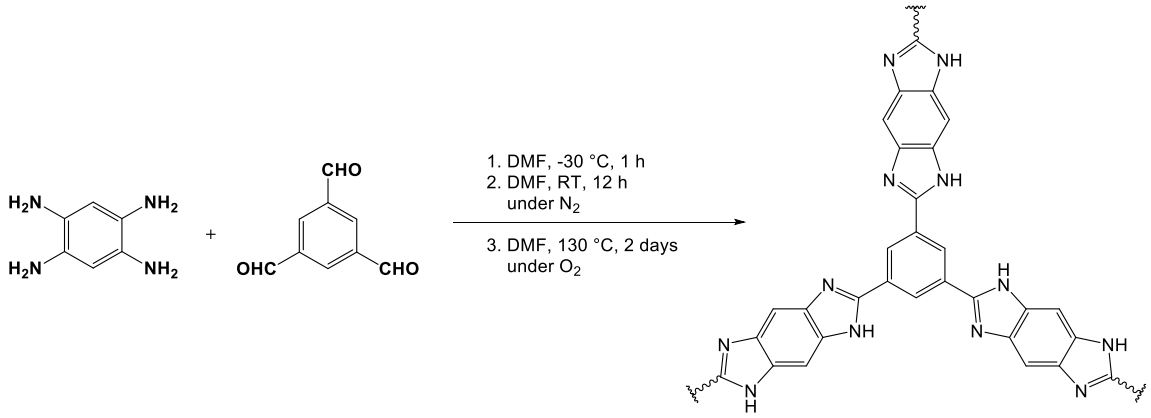
Electronic Supplementary Information

Ultra-Micro Porous Organic Polymer for High Performance Carbon Dioxide Capture and Separation

Ali K. Sekizkardes,*[a] Jeffrey T. Culp,[a,d] Timur Islamoglu, [b] Anne Marti, [a] David Hopkinson, [a] Christina Myers,[a] Hani M. El-Kaderi,[b] and Hunaid B. Nulwala[a,c]

[a.] *U.S. Department of Energy National Energy and Technology Laboratory, Pittsburgh, Pennsylvania 15236, US. Email; ali.sekizkardes@contr.netl.doe.gov Phone: 1 (412) 386-7255.*
[b.] *Department of Chemistry, Virginia Commonwealth University, 1001 W. Main St., Richmond, VA 23284-2006.*
[c.] *Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213.*
[d.] *AECOM PO Box 618 South Park, PA 15219.*

Scheme S1: Reaction scheme of BILP-101.[2]



A 100 mL Schleck flask was charged with 1,2,4,5-benzenetetramine tetrahydrochloride (100 mg, 0.35 mmol), 60 mL anhydrous DMF, and a stirrer-bar. The resultant homogeneous solution was cooled to -30 ^{o}C and treated drop-wise with 1,3,5-triformylbenzene (40 mg, 0.23 mmol) dissolved in anhydrous DMF (15 mL). The temperature was maintained around - 30 ^{o}C for 1 hour during which a dark brown solid formed then the resultant slurry solution was left to warm to room temperature overnight. The flask containing the reaction mixture was flushed with air for 20 minutes and capped tightly. The reaction mixture was then transferred to a static oven and heated gradually to 130 ^{o}C and kept for 2 days to afford a fluffy light brown powder. The solid was isolated by filtration over a medium glass frit and subsequently washed with DMF, acetone, water, 1 M HCl, 1 M NaOH, water, and acetone. After filtration, the product was dried at 120 ^{o}C under vacuum to give BILP-101 as a fluffy brown powder (72 mg, yield 92%). Anal. Calc. for $C_{36}H_{30}N_{12}$.6H20: C, 68.50%; H, 4.70%; N, 26.60%. Found: C, 68.26; H, 3.96%; N, 23.77%. Starting materials and solvents were purchased from Aldrich Chemical Co. and used without further purification.

Figure S1: Thermogravimetric Analysis (TGA) of BILP-101.

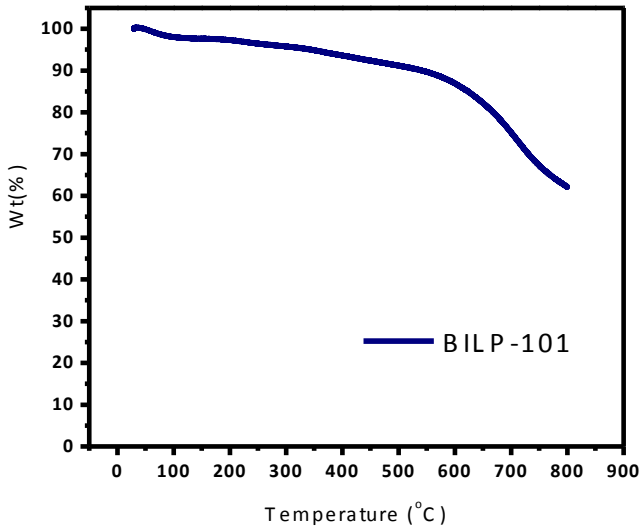


Figure S2: PXRD pattern for BILP-101 showing amorphous morphology.

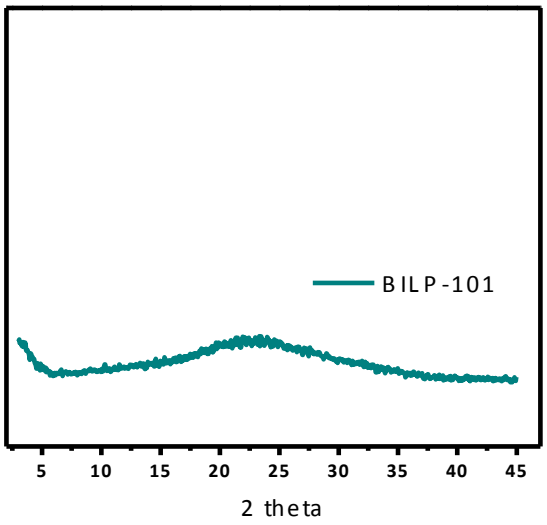
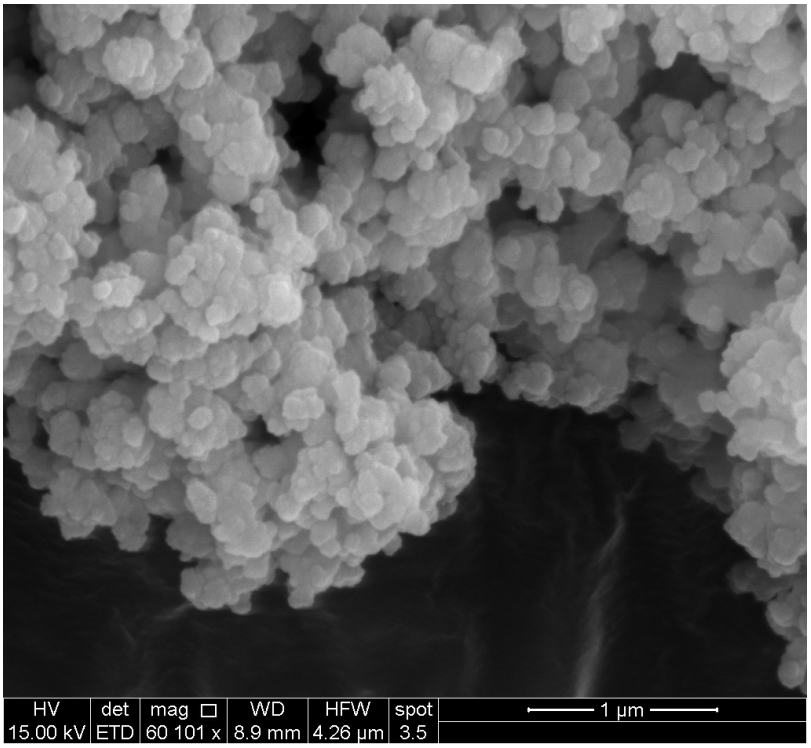
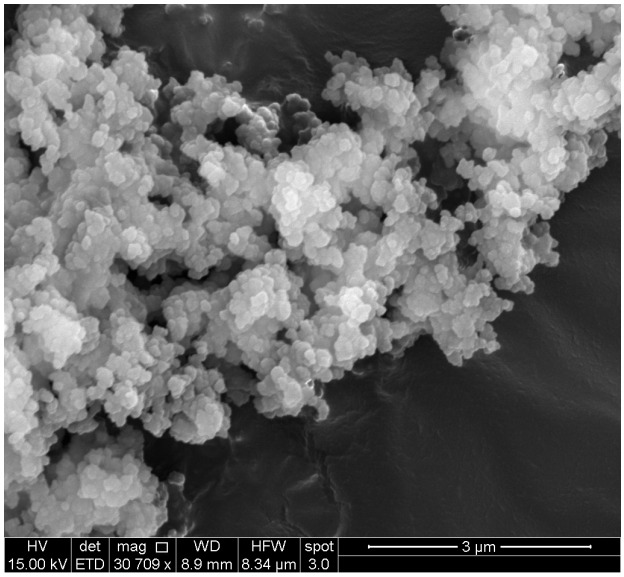


Figure S3: Scanning Electron Microscopy Imaging (SEM) for BILP-101.





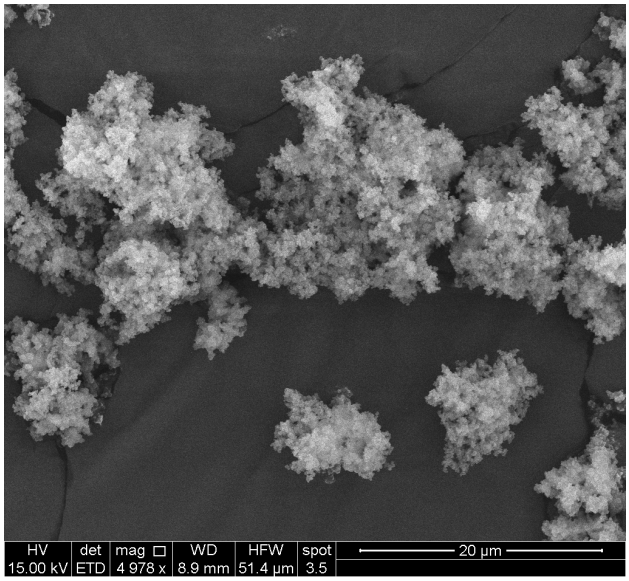


Figure S4: FT-IR spectra (400-4000 cm^{-1}) of BILP-101.

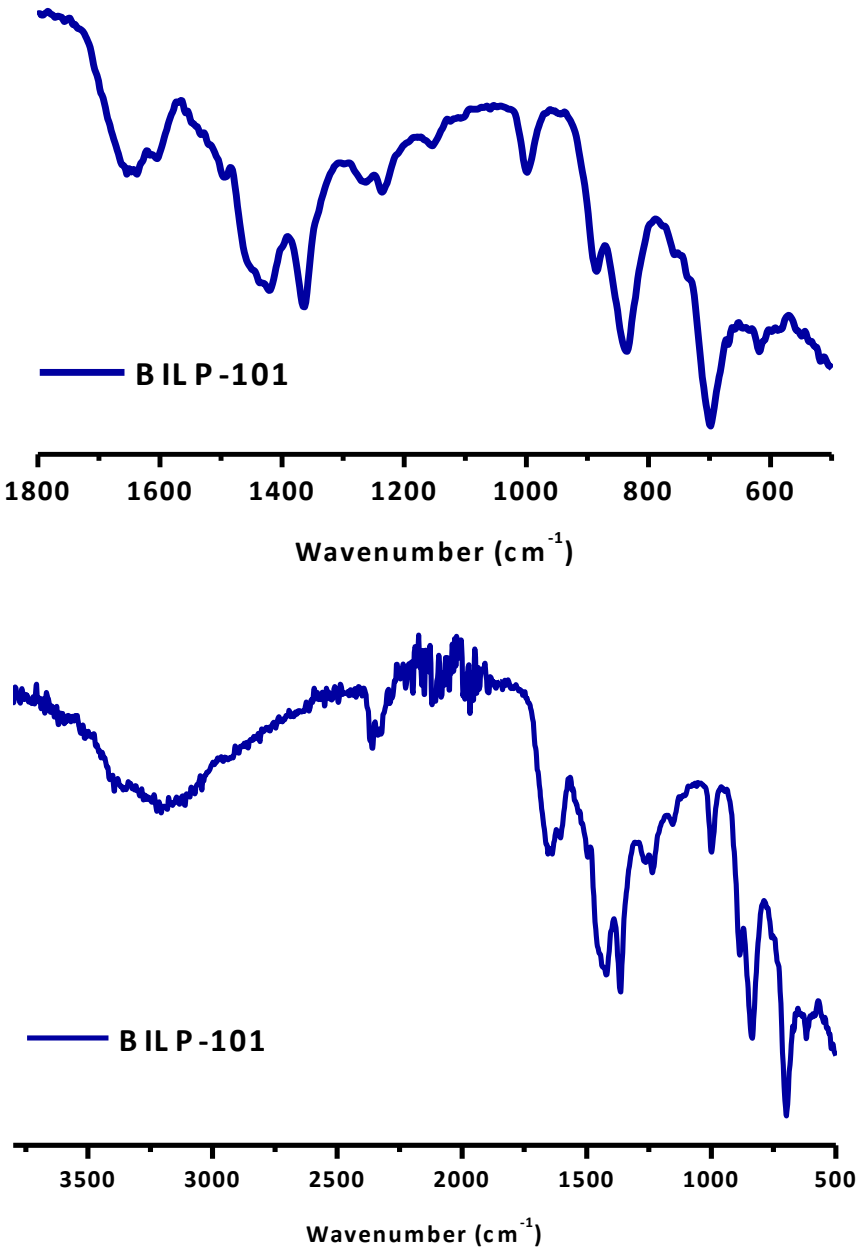


Figure S5: N_2 adsorption isotherm for BILP-101 collected at 77K (non-filled circle) and the calculated NLDFT isotherm is indicated as open circle. The Fitting error is 0.191 %.

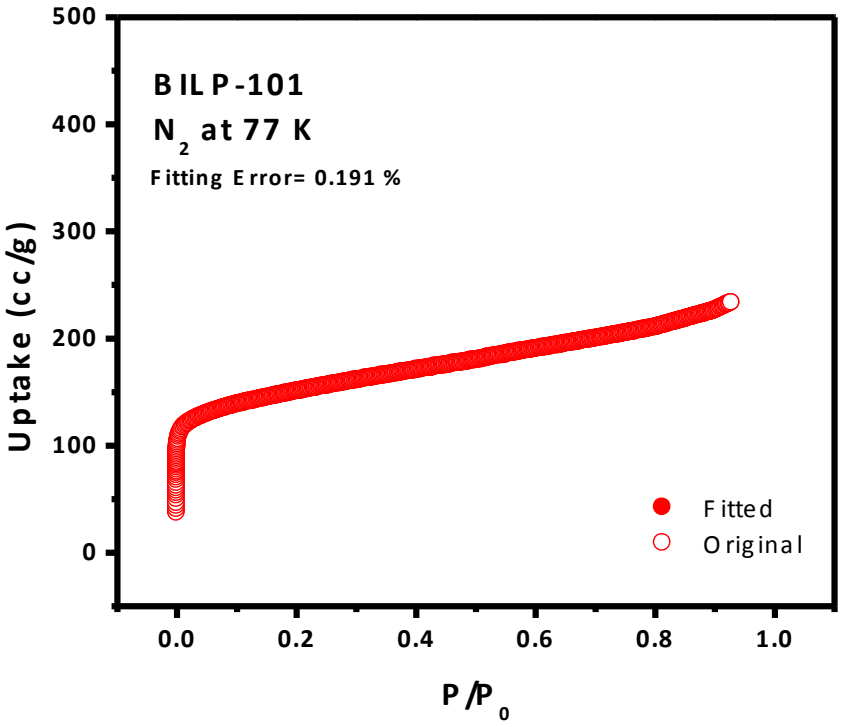


Figure S6: BET plot for BILP-101 calculated from the N_2 isotherm at 77K.

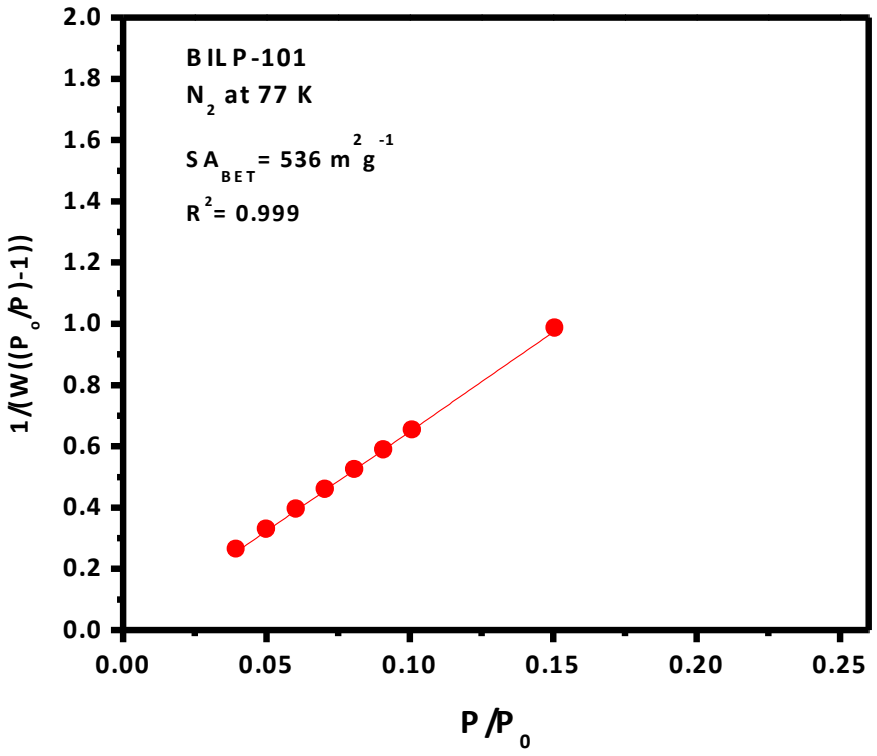


Figure S7: Pore size distribution and pore volume calculation of BILP-101

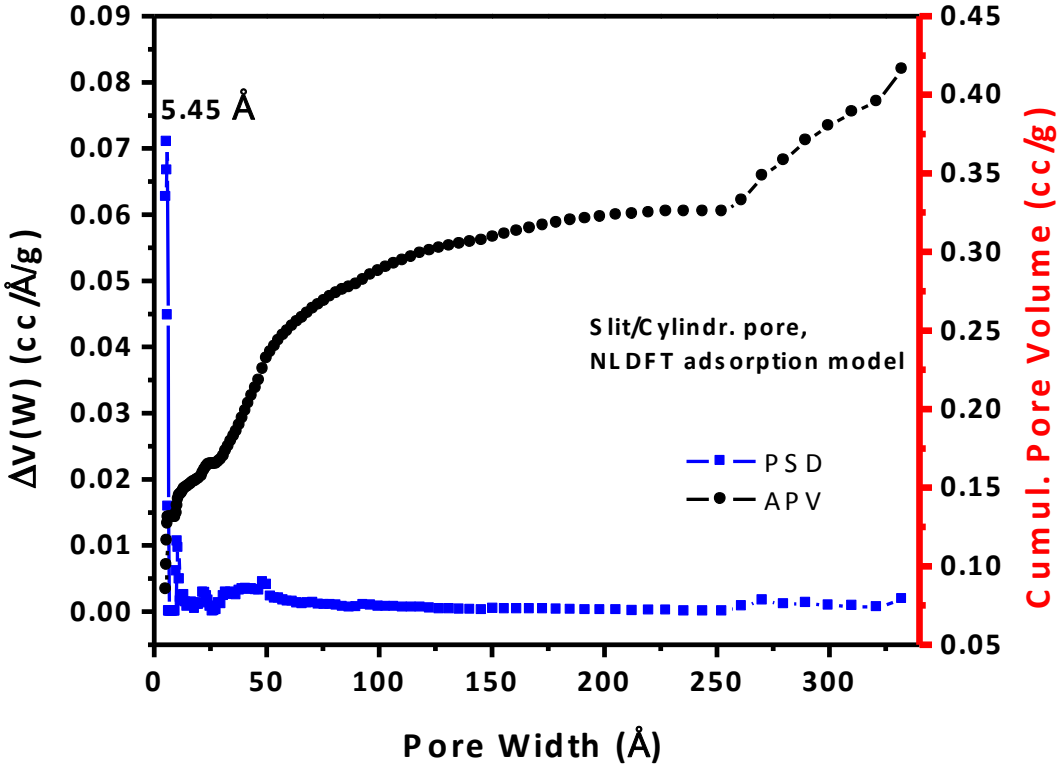


Figure S8a: CO_2 (Red diamond), CH_4 (Blue circle) and N_2 (Green triangle) uptake isotherms collected at 0.2-10 bar and 288 K using gravimetric sorption analysis.

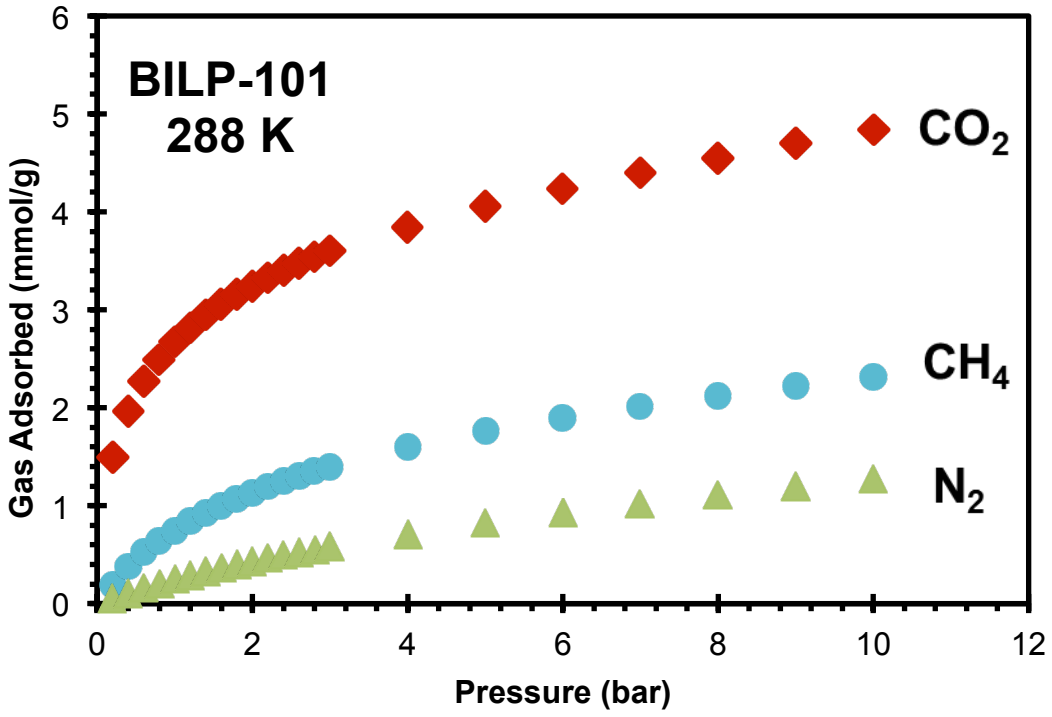


Figure S8b: CO_2 (Red diamond), CH_4 (Blue circle) and N_2 (Green triangle) uptake isotherms collected at 0.2-10 bar and 298 K using gravimetric sorption analysis.

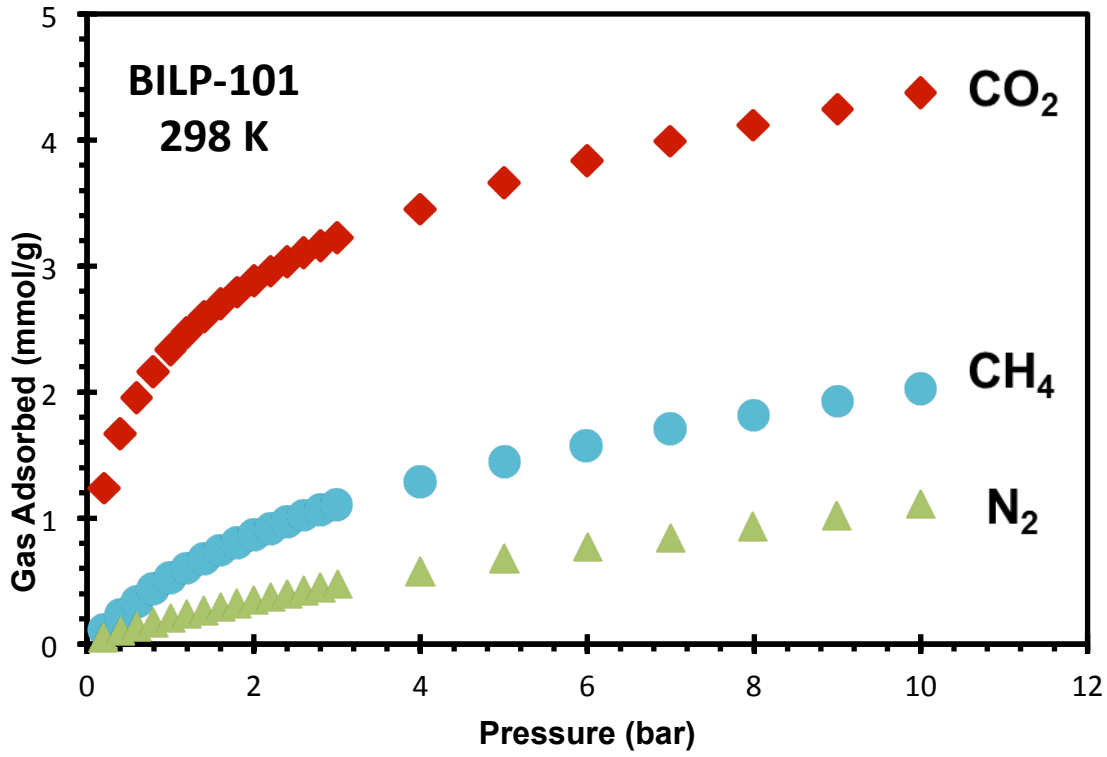


Figure S8c: CO_2 (Red diamond), CH_4 (Blue circle) and N_2 (Green triangle) uptake isotherms collected at 0.2-10 bar 313 K using gravimetric sorption analysis.

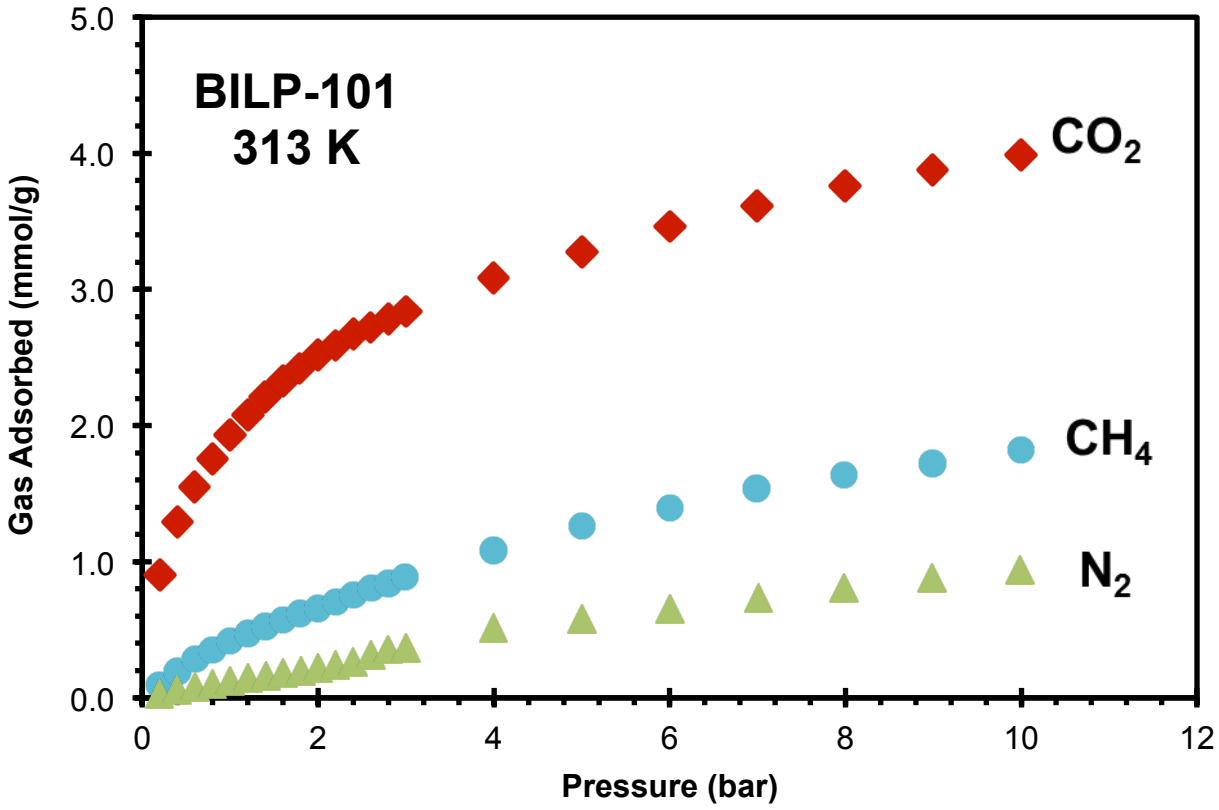


Figure S9: CO_2 regenerability study; five cycles of desorption isotherm at 298 K.

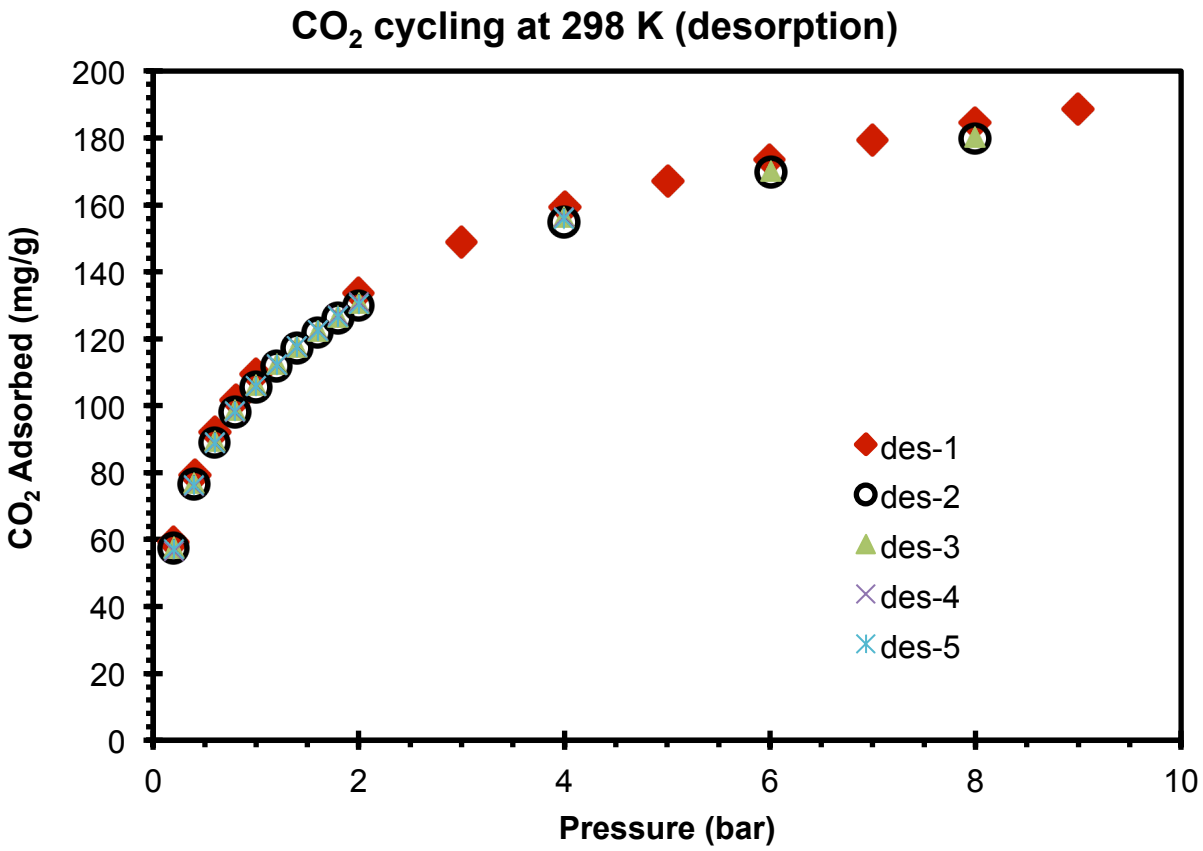


Figure S10: Initial slope gas selectivity studies**.**

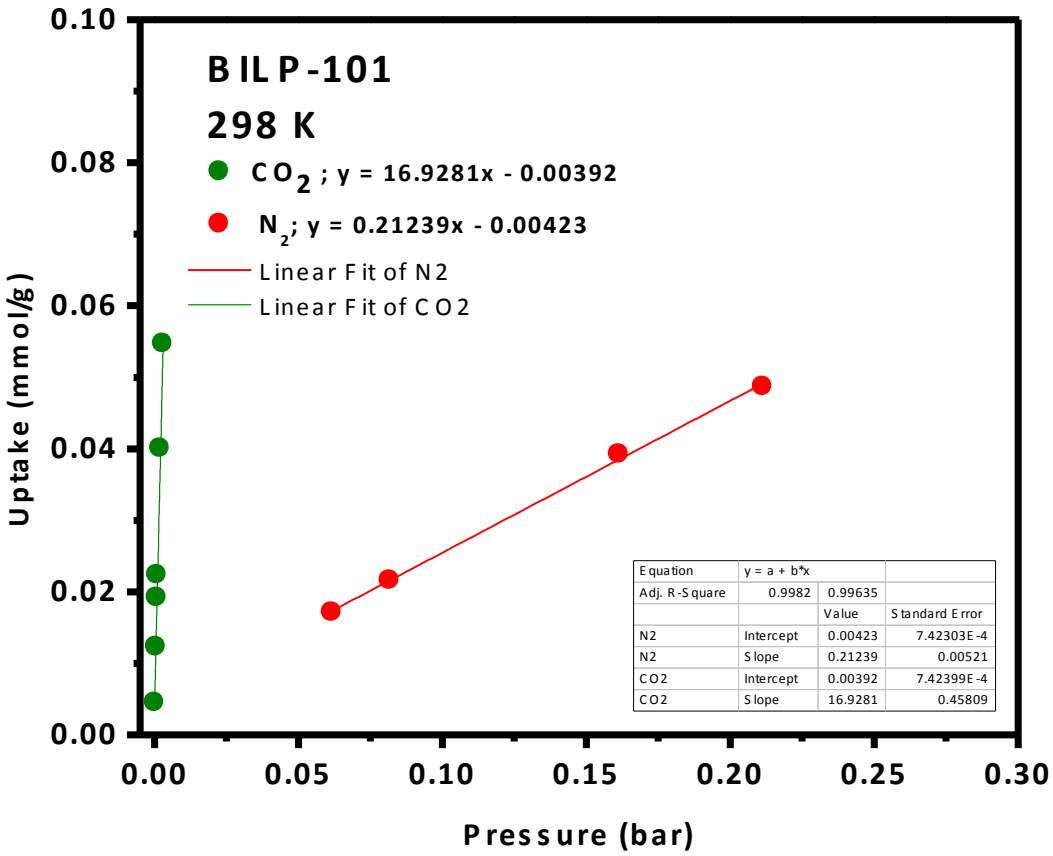


Figure S11: Experimental data (symbol) and corresponding fittings (solid line) of CO_2 (A) and N_2 (B) adsorption isotherms in BILP-101 at 298 K.

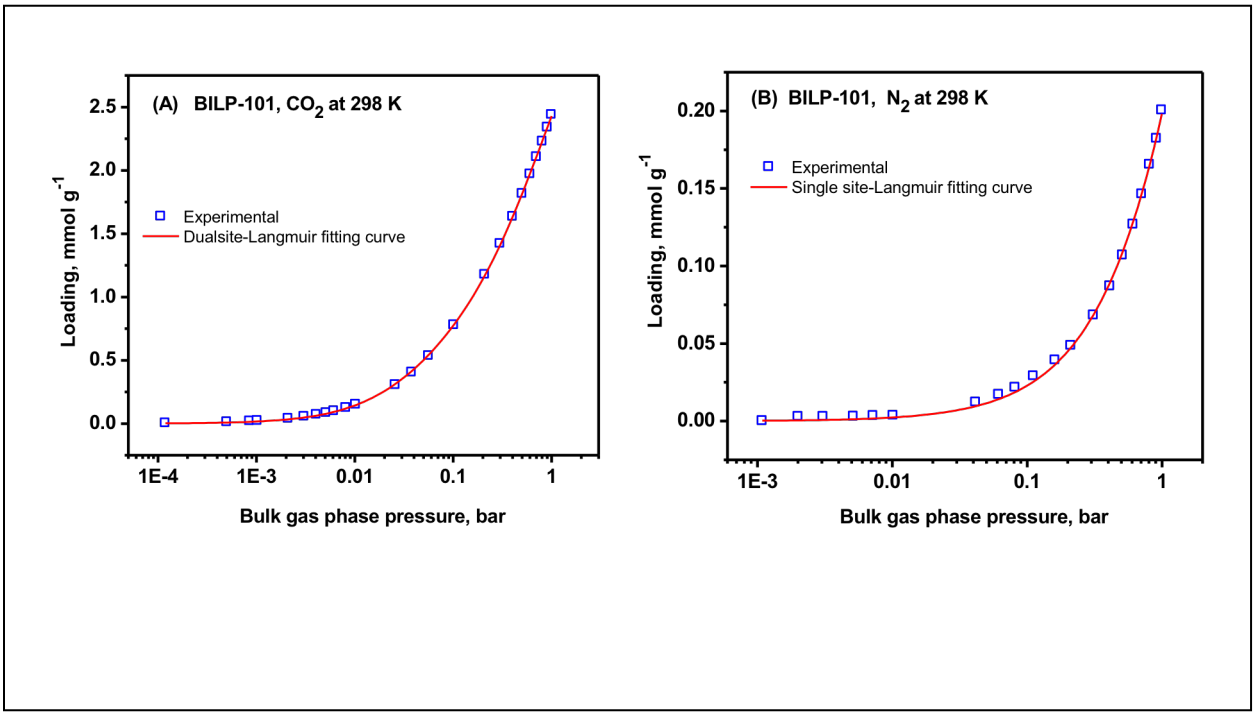


Table S1. Langmuir model fitting parameters of CO_2 and N_2 adsorption isotherms in BILP-101 at 298 K and low pressures (0-1 bar).					
Gas	$q_{sat,A}$	b_A	$q_{sat,B}$	b_B	Adj. R-square
CO_2	3.48809	1.0455	0.68111	18.6841	0.99994
N_2	1.34504	0.17278			0.99901

Equation S1:

The adsorption branch of pure component isotherm of CO_2 was fitted to dual site Langmuir (DSL) isotherm model and N_2 isotherm was fitted to single site Lagmuir isotherm model. Fitting parameters were used to calculate IAST selectivities and then sorbent selection parameters. Details about the calculations were explained previously.[1, 2]

Dual site Langmuir model = $q_A + q_B$; Single site Lagmuir model = q_A

$$q = q_A + q_B = \frac{q_{sat,A} * b_A * p}{1 + b_A * p} + \frac{q_{sat,B} * b_B * p}{1 + b_B * p}$$

where, q is total molar loading (mmol g^{-1}); q_{sat} is saturation loading, (mmol g^{-1}); p is total system pressure, (bar); b is Langmuir constant (bar^{-1}). Subscripts A and B refers to site A and site B, respectively.

Figure S12: IAST Selectivity isotherm of BILP-101 at 298 K.

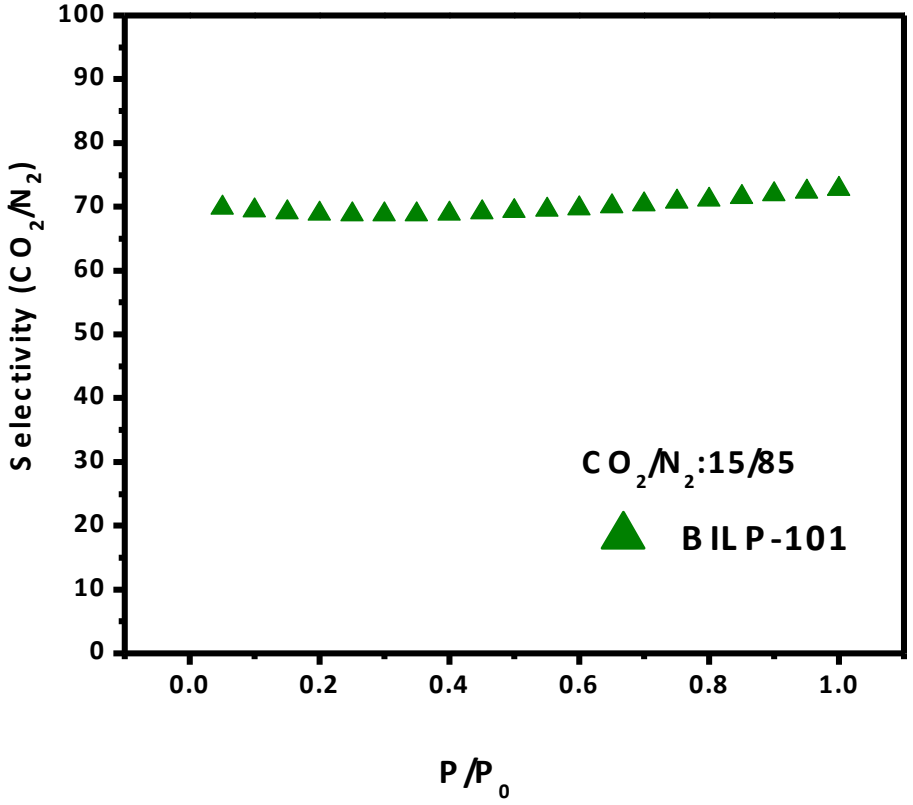


Figure S13: Heats of adsorption of BILP-101 for CO_2 calculated by Clausius-Clapeyron Equation.

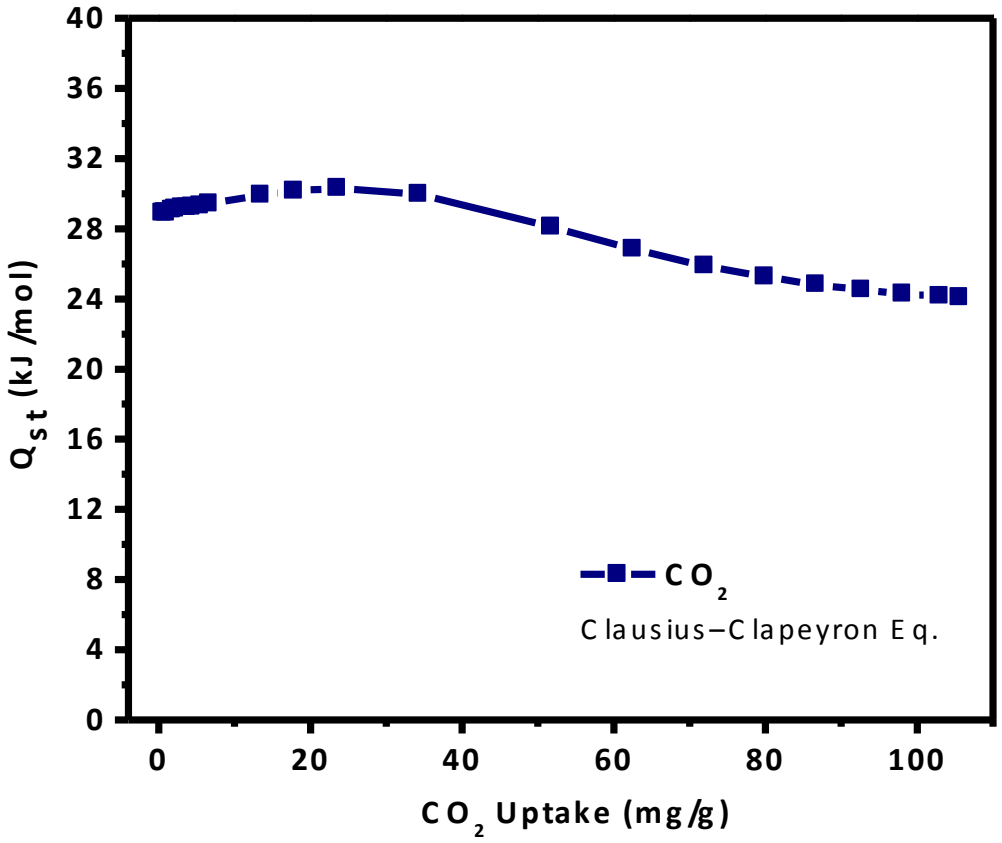


Table S2. BILP-101 and top performing adsorbents for VSA in flue gas (CO_2/N_2 : 10/90) separation at 298K, P_{ads} = 1 bar and P_{des} = 0.1 bar.[1,3]

Adsorbents	N_1^{ads}	ΔN_1	R	α_{12}^{ads}	S
BILP-101	0.95	0.80	84.8	70.3	556.4
BILP-10	0.45	0.41	90.8	35.5	109.0
BILP-12	0.55	0.49	88.7	27.1	72.6
TBILP-1	0.40	0.35	87.0	58.7	334.6
TBILP-2	0.67	0.59	88.3	42.1	192.3
Zeolite-13X	2.49	1.35	54.2	86.2	128
SNU-Cl-va	0.47	0.41	87.3	38.0	262
ZIF-78	0.6	0.58	96.3	34.5	396
ZIF-82	0.41	0.38	92.5	22.7	101
MOF-177	0.16	0.14	87.5	10.3	6.35
MOF-5	0.13	0.10	76.9	11.7	5.63
HKUST-1	0.62	0.55	89.0	20.4	46.2
Ni-MOF-74	4.34	3.2	73.7	41.1	83.5
NoritR1 extra	0.38	0.28	73.7	10.7	5.09

Equation S2:

CO_2 uptake under adsorption conditions (mol kg^{-1})	N_1^{ads}
Working CO_2 capacity (mol kg^{-1}), $N_1^{ads} - N_1^{des}$	ΔN_1
Regenerability (%), $(\Delta N_1/N_1^{ads})x100$	R
Selectivity under adsorption conditions, $(N_1^{ads}/N_2^{ads})x(y_2/y_1)$	α_{12}^{ads}
Sorbent selection parameter, $(\alpha_{12}^{ads})^2/(\alpha_{12}^{des})x\,(\Delta N_1/\Delta N_2)$	S

N: adsorbed amount, y: molar fraction in the bulk phase. Subscripts 1 and 2 correspond to the strongly adsorbed component (CO_2) and the weakly adsorbed component (CH_4 or N_2), respectively. α_{12} : Selectivity of gas component 1 over 2. ads and des correspond to adsorption and desorption conditions, respectively.[3]

References

1. A. L. Myers and J. M Prausnitz,. *AIChE Journal* 1965**, 11**, (1), 121-127.
2. A. K. Sekizkardes, T. Islamoglu, Z. Kahveci and H. M. ElKaderi, l; *J. Mater. Chem. A*, 2014, **2**, 12492.
3. Y. S. Bae and R. Q. Snurr, *Angew. Chem., Int. Edit.*, 2011, **50**, 11586-11596.