO})_2(\text{H}_2\text{O})_9$ (M. Wt. 1603.2 g/mol).

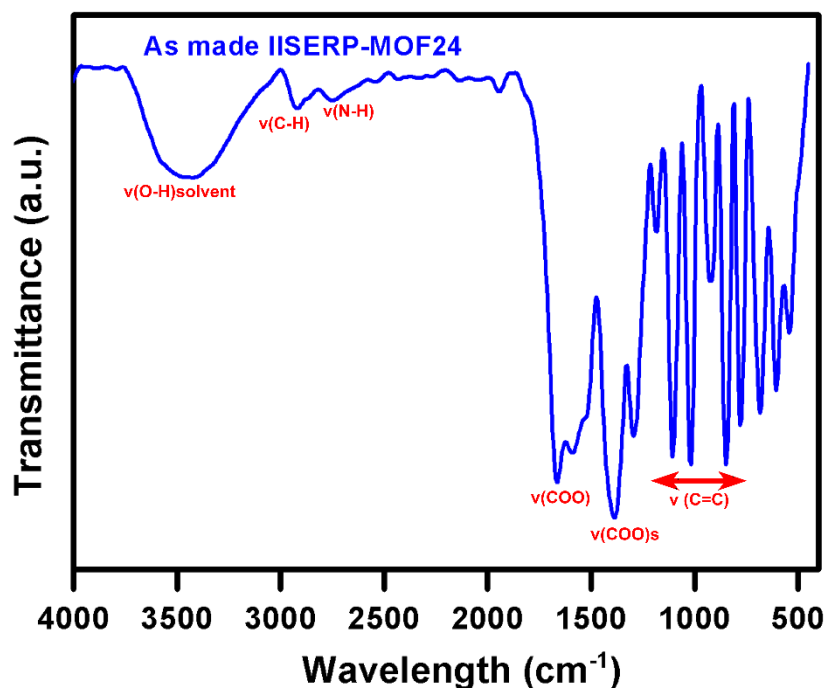


Figure S4. Infrared spectra (IR) of IISERP-MOF24 showing the various stretching and bending modes present. Selected peaks: IR (KBr pellet, cm^{-1}): $\nu(\text{O-H})_{\text{solvent}}$: 3455s; $\nu(\text{C-H})$: 2924; $\nu(\text{N-H})$: 2749; $\nu(\text{COO})$: 1662s and 1593vs, $\nu(\text{COO})_s$ 1396s, 1300 vs; $\nu(\text{C=C})$: 1190 to 780. (Source: *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, Applications in Coordination, Organometallic, and Bioinorganic Chemistry, 6th Edition, Kazuo Nakamoto*).

3. Scanning Electron Microscopy- Energy-dispersive X-ray spectroscopy (EDX) Analysis

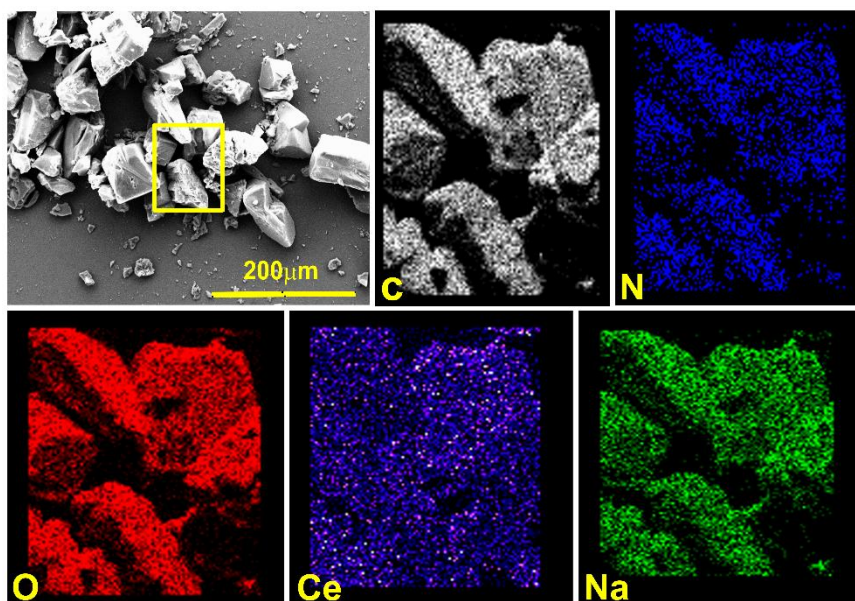


Figure S5. Elemental mapping using Energy-dispersive X-ray analysis (EDXA) technique shows homogeneous distributions of both the Ce and Na in IISERP-MOF24.

Calculation of Ce:Na from SEM-EDX analysis:

From the composition determined from SCXRD analysis $(\text{Ce}_3\text{Na}_3(\text{C}_{14}\text{H}_8\text{O}_4)_3(\text{C}_4\text{H}_5\text{NO}_4)_3 \cdot (\text{C}_3\text{H}_7\text{NO})_2(\text{H}_2\text{O})_9)$, a ratio Ce:Na of 1.00 is expected. EDXA was performed on five different regions of the sample. The results are presented below.

SEM-EDX & elemental analysis of IISERP-MOF24:

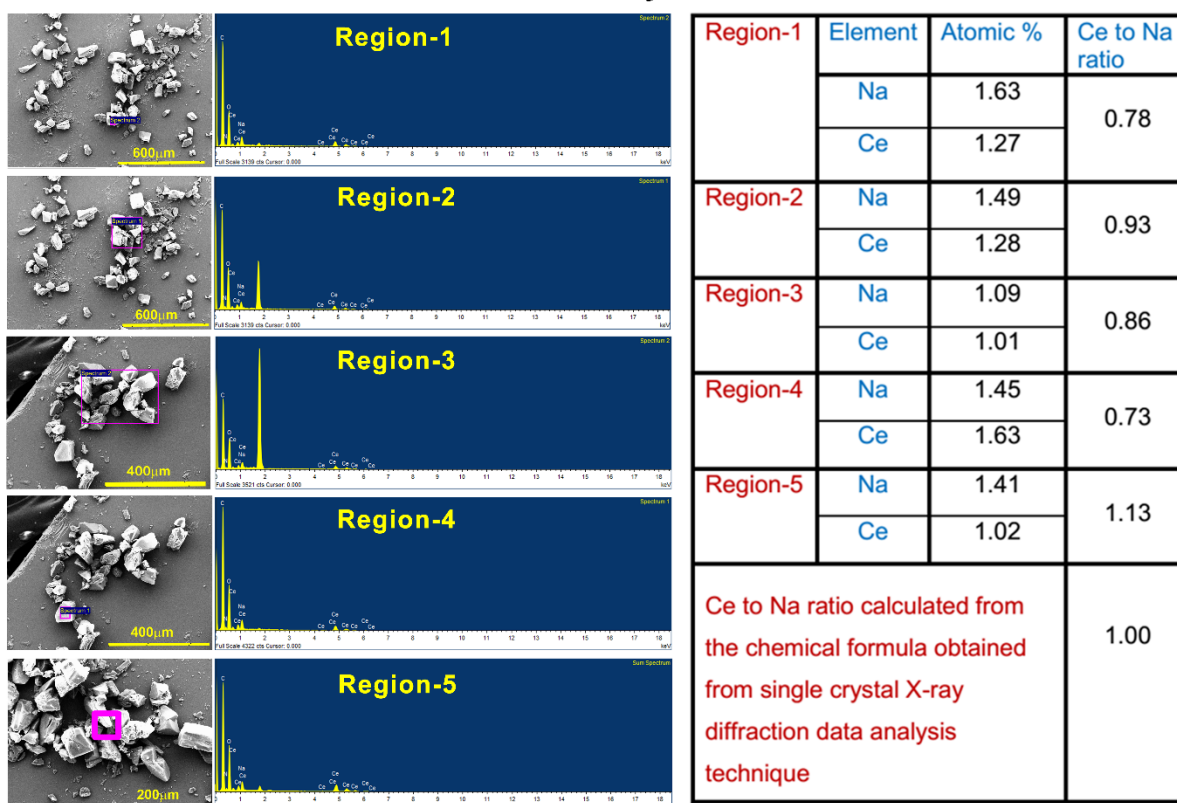


Figure S6. Comparison of the Ce to Na ratio of IISERP-MOF24 from SEM-EDX analysis with that obtained from single crystal X-ray analysis data.

Table-S2. EDAX elemental analysis data

Element	C		N		O		Na		Ce	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
Region-1	51.92	64.92	3.78	4.06	29.97	28.13	2.49	1.63	11.84	1.27
Region-2	46.91	59.40	5.12	5.56	33.94	32.27	2.24	1.49	11.78	1.28
Region-3	47.55	58.75	6.65	7.04	34.62	32.11	1.69	1.09	9.50	1.01
Region-4	49.01	63.34	3.55	3.93	30.56	29.65	2.14	1.45	14.74	1.63
Region-5	49.40	60.87	6.36	6.73	32.40	29.97	2.20	1.41	9.65	1.02

4. Adsorption Analysis

For all gas adsorption analysis was carried out using ~100 mg of IISERP-MOF24. Sample was soaked in THF for 3 days, followed by an evacuation at 150 °C for 12 hrs (10^{-6} mbar) till an outgas rate was ≤ 2 μ bar/min was achieved. Then the sample was transferred to the analysis port of Micromeritics ASAP 2020HD or 3-FLEX instrument. Gas analyses were performed using 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 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):

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

Dual-Site Langmuir (DSL):

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

Ideal Adsorbed Solution Theory (IAST):

IAST calculations were undertaken as described by Prausnitz *et al.*^{S3} The selectivity equation involved in calculation is provided below.

Selectivity:

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

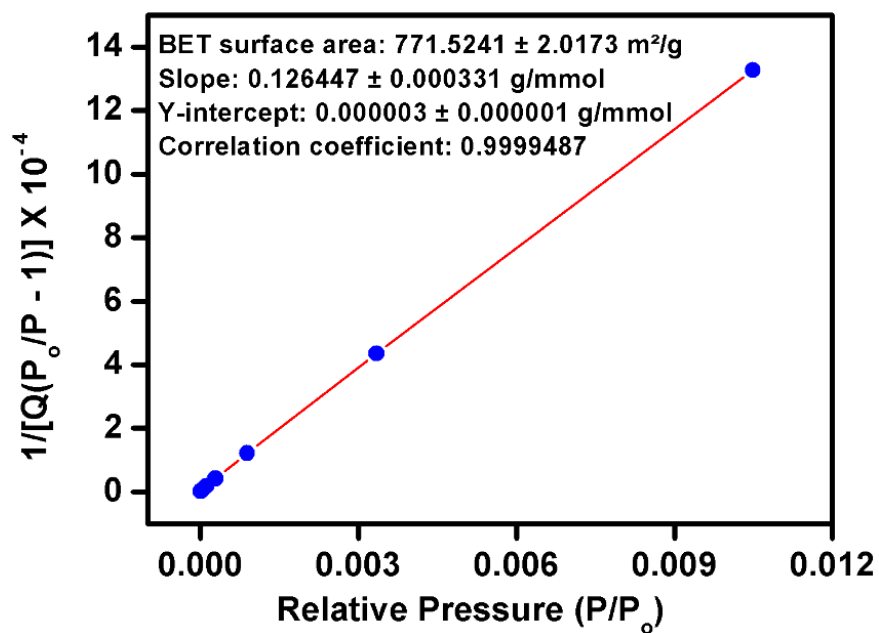


Figure S6. BET fit for the IISERP-MOF24 from the 77 K N₂ isotherm data.

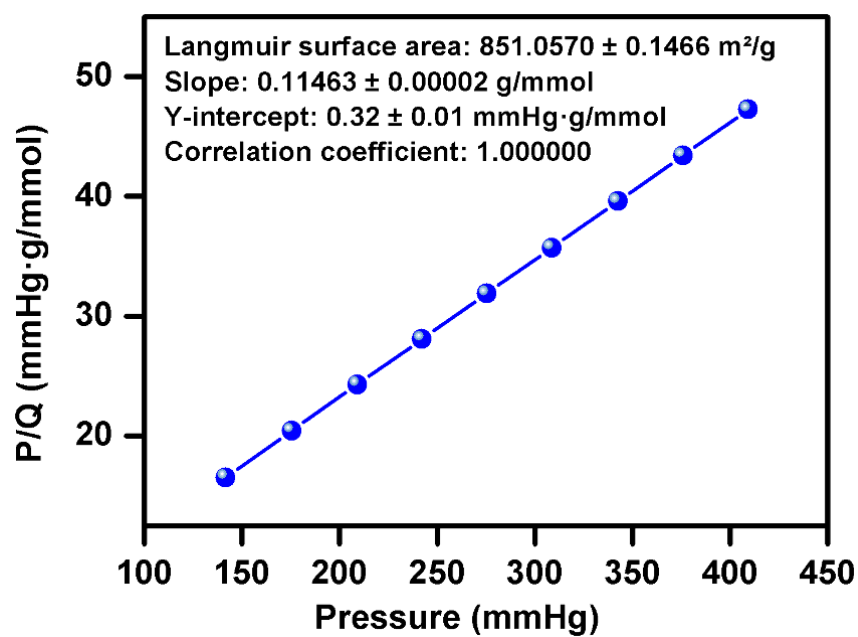


Figure S7. Langmuir fit for the IISERP-MOF24 from the 77 K N₂ isotherm data.

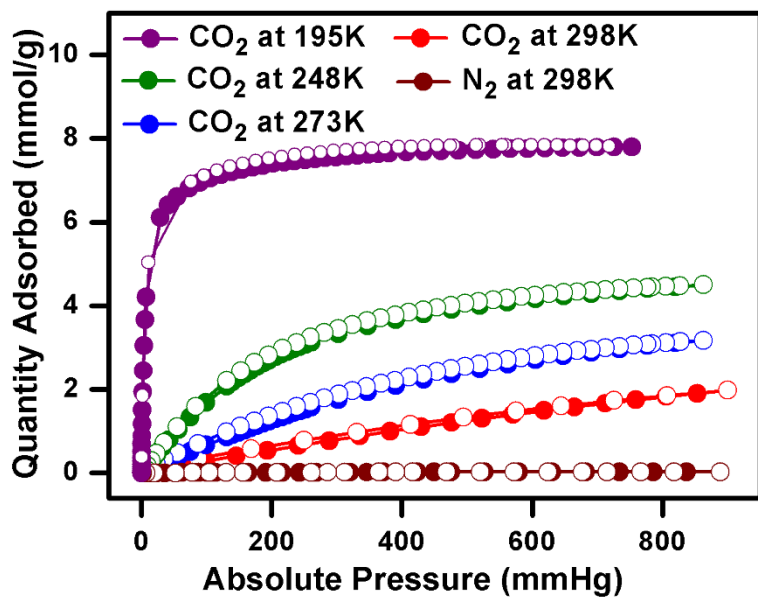


Figure S8. CO₂ isotherms collected at 195, 248, 273 and 298 K along with N₂ isotherms collected at 298K.

Remark: At 298 K, there is no uptake of N₂; whereas there is significant uptake of CO₂. So, IISERP-MOF24 selectively physisorbs CO₂ over N₂.

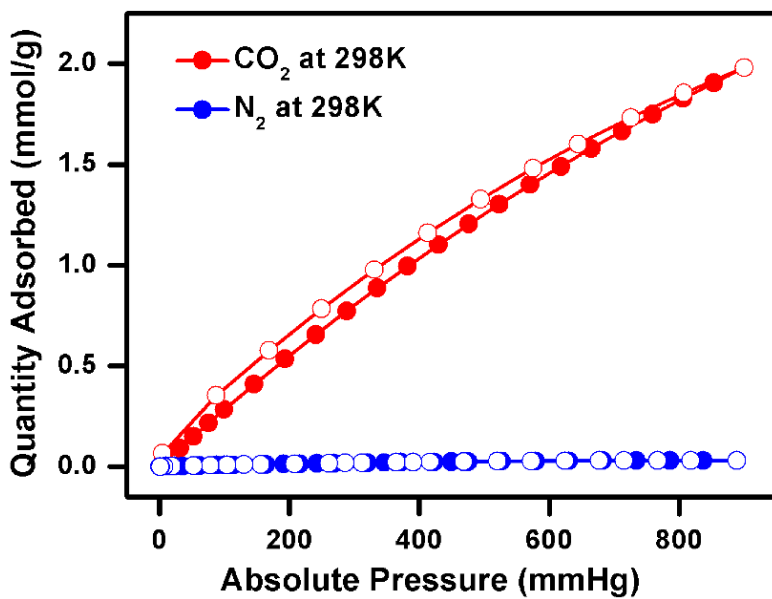


Figure S9. CO₂ and N₂ adsorption isotherms at 298 K showing the selectivity of IISERP-MOF24 towards CO₂ at 298 K and 1 bar.

Virial analysis:

Heat of adsorption for CO₂ in IISERP-MOF24 was obtained by fitting the Virial equation (Equ. (1)) to the CO₂ adsorption isotherms measured from 0- 1 bar at 248, 273 and 298 K.

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

Where, P is pressure, V_a is amount adsorbed, T is temperature, and A₀, A₁, A₂ ... , A₆ and B₀, B₁ are temperature independent empirical parameters.

Table S3: Summary of the fitted Virial parameters for IISERP-MOF24.

A0	-2674.227686
A1	-379.4005948
A2	68.13796624
A3	3.61670552
A4	2.581397795
A5	-1.118482926
A6	0.161750942
B0	15.15554664
B1	1.248964199
B2	-0.181475587
B3	0.01295927
B4	-0.008084079

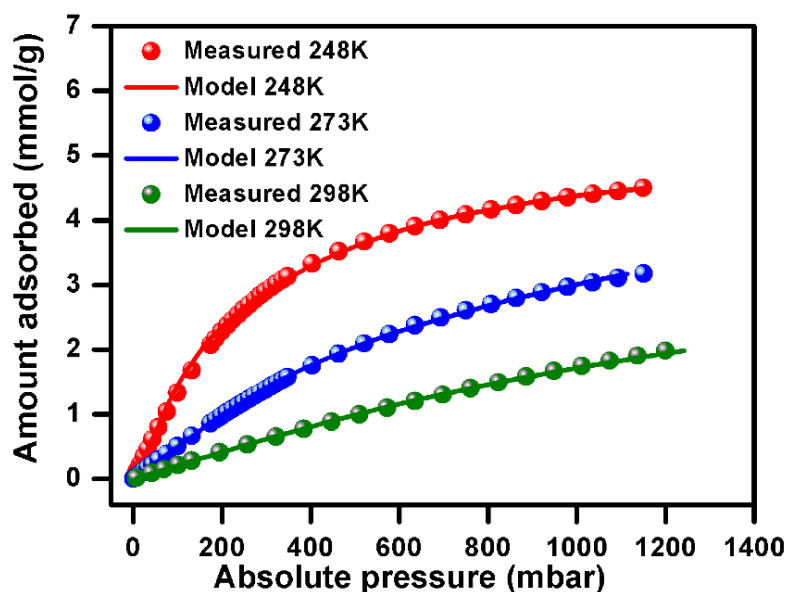


Figure S10. Comparison of experimental isotherms to the ones obtained from Virial modelling carried out using CO₂ isotherms collected at 248, 273, and 298 K.

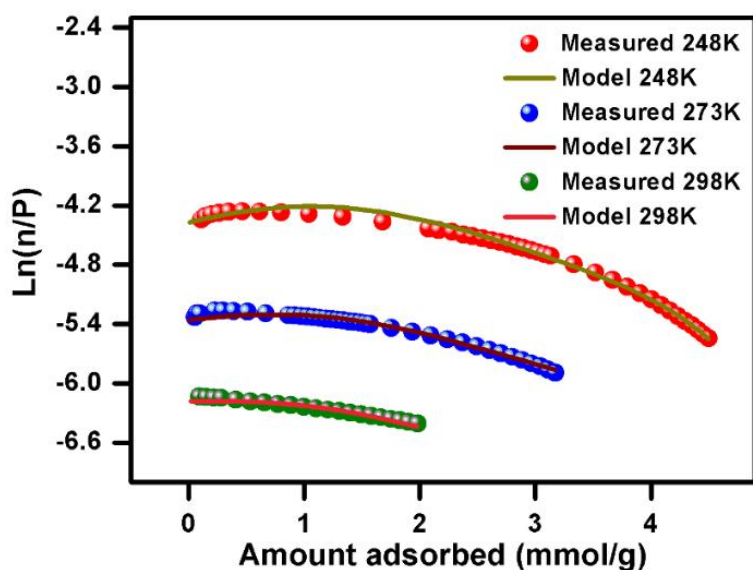


Figure S11. Virial fits for the CO₂ isotherms collected at 248, 273, and 298 K.

IAST selectivities:

CO₂/N₂ selectivity was calculated for IISERP-MOF24 using the experimental single component CO₂ and N₂ isotherms and ideal adsorbed solution theory (IAST) with a nominal composition of 15CO₂:85N₂ (conditions of relevance to post combustion CO₂ capture). A total pressure of 1 bar and temperatures of 298 K & 273 K were employed. IISERP-MOF24 has a CO₂/N₂ selectivity of 67 and 105. This unusually high selectivity is due to ultra-low nitrogen uptake for the MOF at these temperatures.

IAST fitting parameters for IISERP-MOF24 (CO₂/N₂):

At 273K

Gas A =CO₂

Gas B = N₂

Gas Mixture			
YA =	0.15		
YB =	0.85		
Gas A Constants		Gas B Constants	
qA1 =	4.993007085	qA1 =	0.06135295
qA2 =	0	qA2 =	0
kA1 =	0.000624444	kA1 =	0.00024766
kA2 =	0	kA2 =	0
na1 =	1.127025588	na1 =	1.37724099
na2 =	0	na2 =	0
HA1 =	0	HB1 =	0
HA2 =	0	HB2 =	0

At 298K

Gas A =CO₂

Gas B = N₂

Gas Mixture			
YA =	0.15		
YB =	0.85		
Gas A Constants		Gas B Constants	
qA1 =	6.458188067	qA1 =	0.03890991
qA2 =	0	qA2 =	0
kA1 =	0.00027967	kA1 =	0.00033726
kA2 =	0	kA2 =	0
na1 =	1.03926659	na1 =	1.31047808
na2 =	0	na2 =	0
HA1 =	0.001806162	HB1 =	1.3123E-05
HA2 =	0	HB2 =	0

With increase of the temperature, thermal energy of the gas molecules increases and the difference in binding energies of CO₂ and N₂, which are reasonably constant with respect to temperature, becomes less significant, and the selectivity gradually decreases. That is why selectivity at 298 K is less than 273 K. Again, there is a difference of CO₂/N₂ selectivities at low pressures between two different temperatures (273 K & 298 K) because at low pressure region at 273 K first selectivity decreases and then increases at high pressure region whereas at 298 K the selectivity increases from starting onwards. This is probably due to temperature effect on the framework. Since, BPDC units act as a pillaring agent its two phenyl rings can flip around the C-C single bond under the partial pressure of CO₂ at room temperature to bring a gatepass for CO₂ entrance from starting onwards while at 273 K the flipping of phenyl rings are restricted due to low energy input which creates obstacle for CO₂ entrance at low pressure region. At high pressure region at 273 K the CO₂ partial pressure is high enough to bring gatepass for CO₂ entrance and that is why selectivity increases gradually. The selectivity increases in both the cases as there is various types of interactions such as CO₂-framework, CO₂...Na⁺ and CO₂...CO₂ interactions.

CO₂ cycling Experiment Procedure:

Isotherm cycling experiments were done using ASAP 2020HD instrument associated with Iso-Cycling software. About 100 mg of samples were loaded in the sample cell and activated until the outgas rate was $\leq 2 \mu\text{bar}/\text{min}$. The iso-cycling program was created with 15 cycles, each cycle having 14 to 15 data points (equilibration time 100 sec) in between 0.015 bar to 1.2 bar. After each cycle, the material was maintained under vacuum for 10 mins before continuing the subsequent cycles.

Rate of adsorption studies- CO₂ self-diffusion coefficients calculations and analysis Diffusion coefficient determination from Rate of Adsorption (ROA) measurements:

Rate of adsorption (ROA) experiments were carried out on the Micromeritics ASAP2020HD instrument equipped with a ROA software capabilities. An extremely high resolution isotherm measurement was carried out using the ASAP2020HD instrument at 273 K in the pressure range of 0-1 bar. The diffusion coefficient was calculated as a function of CO₂ loading. For this purpose, 8 different loading points were used and each of the ROA data was fitted to a spherical pore model⁵⁴ F = fractional uptake; τ = non-dimensional time given by $\tau = Dt/R^2$, where R = particle size; t = time (secs); D = apparent diffusivity. The single-component diffusion coefficient was estimated to be $8.1932 \times 10^{-9} \text{ m}^2/\text{s}$ for IISERP-MOF24 taking the average of these eight points. Note: the kinetics of the low loadings (< 1 mmol/g) were extremely hard to model.

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \text{Exp}(-n^2\pi^2\tau)$$

5. Stability studies

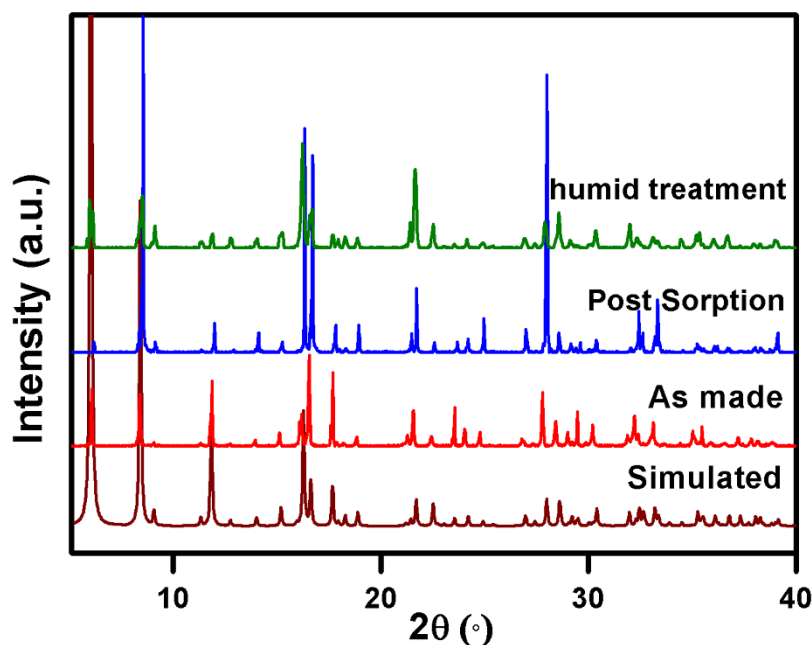


Figure S12. PXRD comparisons indicating the complete retention of crystallinity by IISERP-MOF24 following repeated heating and cooling during multiple gas adsorption runs followed by exposure to open atmosphere. For the humid treatment, the sample was exposed to a humid stream of N₂ (75%RH) for about 12 hrs.

IISERP-MOF24 has excellent shelf-life - complete retention of porosity even after 6 months on the shelf.

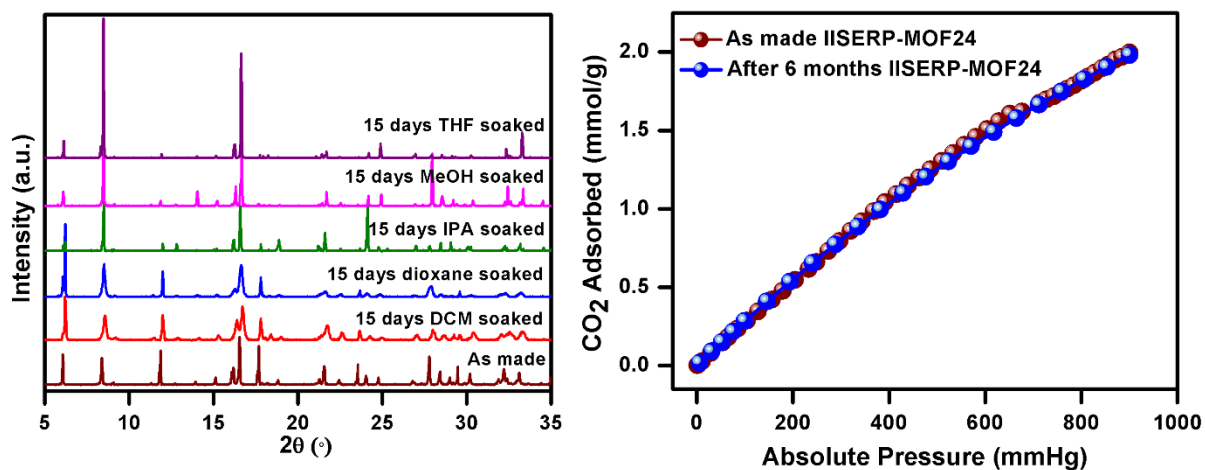


Figure S13. Stability studies: left: PXRDs showing the exceptional solvent stability of IISERP-MOF24, Right: IISERP-MOF24 retains complete porosity even after 6 months keeping on shelf.

The complete retention of crystallinity was also observed in the microscopic crystal images of IISERP-MOF24 for pre- & post- sorption treated samples.

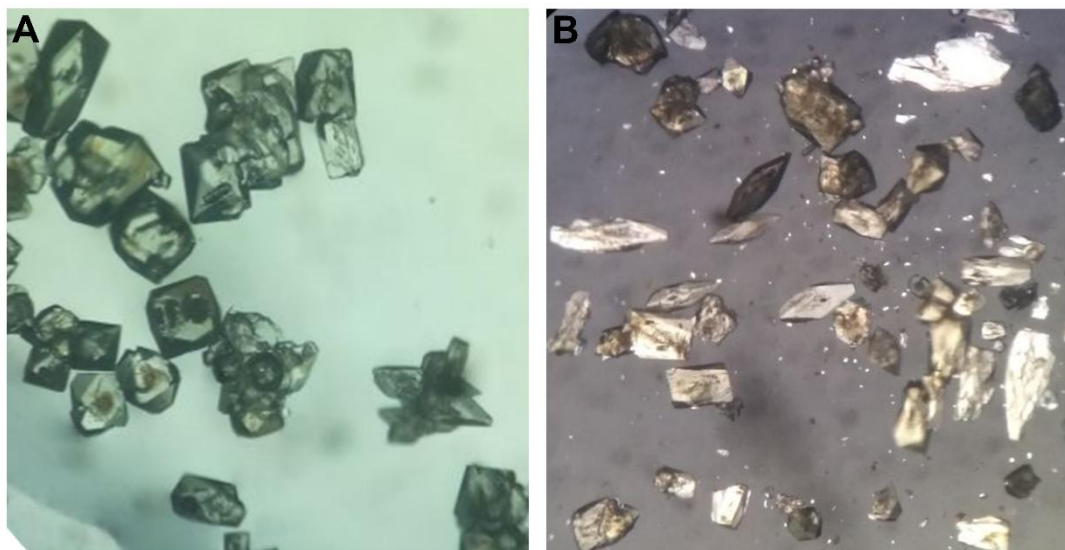


Figure S14. Optical microscopic images showing comparisons between the state of (A) pre-sorption and (B) post-sorption sample of IISERP-MOF24.

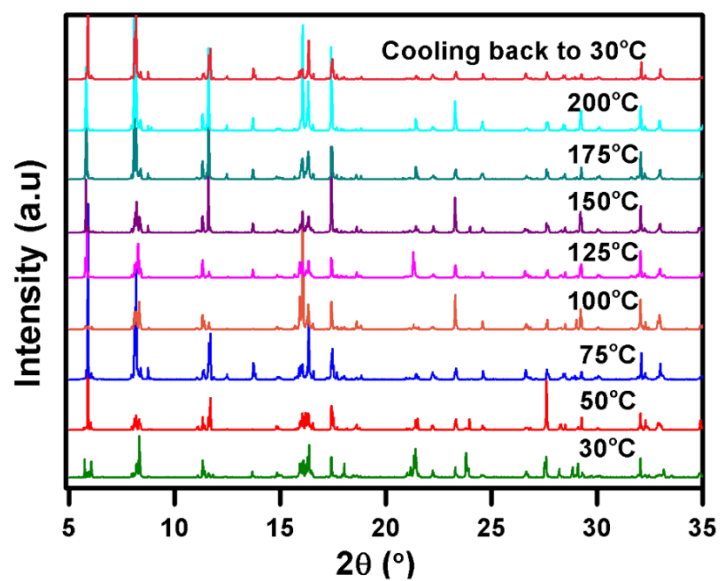


Figure S15. Variable temperature PXRD for displaying complete retention of crystallinity to temperatures as high as 200 °C.

6. Simulation Studies:

All the simulations have been carried out using Material Studio program V.6.0 (Accelrys). The adsorption isotherms were simulated using the Grand Canonical Monte Carlo routine embedded in the Materials Studio V6 software. For this, considering that CO₂ is a small probe with no torsional degree of freedom, a Metropolis algorithm was employed. Universal force field was used. The isotherm simulations were carried out over three times and the error bars were calculated. The simulated isotherm matched well with the experimental one (Fig. S16). From this GCMC simulated structure, the most probable densities of CO₂ were found to be well distributed in the entire pore space. For the binding site location, the framework was frozen and the CO₂ molecules were allowed to find the again using the GCMC routine. An automated temperature control and Universal force field were used with about 1000000 steps per cycle. Applying rotational and translation freedom did not make much of a change in the positions or the orientations in the minimized structure. Energy distribution, density and energy field were all optimized. The CO₂ positions were obtained from the lowest energy configuration have been shown in Figure 4.

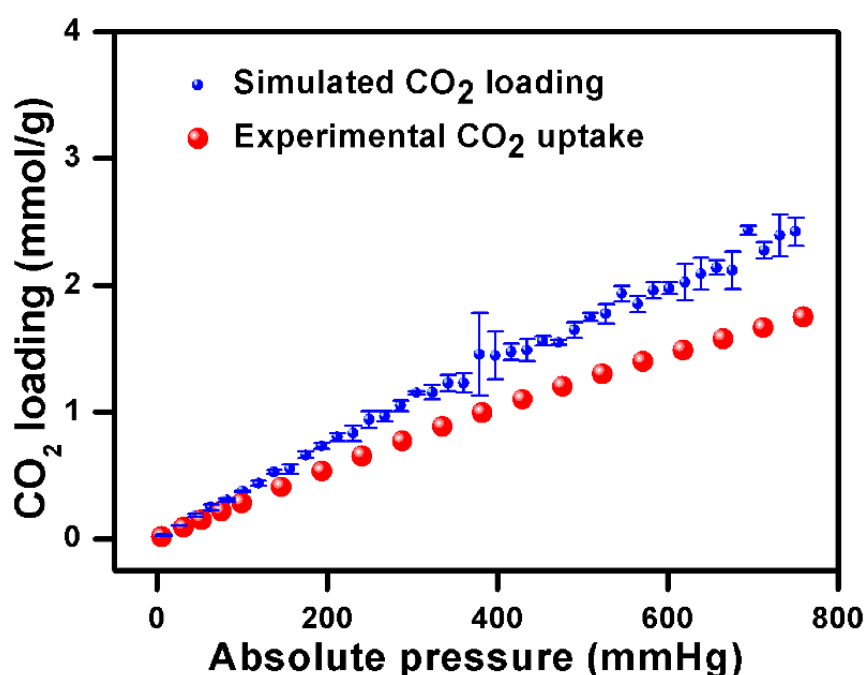


Figure S16. Experimental and simulated CO₂ adsorption isotherms of IISERP-MOF24 at 298 K (0 to 1 bar). The isotherms were simulated using the Grand Canonical Monte Carlo methods embedded in the Materials Studio V6.

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