

## Electronic Supplementary Information

### A Charge-Separated Diamondoid Metal-Organic Framework

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**1. Materials and Methods:** All reagents and solvents were used as received from Sigma-Aldrich or VWR unless otherwise noted. Ether, acetonitrile (CH<sub>3</sub>CN), triethylamine (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were distilled over calcium hydride (CaH<sub>2</sub>) followed by degassing through several freeze-pump-thaw cycles before use. NMR experiments, including 300.13 MHz proton, 96.25 boron and 282.23 MHz fluorine spectra, were recorded on a Bruker Advance III 300 MHz solution spectrometer. The 125.76 MHz carbon spectrum was recorded on a Bruker Advance 500 MHz solution spectrometer. Proton and carbon NMR spectra were referenced with respect to internal solvent signals. Boron and fluorine NMR were externally referenced to BF<sub>3</sub>•Et<sub>2</sub>O (δ = 0 ppm) and C<sub>6</sub>F<sub>6</sub> (δ = -164.9 ppm) respectively. Single crystal X-ray data were collected on a Bruker Kappa APEX II CCD system equipped with a graphite monochromator and a Mo K-α fine-focus tube (λ = 0.71073 Å). Powder XRD was recorded on a Rigaku Smart Lab Diffractometer in Bragg-Brentano mode using Cu K-α radiation (λ = 1.54 Å) at room temperature. All gas adsorption isotherms were measured on a Quantachrome Autosorb AS1 instrument. UHP grade gases were used for the gas adsorption analysis. Before the analysis, about 100 mg of sample was outgassed for 25 hours at 60 °C. Liquid nitrogen was used as a cooling bath to maintain the temperature of 77 K. Other temperatures were maintained by using water bath. To confirm the accuracy of the results, all gas adsorption experiments were repeated 3 times. Thermogravimetric analysis was carried out using a TA SDT Q600 TGA/DSC instrument at a heating rate of 2 °C/minute from room temperature to 600°C under nitrogen.

#### 2. Synthetic procedures

Compounds **1–3** were synthesized according to literature procedures.<sup>1</sup>

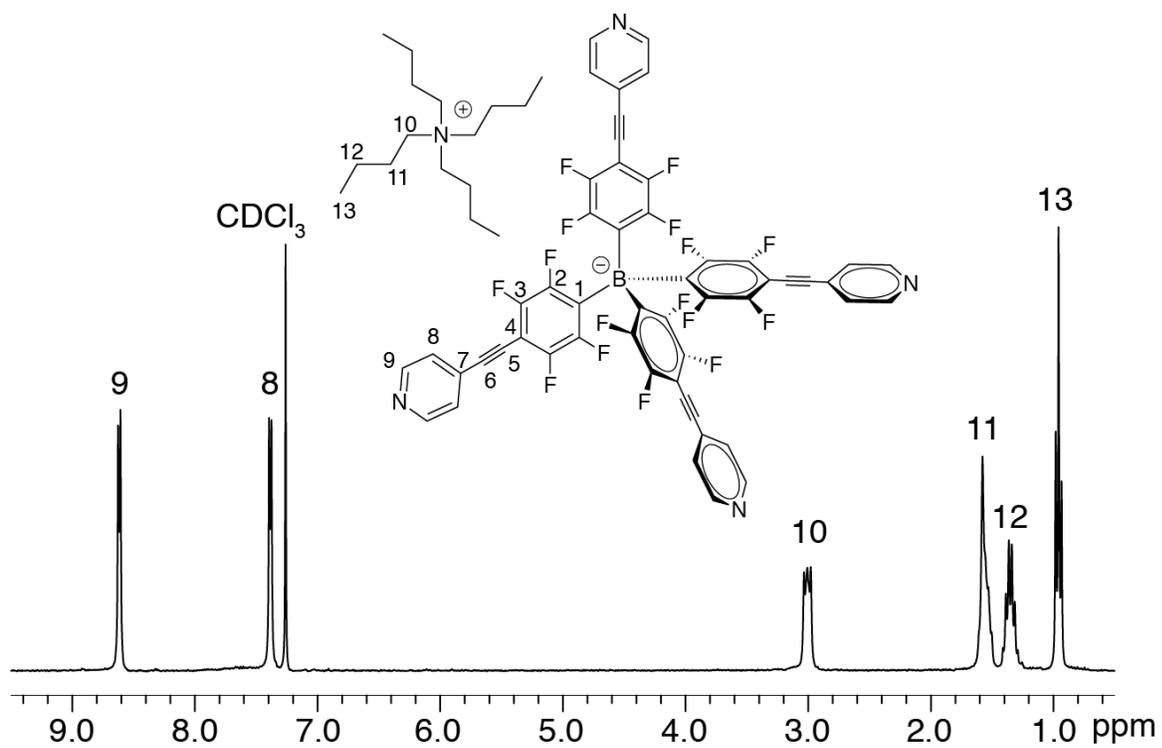
Compound **1** (Triisopropyl((2,3,5,6-tetrafluorophenyl)ethynyl)silane, C<sub>17</sub>H<sub>22</sub>F<sub>4</sub>Si). 11.45 g (50 mmole) of 3-bromo-1,2,4,5-tetrafluorobenzene, 10.032 g (55 mmole, 1.1 eq.) of TiPS-acetylene, 0.95 g (5 mmole, 10%) of CuI, 2.88 g (2.5 mmole, 5%) of Pd(PPh<sub>3</sub>)<sub>4</sub> were dissolved in a 16:1 mixture of toluene and Triethyl amine (80 mL toluene and 5 mL TEA) in a pressure vessel under argon. The reaction mixture was heated at 80°C overnight. Solvent was evaporated and the compound was dissolved in 500 mL of hexane and filtered through silica. After the evaporation of solvent, the compound was further purified by distillation to yield 12 g (72.6 %) of pure compound as a colorless liquid. <sup>1</sup>H NMR: (CDCl<sub>3</sub>, 298 K) δ ppm 7.06 (m, 1H), 1.56 (m, 2H), <sup>19</sup>F NMR: (CDCl<sub>3</sub>, 298 K) δ ppm, -134.88 (m, 2F), -137.68 (m, 2F).

Compound **2** (Lithium tetrakis(2,3,5,6-tetrafluoro-4-((triisopropylsilyl)ethynyl)phenyl)borate C<sub>68</sub>H<sub>84</sub>BF<sub>16</sub>LiSi<sub>4</sub>). 5g (15.13 mmole) of **1** was dissolved in 100 mL anhydrous diethyl ether in a Schlenk flask under argon. Then 6 mL (15 mmole, 2.5M in hexane, 1 eq.) of nBuLi was added dropwise to the reaction mixture at -78°C under nitrogen. The reaction was stirred continuously for two hours and then 3.8 mL

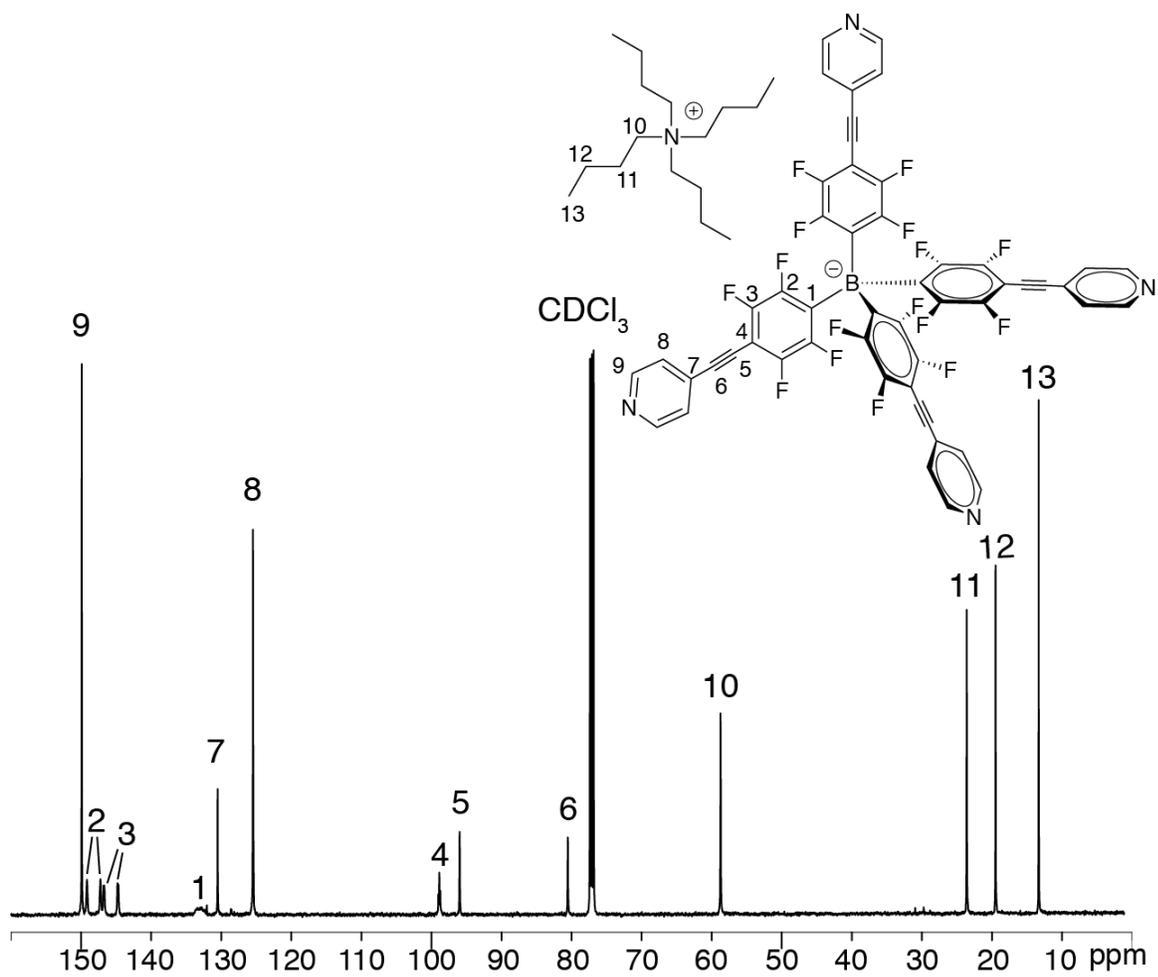
(3.8 mmole, 1M in heptane, 0.25 eq.) of  $\text{BCl}_3$  was added to the reaction at  $-78^\circ\text{C}$ . The reaction was stirred for 2 hours at  $-78^\circ\text{C}$  and then warmed up to the room temperature and stirred overnight forming a white suspension. After evaporating the solvent, the white solid obtained was dissolved in a little amount of methylene chloride and precipitated in hexane to afford 3.59 g (71.23%) of pure compound as a white powder.  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ , 298 K)  $\delta$  ppm, 1.113 (m, 84 H),  $^{11}\text{B}$  NMR: ( $\text{CDCl}_3$ , 298 K)  $\delta$  ppm, -16.48,  $^{19}\text{F}$  NMR: ( $\text{CDCl}_3$ , 298 K)  $\delta$  ppm, -131.39 (s, 8F), -139.28 (s, 8F).

Compound **3** (Tetrabutylammonium tetrakis(4-ethynyl-2,3,5,6-tetrafluorophenyl)borate  $\text{C}_{48}\text{H}_{40}\text{BF}_{16}\text{N}$ ). 2.78 g (2.08 mmole) of **2** was dissolved in 30 mL of THF and mixed with 3.26 g (12.48 mmole, 6 eq.) of tetrabutyl ammonium fluoride (TBAF). The reaction was stirred overnight at room temperature. Solvent was evaporated under vacuum to obtain a white colored solid which was dissolved in 250 mL of methylene chloride. Then the compound was filtered through silica and pumped under vacuum to evaporate the solvent. The residue obtained was dissolved in a little amount of methylene chloride and precipitated in hexane to afford 1.34 g (68.36%) of pure compound as a white colored powder.  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ , 298 K):  $\delta$  ppm, 3.44 (s, 4H), 2.96 (m, 8H), 1.54 (m, 8H), 1.15 (m, 8 H), 0.95 (t, 12 H).  $^{11}\text{B}$  NMR: ( $\text{CDCl}_3$ , 298 K):  $\delta$  ppm, -16.45.  $^{19}\text{F}$  NMR: ( $\text{CDCl}_3$ , 298 K)  $\delta$  ppm, -130.27 (s, 8F), -139.62(s, 8F).

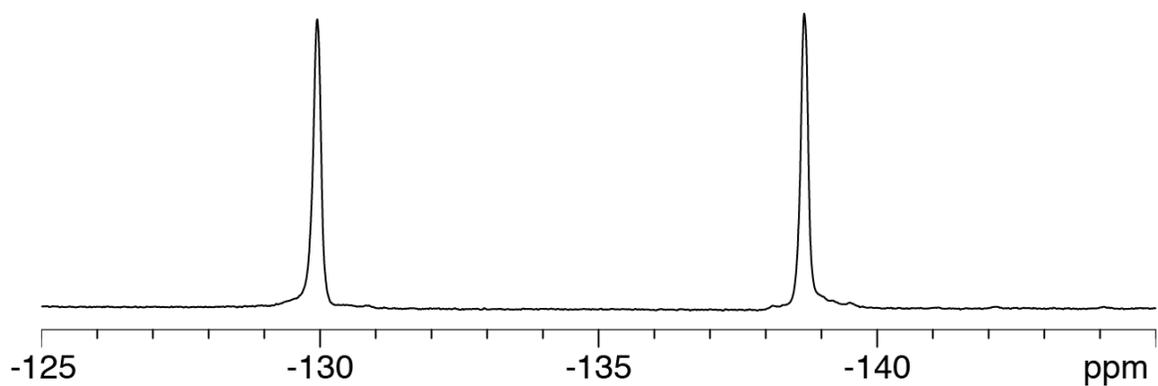
Compound **4** (Tetrabutylammonium tetrakis(pyridine-4-ethynyl-2,3,5,6-tetrafluorophenyl)borate  $\text{C}_{68}\text{H}_{52}\text{BF}_{16}\text{N}_5$ ). Compound **3** (400 mg, 0.42 mmol), 4-bromopyridine hydrochloride (351 mg, 1.806 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (24 mg, 0.021 mmol), and  $\text{CuI}$  (7 mg, 0.042 mmol) were dissolved in a mixture of triethylamine (1.5 mL) and  $\text{CH}_3\text{CN}$  (6 mL) into a pressure vessel equipped with a magnetic stir bar under argon. The vessel was sealed and immersed into an oil bath preset at  $90^\circ\text{C}$  with stirring for 24 h. The reaction mixture was then cooled to room temperature, diluted with a large excess of 1:5 dichloromethane:hexane mixture, and stirred for 6 hours. After filtration, the residue obtained was recrystallized from methanol and water to afford borate **4** as a light yellow compound (380 mg, 73% yield).  $^1\text{H}$  NMR: (300.13 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  (ppm) = 8.62 (d,  $^3J_{\text{HH}} = 6$  Hz, 8H), 7.39 (d,  $^3J_{\text{HH}} = 6$  Hz, 8H), 3.01(m, 8H), 1.58 (m, 8 H), 1.36 (m, 8H), 0.95 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 12 H).  $^{13}\text{C}$  NMR: (125.76 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  (ppm) = 13.3, 19.5, 23.6, 58.7, 80.5, 96.0, 98.9 (t,  $^2J_{\text{CF}} = 14$  Hz), 125.5, 130.5, 132-134 (br), 145.7 (d,  $^1J_{\text{CF}} = 255$  Hz), 148.2 (d,  $^1J_{\text{CF}} = 241$  Hz), 149.9.  $^{11}\text{B}$  NMR: (96.25 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  (ppm) = -16.32.  $^{19}\text{F}$  NMR (282.40 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  (ppm) = -129.94 (s, 8F), -139.69(s, 8F).



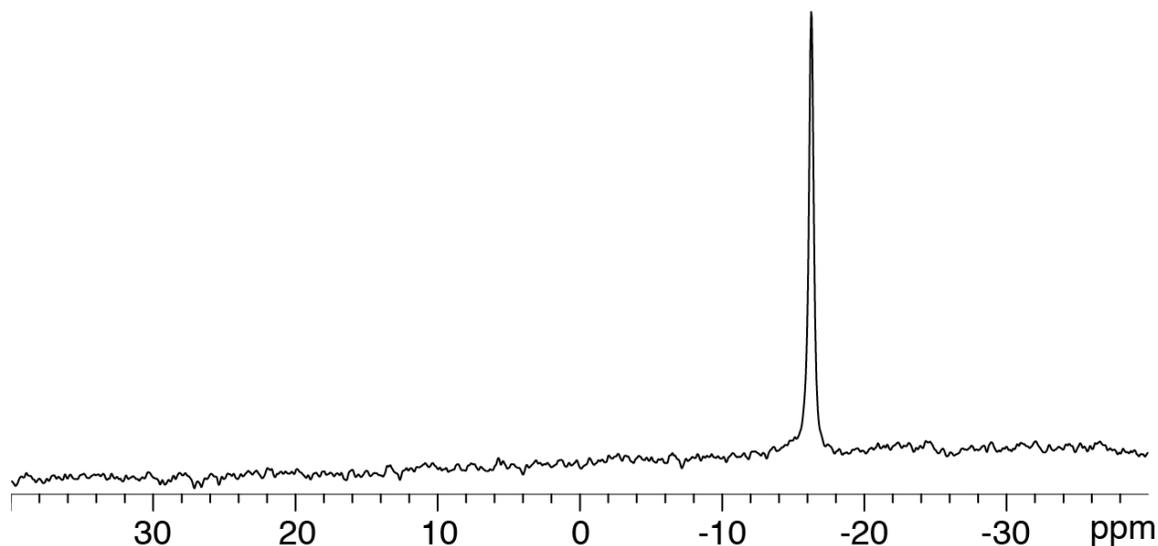
**Figure S1.**  $^1\text{H}$  NMR spectrum of **4** in  $\text{CDCl}_3$ .



**Figure S2.**  $^{13}\text{C}$  NMR spectrum of **4** in  $\text{CDCl}_3$ .



**Figure S3.**  $^{19}\text{F}$  NMR spectrum of **4** in  $\text{CDCl}_3$ .



**Figure S4.**  $^{11}\text{B}$  NMR spectrum of **4** in  $\text{CDCl}_3$ .

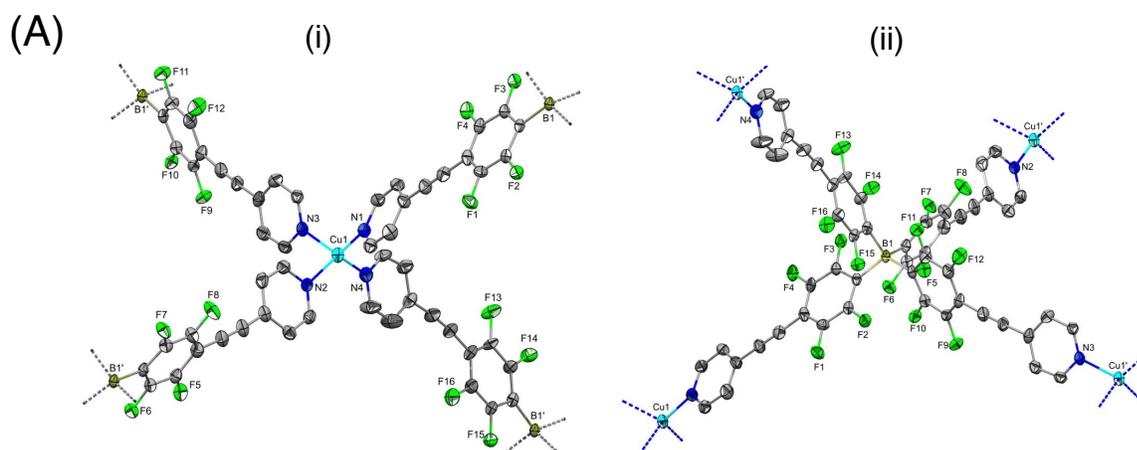
**Synthesis of UNM-1.** A solution of borate **4** (20 mg, 0.015 mmol) in 1 mL of  $\text{CH}_2\text{Cl}_2$  was placed in a long 20 mL glass vial and 7 mL of  $\text{CH}_3\text{CN}$  was layered on the top. Then a solution of 15 mg of  $(\text{CH}_3\text{CN})_4\text{CuBF}_4$  (0.045 mmol, 3 eq.) in 1 mL of  $\text{CH}_3\text{CN}$  was added on the top of the two layers. The contents were mixed slowly under argon. After 3 days orange colored needle shaped crystals were obtained. The crystals were washed several times with acetonitrile, dichloromethane and air dried to obtain 12 mg (74.4%) of **UNM-1** for single crystal X-ray diffraction and gas adsorption analysis.

### 3. Single crystal X-ray Diffraction.

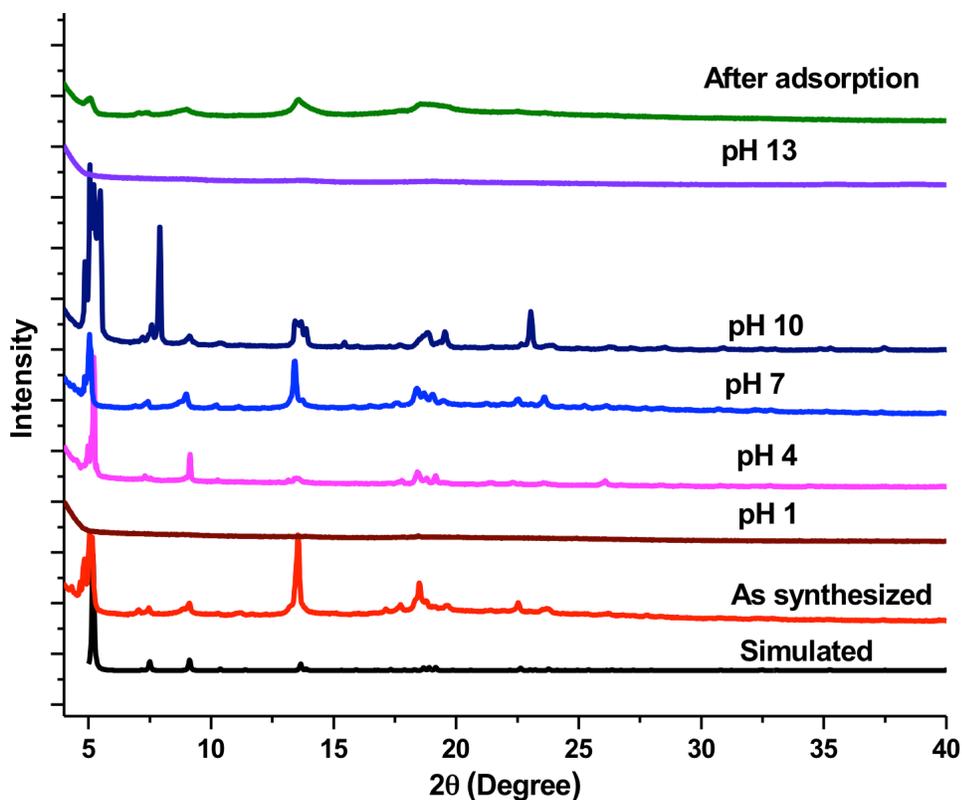
A single crystal of **UNM-1** was coated with Paratone oil and mounted on a MiTeGen Micro Loop that had been previously attached to a metallic pin using epoxy for the X-ray crystallographic analysis. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The structure was solved and refined using the Bruker SHELXTL Software Package. Non-hydrogen atoms were refined anisotropically. Solvent accessible voids were accounted for by SQUEEZE. Crystal data, structure refinements and crystal structure are given below.

**Table S1.**

<b>Chemical formula</b>	C <sub>52</sub> H <sub>16</sub> BCuF <sub>16</sub> N <sub>4</sub>	
<b>Formula weight</b>	1075.04 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71073 Å	
<b>Crystal size</b>	0.380 x 0.428 x 0.488 mm	
<b>Crystal system</b>	tetragonal	
<b>Space group</b>	I -4	
<b>Unit cell dimensions</b>	a = 23.5586(7) Å	α = 90°
	b = 23.5586(7) Å	β = 90°
	c = 24.6516(9) Å	γ = 90°
<b>Volume</b>	13681.8(10) Å <sup>3</sup>	
<b>Z</b>	8	
<b>Density (calculated)</b>	1.044 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	0.392 mm <sup>-1</sup>	
<b>F(000)</b>	4272	
<b>Theta range for data collection</b>	2.10 to 25.71°	
<b>Index ranges</b>	-24<=h<=28, -28<=k<=24, -30<=l<=24	
<b>Reflections collected</b>	31438	
<b>Independent reflections</b>	12964 [R(int) = 0.0408]	
<b>Coverage of independent reflections</b>	99.8%	
<b>Absorption correction</b>	Multi-Scan	
<b>Max. and min. transmission</b>	0.8650 and 0.8320	
<b>Function minimized</b>	Σ w(F <sub>o</sub> <sup>2</sup> - F <sub>c</sub> <sup>2</sup> ) <sup>2</sup>	
<b>Data / restraints/ parameters</b>	12964 / 0 / 668	
<b>Goodness-of-fit on F<sup>2</sup></b>	0.937	
<b>R<sub>1</sub> (I&gt;2σ(I))</b>	0.0314	
<b>wR<sub>2</sub> (all data)</b>	0.0697	



**Figure S5.** The Coordination environment around (A): (i) Cu (I) atom and (ii): boron atom in the crystal structure of **UNM-1**.



**Figure S6.** PXRD patterns of **UNM-1**, from bottom to top: simulated from single crystal XRD data (black), as synthesized (red), sample after soaking for 48 h in HCl solutions of pH 1 (maroon) and pH 4 (pink), neutral water (pH 7, blue), NaOH solutions of pH 10 (nacy blue) and pH 13 (purple) and, after all adsorption experiments (green).

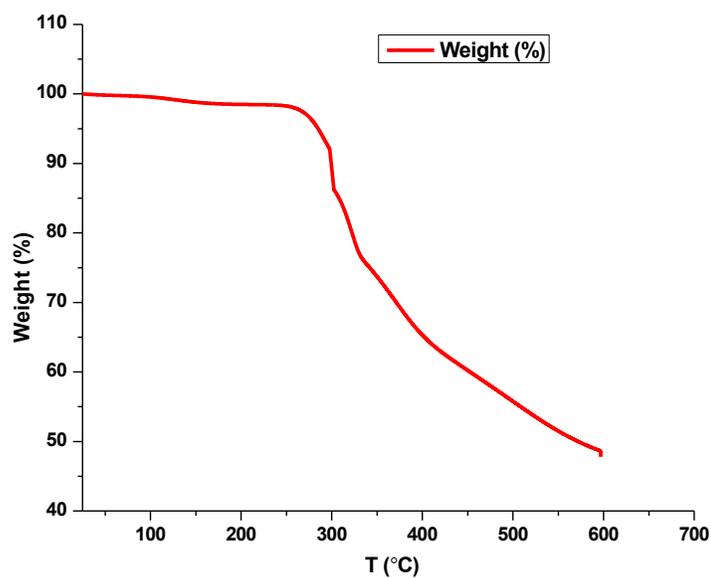


Figure S7. Thermogravimetric analysis (TGA) histogram of **UNM-1** under N<sub>2</sub> environment.

#### 4. Surface area and pore size measurement

**A. Surface Area Determination:** The surface area of **UNM-1** is determined by 7 points N<sub>2</sub> - BET isotherm and Langmuir isotherms using gaseous nitrogen as an adsorbate at 77 K.

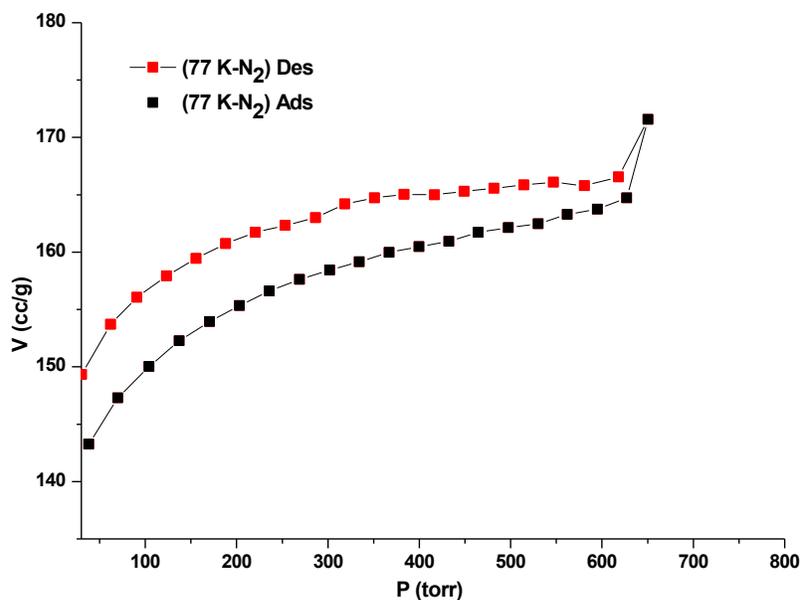


Figure S8. N<sub>2</sub> adsorption/desorption isotherm of **UNM-1** at 77 K.

**Brunauer-Emmett-Teller (BET)** method: The BET equation used for the surface area determination is given as:

$$\frac{1}{W(P_0/P) - 1} = \frac{1}{W_m C} + \frac{C - 1}{W_m C} \left( \frac{P}{P_0} \right) \quad (\text{Eq. 1})$$

W = weight of gas adsorbed, P/P<sub>0</sub> = relative pressure, W<sub>m</sub> = weight of adsorbate forming a monolayer and C is the BET constant, which is related to the magnitude of the adsorbent/adsorbate interactions. Using nitrogen as the adsorbate, the linear plot of 1/[W(P<sub>0</sub>/P)-1] vs P/P<sub>0</sub> gave the surface area of 621 m<sup>2</sup>/g for **UNM-1 (Figure S9, top)**

**Langmuir method:** Langmuir equation used for the surface area calculation is given below:

$$\frac{W}{W_m} = \frac{C(P/P_0)}{1 + C(P/P_0)} \quad (\text{Eq. 2})$$

Where W is the weight of adsorbate, W<sub>m</sub>= weight in a monolayer at P/P<sub>0</sub> respectively. C is the constant associated with the energy of adsorption. Equation (2), in the form of a straight line can be written as:

$$\frac{P/P_0}{W} = \frac{1}{CW_m} + \frac{P/P_0}{W_m} \quad (\text{Eq. 3})$$

For surface area determination (P/P<sub>0</sub>)/W is linearly plotted as a function of P/P<sub>0</sub>. The Langmuir surface area of **UNM-1** was found to be 915 m<sup>2</sup>/g (Figure S9, bottom).

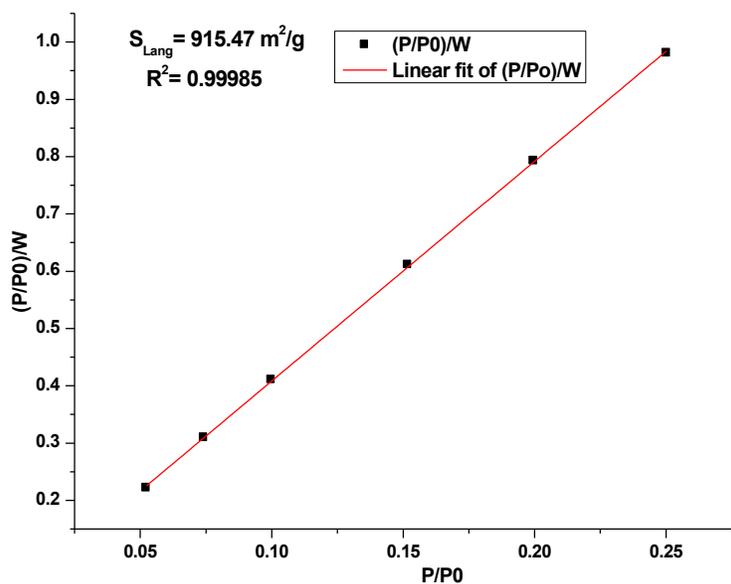
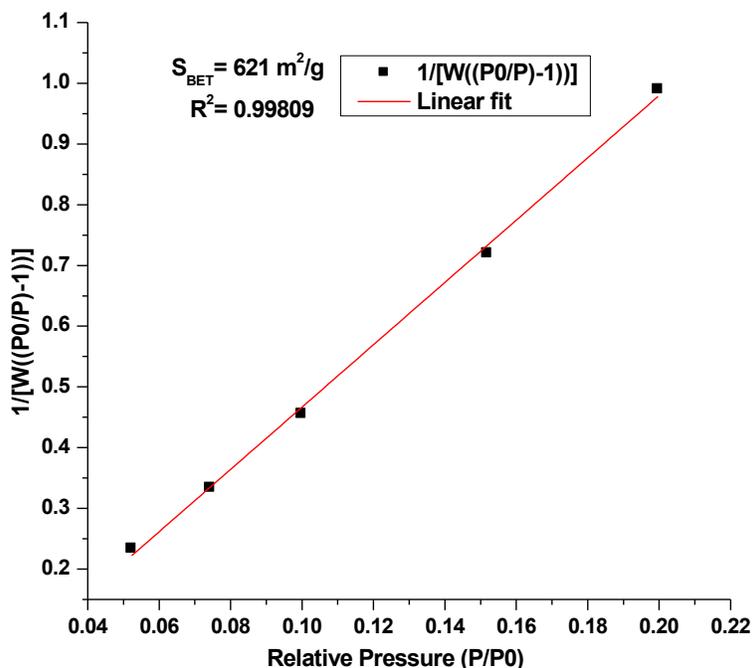
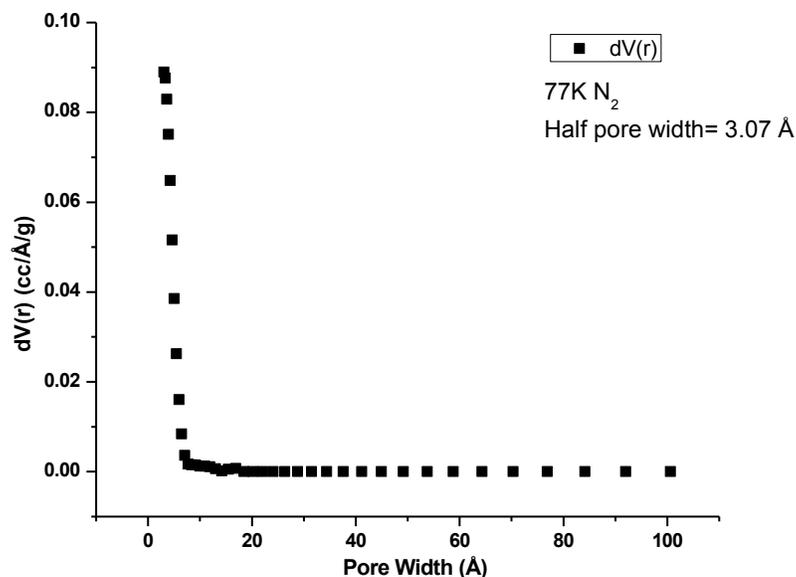


Figure S9. BET (top) and Langmuir (bottom) plots of  $\text{N}_2$  adsorption of **UNM-1** at 77K.

## 5. Pore size measurement

Pore size of **UNM-1** was estimated by fitting  $\text{N}_2$  adsorption isotherm at 77 K using non-local density functional theory (NLDFT). Here,  $\text{N}_2$  adsorption at 77K on carbon for slit pore was used as the calculation model with QSDFT (Quenched Solid Density Functional Theory) equilibrium model as the kernel in the Quantachrome AS1Win software. QSDFT has the advantage on the contrary to regular NLDFT, as it

considers surface roughness and heterogeneity. This model is applicable to micro/meso porous materials with 0.35 nm to 40 nm.



**Figure S10.** Pore size distribution of **UNM-1** obtained by fitting the  $N_2$  adsorption isotherm at 77 K using non-local density functional theory (NLDFT).

## 6. $CO_2/N_2$ adsorption selectivity calculation by using Binary Mixture selectivity calculation (Ideal adsorbed solution theory, IAST)

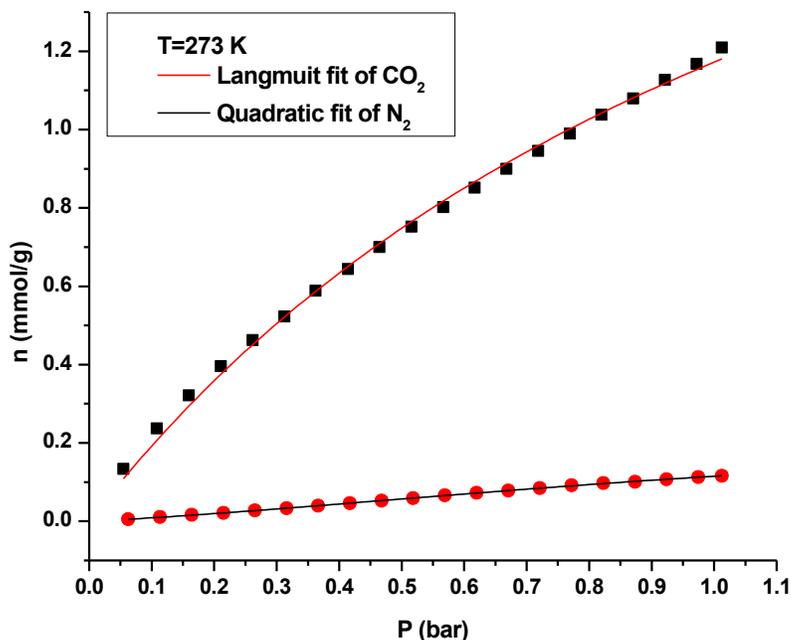
IAST is a thermodynamic model developed by Myer and Prausnitz which predicts the multicomponent adsorption isotherm from pure component adsorption isotherm at same temperature.<sup>2</sup> This method is widely used for the adsorption selectivity calculation of metal organic framework and covalent organic framework. By using IAST, adsorption selectivity is calculated as:

$$S_{a/b} = \frac{x_a/y_a}{x_b/y_b} \quad (Eq. 4)$$

Where,  $x_a$  and  $y_a$  are the mole fraction of component 'a' in adsorbed and gas phase. Similarly,  $x_b$  and  $y_b$  are the mole fraction of component 'b' in adsorbed and gas phase.

Based on previous work,<sup>3-5</sup> the ideal flue gas mixture containing 15%  $CO_2$  and 85%  $N_2$  is assumed for calculation by using the pyIAST code developed by Cory M. Simon<sup>6</sup> at 273 K, 298 K, 303 K, 313K and 323 K. Below are the results obtained by pyIAST calculations at different temperatures. The plots shown here are generated by fitting the experimental data to the parameters obtained from pyIAST in Origin software. Note, the  $CO_2$  data is best fitted by using Langmuir model and the  $N_2$  data is best fitted by using the quadratic model.

**A. 273 K**



**Figure S11.** Fitting of CO<sub>2</sub> and N<sub>2</sub> adsorption isotherm at 273 K. Dots represents experimental data, lines are fitting curves.

**Table S2.** N<sub>2</sub> - Quadratic Parameters

M (mmol/g)	K <sub>A</sub> (bar <sup>-1</sup> )	K <sub>B</sub> (bar <sup>-2</sup> )	R <sup>2</sup>
0.139144	0.545797	0.624341	0.99973

$$n(P) = M \frac{(K_A + 2K_B P)P}{1 + K_A P + K_B P^2} \quad (\text{Eq. 5})$$

Where, n is the amount adsorbed (mmol/g), P is the pressure (bar) M is the saturation loading and K<sub>A</sub> (bar<sup>-1</sup>) and K<sub>B</sub> (bar<sup>-2</sup>) are constants.

**Table S3.** CO<sub>2</sub> - Langmuir Parameters

M (mmol/g)	K (bar <sup>-1</sup> )	R <sup>2</sup>
2.703687	0.765012	0.99718

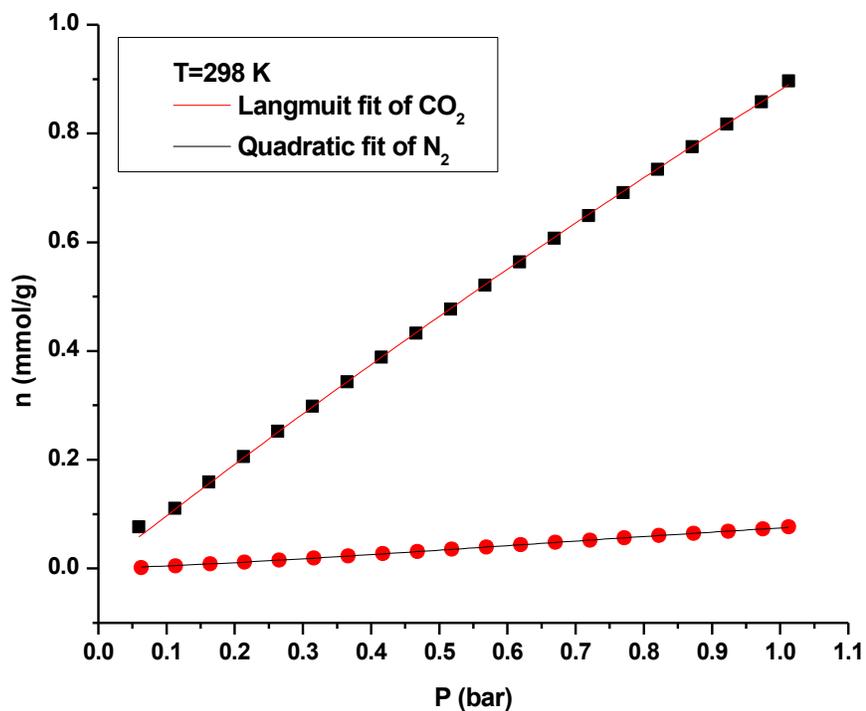
$$n(P) = M \frac{KP}{1 + KP} \quad (\text{Eq. 6})$$

Where n is the amount adsorbed (mmol/g), P is the pressure (bar<sup>-1</sup>) M is the saturation loading and K is a constant.

**Table S4.** IAST adsorption selectivity calculated for mixed gas (15% CO<sub>2</sub> : 85% N<sub>2</sub>) at 273 K

Total Pressure	IAST CO <sub>2</sub> molar fraction	IAST N <sub>2</sub> molar fraction	Selectivity
0.06	0.80103	0.19896	22.8144853
0.11	0.78786	0.21214	21.0452531
0.16	0.77904	0.22096	19.9790007
0.21	0.77308	0.22692	19.3054234
0.26	0.76916	0.23084	18.8813608
0.31	0.76679	0.23321	18.6318911
0.36	0.76559	0.2344	18.5082907
0.41	0.76533	0.23467	18.4807176
0.46	0.76581	0.23419	18.5302105
0.51	0.7669	0.2331	18.6433576
0.56	0.76847	0.23153	18.8082034
0.61	0.77044	0.22956	19.0182378
0.67	0.77323	0.22676	19.3227936
0.72	0.77584	0.22416	19.6128956
0.77	0.77866	0.22134	19.9349718
0.82	0.78165	0.21835	20.2855507
0.87	0.78477	0.21523	20.6617572
0.92	0.78799	0.21201	21.0616323
0.97	0.79131	0.20869	21.4868465
1	0.79332	0.20667	21.7519717

## B. 298 K



**Figure S12.** Fitting of  $\text{CO}_2$  and  $\text{N}_2$  adsorption isotherm at 298 K. Dots represents experimental data, lines are fitting curves.

**Table S5.**  $\text{N}_2$  - Quadratic Parameter

$M$ (mmol/g)	$K_A$ ( $\text{bar}^{-1}$ )	$K_B$ ( $\text{bar}^{-2}$ )	$R^2$
0.110403	0.363959	0.421614	0.99967

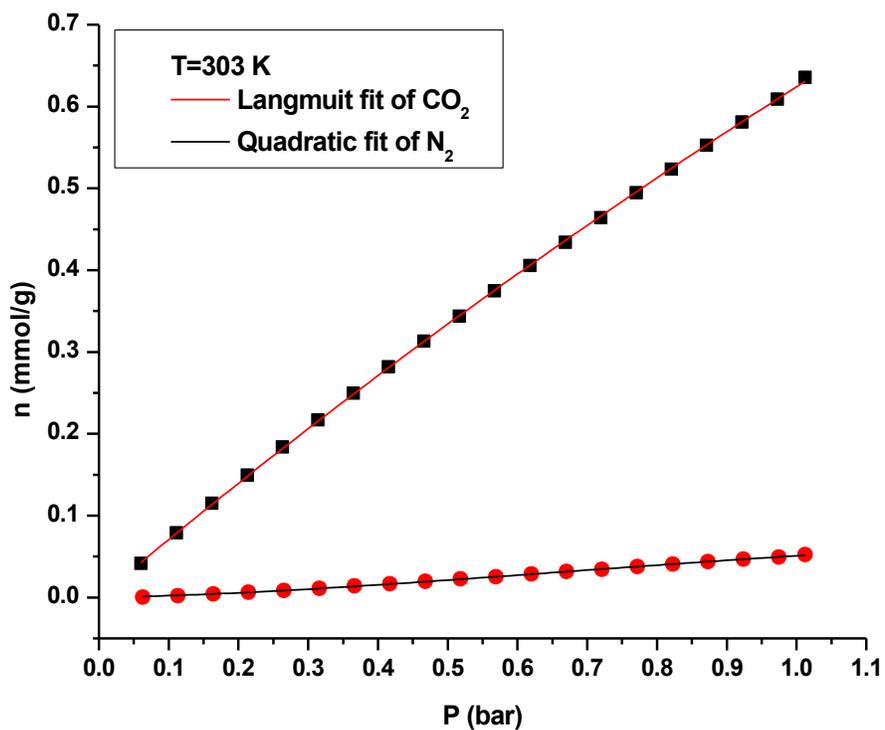
**Table S6.**  $\text{CO}_2$  - Langmuir Parameters

$M$ (mmol/g)	$K$ ( $\text{bar}^{-1}$ )	$R^2$
8.600484	0.113949	0.99963

**Table S7.** IAST adsorption selectivity calculated for mixed gas (15% CO<sub>2</sub> : 85% N<sub>2</sub>) at 298 K.

Total Pressure	IAST CO <sub>2</sub> molar fraction	IAST N <sub>2</sub> molar fraction	Selectivity
0.06	0.78101	0.21899	20.2097052
0.11	0.76445	0.23555	18.3905045
0.16	0.75219	0.24781	17.2003148
0.21	0.74283	0.25717	16.3680445
0.26	0.73559	0.26441	15.7646962
0.31	0.72998	0.27002	15.3194331
0.36	0.72566	0.27424	14.9944331
0.41	0.7224	0.27776	14.7379032
0.46	0.72001	0.27999	14.5721514
0.51	0.71835	0.28165	14.452867
0.56	0.71732	0.28268	14.3795576
0.61	0.71683	0.28327	14.3398054
0.67	0.71683	0.28317	14.3448694
0.72	0.71726	0.28274	14.3753036
0.77	0.71803	0.28197	14.4300339
0.82	0.71908	0.28092	14.5051497
0.87	0.7204	0.2796	14.6003815
0.92	0.72193	0.27807	14.7118951
0.97	0.72366	0.27634	14.8394731
1	0.72479	0.27521	14.9236704

**C. 303 K**



**Figure S13.** Fitting of CO<sub>2</sub> and N<sub>2</sub> adsorption isotherm at 303 K. Dots represents experimental data, lines are fitting curves.

**Table S8.** N<sub>2</sub> - Quadratic Parameter

M (mmol/g)	K <sub>A</sub> (bar <sup>-1</sup> )	K <sub>B</sub> (bar <sup>-2</sup> )	R <sup>2</sup>
0.066380	0.224045	0.580506	0.99948

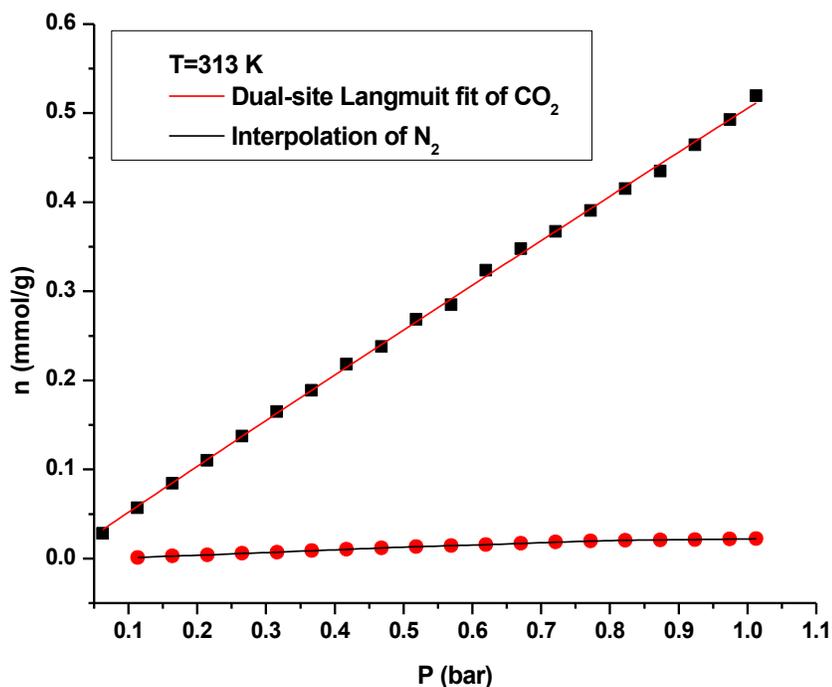
**Table S9.** CO<sub>2</sub> - Langmuir Parameters

M (mmol/g)	K (bar <sup>-1</sup> )	R <sup>2</sup>
4.738390	0.151683	0.99992

**Table S10.** IAST adsorption selectivity calculated for mixed gas (15% CO<sub>2</sub> : 85% N<sub>2</sub>) at 303K.

Total Pressure	IAST CO <sub>2</sub> molar fraction	IAST N <sub>2</sub> molar fraction	Selectivity
0.06	0.83417	0.16583	28.5048745
0.11	0.80811	0.19189	23.8641409
0.16	0.78997	0.21003	21.313606
0.21	0.77655	0.22345	19.69322
0.26	0.76636	0.23364	18.5871711
0.31	0.75858	0.24142	17.8055671
0.36	0.75264	0.24736	17.2419146
0.41	0.74818	0.25182	16.8361793
0.46	0.74491	0.25509	16.5477152
0.51	0.74264	0.25736	16.3518431
0.56	0.7412	0.2588	16.2292633
0.61	0.74046	0.25953	16.1674566
0.67	0.74035	0.25965	16.1575839
0.72	0.7408	0.25201	16.65754
0.77	0.74167	0.25833	16.2692262
0.82	0.74291	0.25709	16.3749011
0.87	0.74445	0.25555	16.5077284
0.92	0.74626	0.25374	16.6659047
0.97	0.74831	0.2517	16.8471328
1	0.74963	0.25037	16.9665029

**D. 313 K**



**Figure S14.** Fitting of CO<sub>2</sub> and N<sub>2</sub> adsorption isotherm at 313 K. Dots represents experimental data, lines are fitting and interpolating curves. N<sub>2</sub> (313 K) adsorption data was linearly interpolated because none of the other available model of pyIAST produced the good fit.

**Table S11.** CO<sub>2</sub> – Dual-Site Langmuir Parameters

M <sub>1</sub> (mmol/g)	M <sub>2</sub> (mmol/g)	K <sub>1</sub> (bar <sup>-1</sup> )	K <sub>2</sub> (bar <sup>-1</sup> )	R <sup>2</sup>
-2.802783	6.146601	-0.047517	0.063223	0.9992

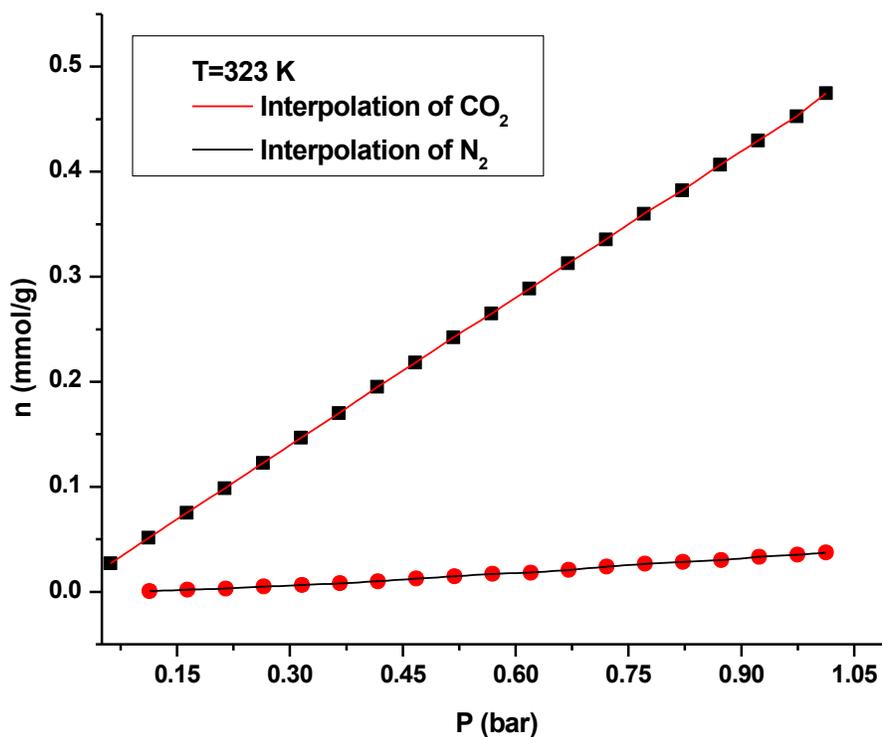
$$n(P) = M_1 \frac{K_1 P}{1 + K_1 P} + M_2 \frac{K_2 P}{1 + K_2 P} \quad (\text{Eq. 7})$$

Where M<sub>1</sub> and M<sub>2</sub> (mmol/g) are the number of adsorption sites of type 1 and type 2. K<sub>1</sub> and K<sub>2</sub> are the constants.

**Table S 12.** IAST adsorption selectivity calculated for mixed gas (15% CO<sub>2</sub> : 85% N<sub>2</sub>) at 313K.

Total Pressure	IAST CO <sub>2</sub> molar fraction	IAST N <sub>2</sub> molar fraction	Selectivity
0.06	0.85075	0.14925	32.3009492
0.11	0.8265	0.1735	26.9942363
0.16	0.81487	0.18513	24.9424549
0.21	0.80942	0.19058	24.0671284
0.26	0.81033	0.18967	24.2097854
0.31	0.81633	0.18367	25.185768
0.36	0.82528	0.17472	26.7661783
0.41	0.83576	0.16424	28.8356876
0.46	0.84694	0.15306	31.3558517
0.51	0.85829	0.14171	34.3211018
0.56	0.86945	0.13051	37.7510025
0.61	0.88035	0.11965	41.6936899
0.67	0.89273	0.10727	47.1595351
0.72	0.90244	0.09756	52.4172475
0.77	0.91156	0.08844	58.4069049
0.82	0.92006	0.07994	65.2198315
0.87	0.92795	0.07205	72.9824196
0.92	0.93524	0.06476	81.8359069
0.97	0.94195	0.05805	91.9503302
1	0.9457	0.0543	98.6918355

**E. 323 K**



**Figure S15.** Fitting of  $\text{CO}_2$  and  $\text{N}_2$  adsorption isotherm at 323 K. Dots represents experimental data, lines are interpolating curves. Both  $\text{N}_2$  (323 K) and  $\text{CO}_2$  (323 K) adsorption data were linearly interpolated because good fit was not obtained by any other model available in pyIAST.

**Table S 13.** IAST adsorption selectivity calculated for mixed gas (15% CO<sub>2</sub> : 85% N<sub>2</sub>) at 323K.

Total Pressure	IAST CO <sub>2</sub> molar fraction	IAST N <sub>2</sub> molar fraction	Selectivity
0.06	0.86208	0.13792	35.4199536
0.11	0.8248	0.1752	26.6773212
0.16	0.80018	0.19982	22.6921896
0.21	0.78123	0.21877	20.235727
0.26	0.76688	0.23311	18.6420717
0.31	0.75576	0.24424	17.5345562
0.36	0.74975	0.25025	16.977356
0.41	0.74797	0.25203	16.8174291
0.46	0.7492	0.2508	16.927698
0.51	0.75259	0.24741	17.2372849
0.56	0.75749	0.24251	17.7000674
0.61	0.76345	0.23655	18.2888043
0.67	0.77154	0.22846	19.1370918
0.72	0.7788	0.22121	19.9502735
0.77	0.78634	0.21366	20.8552217
0.82	0.79404	0.20596	21.8467664
0.87	0.80182	0.19818	22.9268678
0.92	0.80959	0.19041	24.0936751
0.97	0.81729	0.18271	25.3478737
1	0.82186	0.17813	26.1449877

## 7. Calculation of isosteric heat of gas adsorption

Isosteric heat of CO<sub>2</sub> adsorption of **UNM-1** is calculated by the following two methods. The adsorption isotherms measured at 273 K, 298 K and 313 K in the pressure range from 0 to 760 torr are used for the calculation.

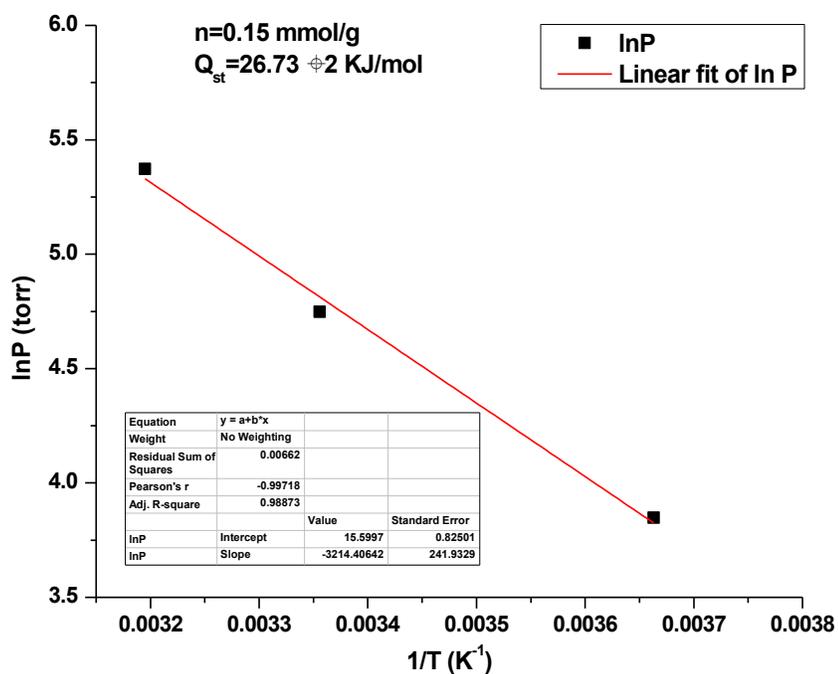
**A. Direct Method.** Clausius-Clayperon equation for the determination of isosteric heat of adsorption ( $Q_{st}$ ) given as:

$$Q_{st} = - \left[ \frac{d \ln P}{d(1/T)} \right] n \quad (Eq. 8)$$

Integration of equation 8 gives:

$$\ln(P)_n = -\frac{(Q_{st}/R)}{(1/T)} + C \quad (Eq. 9)$$

Where P is the Pressure in torr at temperature T in K, n is the amount of gas adsorbed in mmol/g, R is universal gas constant and C is a constant. The corresponding value of 'P' at each given 'n' is determined from the fitted isotherm at 273 K, 298 K and 313 K. The slope obtained from the linear regression of ln P versus 1/T at a given 'n' is used to calculate Q<sub>st</sub> according to equation 9.<sup>7,8</sup>



**Figure S16.** The Vant' Hoff isochores for CO<sub>2</sub> adsorption on **UNM-1** (n=0.15 mmol/g).

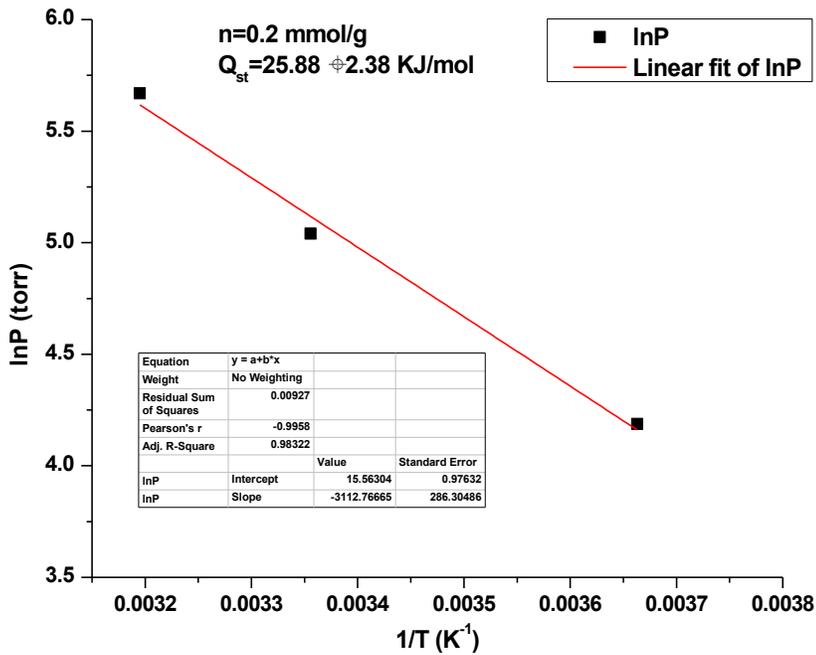


Figure S17. The Vant' Hoff isochores for CO<sub>2</sub> adsorption on **UNM-1** ( $n=0.2 \text{ mmol/g}$ ).

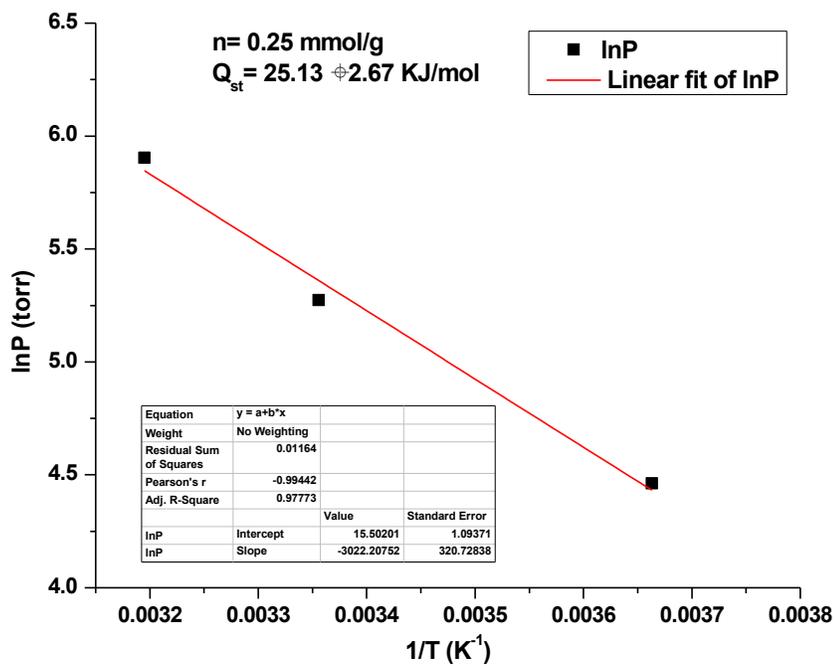


Figure S18. The Vant' Hoff isochores for CO<sub>2</sub> adsorption on **UNM-1** ( $n=0.25 \text{ mmol/g}$ ).

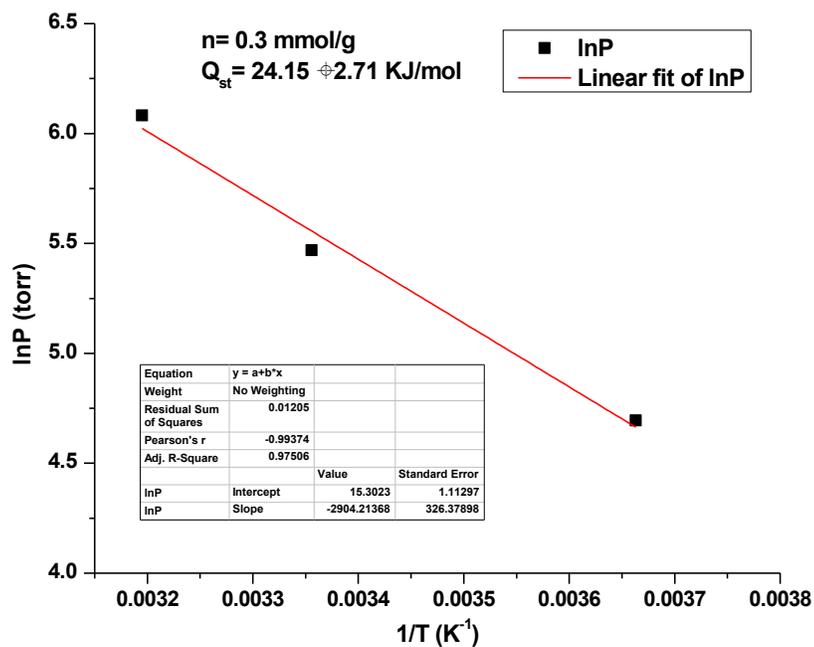


Figure S19. The Vant' Hoff isochores for CO<sub>2</sub> adsorption on **UNM-1** ( $n=0.3 \text{ mmol/g}$ ).

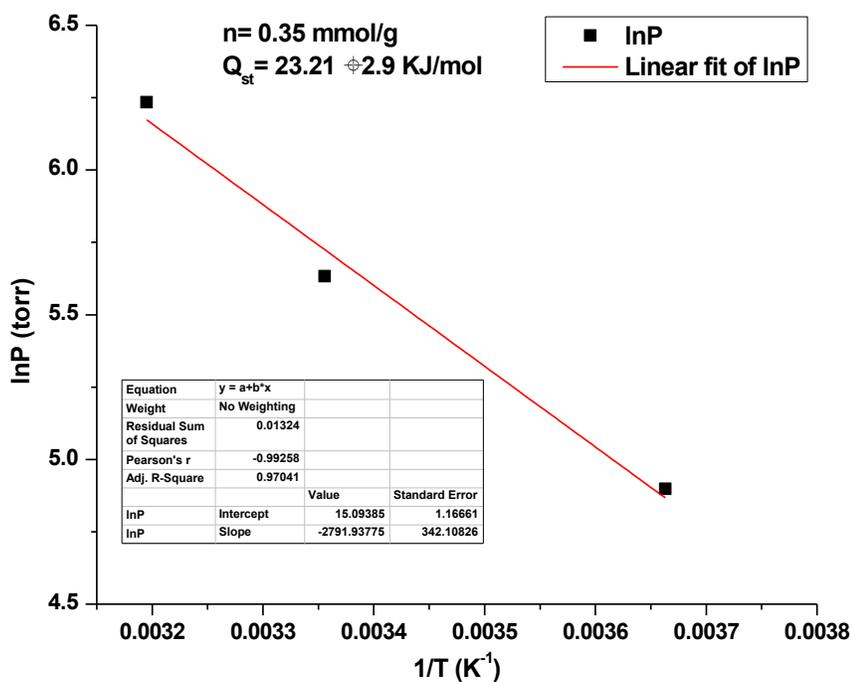


Figure S20. The Vant' Hoff isochores for CO<sub>2</sub> adsorption on **UNM-1** ( $n=0.35 \text{ mmol/g}$ ).

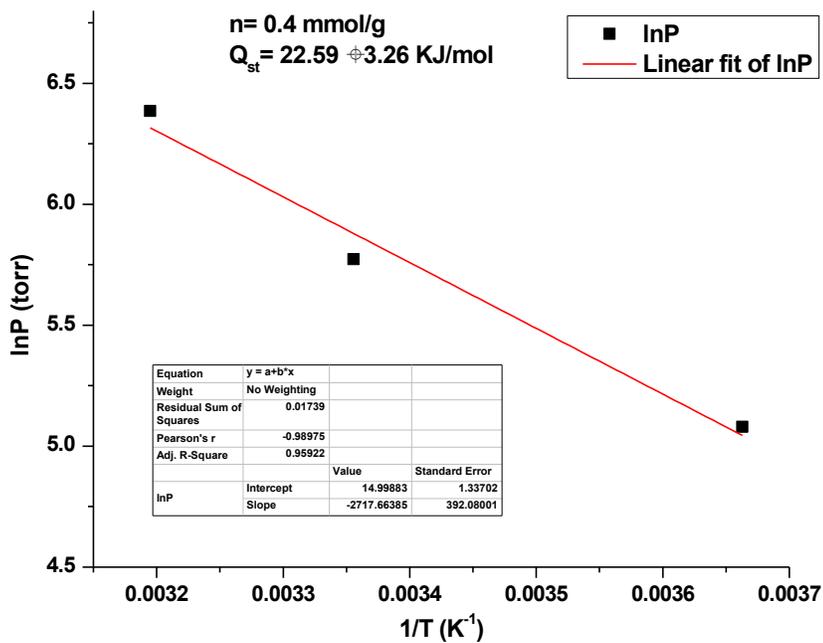


Figure S21. The Vant' Hoff isochores for CO<sub>2</sub> adsorption on **UNM-1** ( $n=0.4 \text{ mmol/g}$ ).

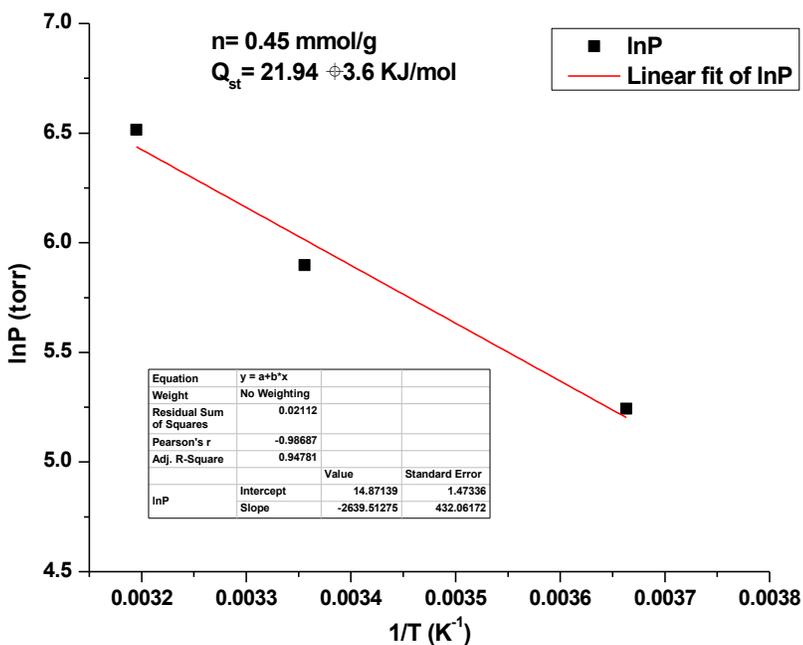


Figure S22. The Vant' Hoff isochores for CO<sub>2</sub> adsorption on **UNM-1** ( $n=0.45 \text{ mmol/g}$ ).

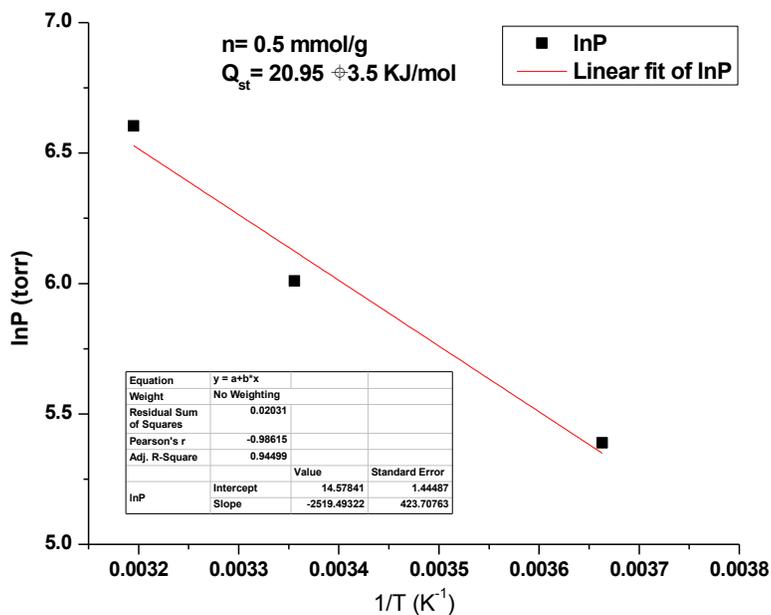


Figure S23. The Vant' Hoff isochores for CO<sub>2</sub> adsorption on **UNM-1** (n=0.5 mmol/g).

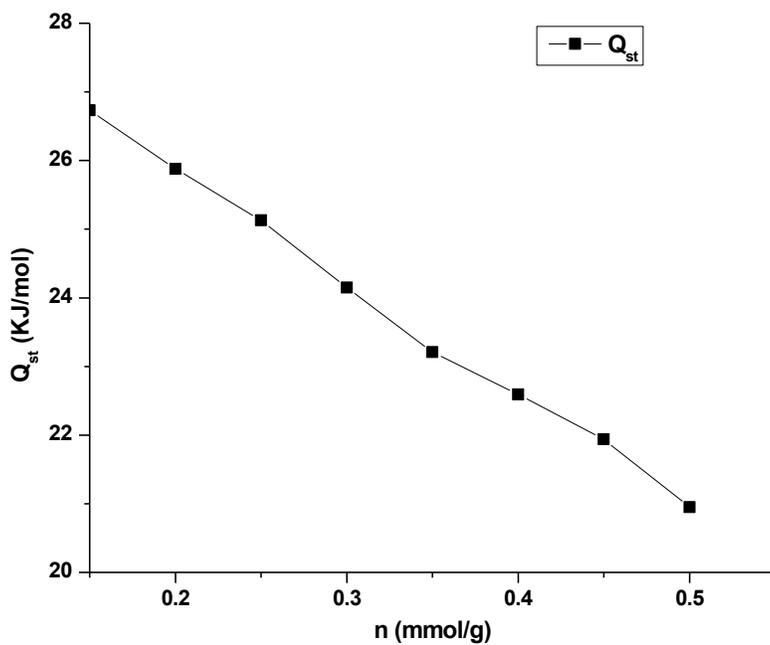


Figure S24. Isosteric heat of CO<sub>2</sub> adsorption for **UNM-1** at different loading calculated by direct method.

## B. Virial Method

The coverage dependent  $Q_{st}$  is determined by fitting the isotherms data to the following 'virial equation':

$$\ln P = \ln n + \frac{1}{T} \sum_{i=0}^m a_i n^i \quad (Eq. 10)$$

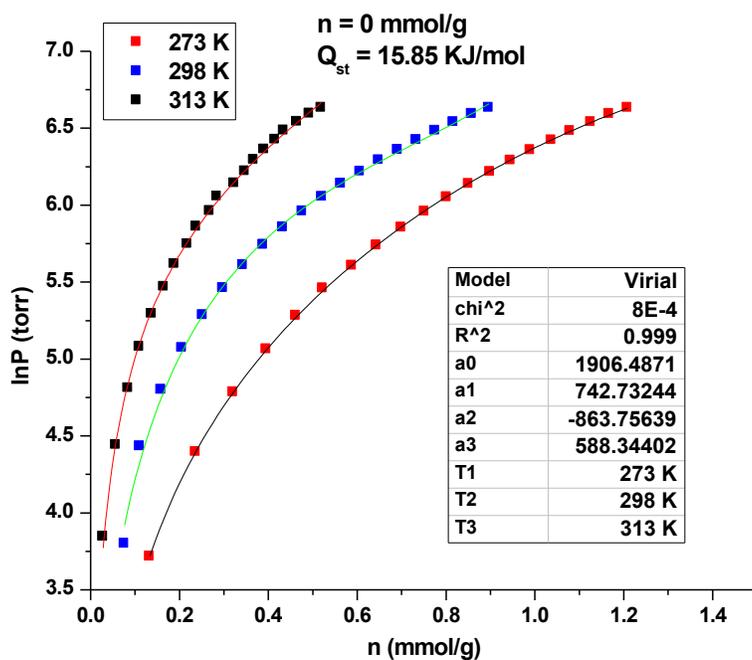
Where,  $n$  is the amount adsorbed in mmol/g at pressure  $P$  (torr) and temperature  $T$  (K).  $a_i$  is the virial coefficient and  $m$  represent the number of coefficients required to adequately describe the isotherms ( $m$  is increased until the best fit is obtained and the average value of the squared deviations is minimized). The values of these virial coefficients are then used to calculate the isosteric heat of adsorption according to the following expression:

$$Q_{st} = -R \sum_{i=0}^m a_i n^i \quad (Eq. 11)$$

' $Q_{st}$ ' at zero coverage is calculated according to equation 12.

$$Q_{st} = -R \sum_{i=0}^m a_0 \quad (Eq. 12)$$

The fitted isotherm and fitting parameters for  $\text{CO}_2$  are given in fig. S25.



**Figure S25.** Virial fitting of  $\text{CO}_2$  adsorption isotherm for **UNM-1**. Experimental data are the dots, lines are fitting and the parameters are given in the table within the plot.

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