

Electronic Supporting Information

New Insights into carbon dioxide interactions with benzimidazole-linked polymers

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Table of Contents

Section S1: *DFT modeling and CO₂ interaction with BILPs*

Section S2: *Synthesis of aryl-aldehyde and the BILPs*

Section S3: *Characterization of BILPs*

TGA (Thermal gravimetric analysis)

Scanning Electron Microscopy Imaging (SEM)

XRD-pattern for BILPs

FT-IR Spectroscopy of Starting Materials and BILPs

Solid-state ¹³C CP-MAS NMR spectra for BILPs

Section S4: *Low-Pressure (0 – 1.0 bar) Gas Adsorption Measurements for BILPs*

Section S1: Computational Method for CO₂ interaction with BILPs

Benzimidazole-linked polymers, BILP-15 and BILP-14, were modeled by their corresponding benzimidazole-containing units biphenylimidazole (BILP-15) and benzimidazole (BILP-14) to ease the computational demand. The binding affinities, E_b per CO₂ were calculated by determining the equilibrium geometries and corresponding total energies of these complexes.

We define E_b as,

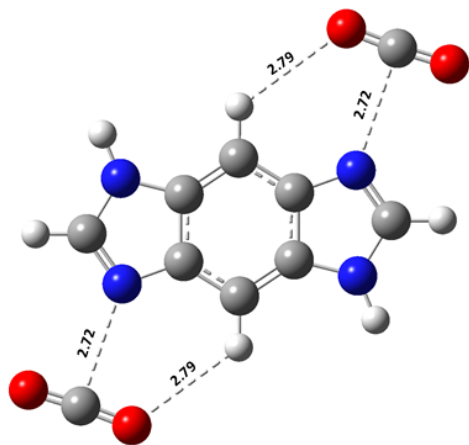
$$E_b = \{E[\text{BILP-15}@n\text{CO}_2] - E[\text{BILP-15}] - n \cdot E[\text{CO}_2]\} / n \quad \text{and}$$

$$E_b = \{E[\text{BILP-14}@n\text{CO}_2] - E[\text{BILP-14}] - n \cdot E[\text{CO}_2]\} / n; \text{ for } n = 2, 4$$

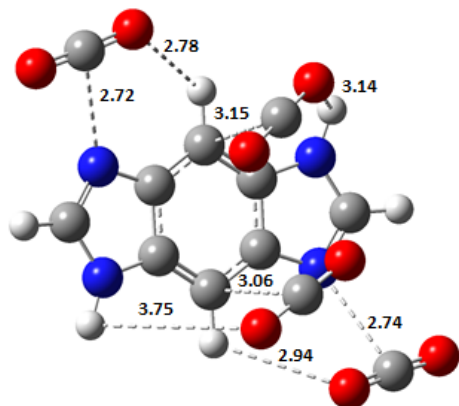
Where, $E[\text{BILP-15}@n\text{CO}_2]$ and $E[\text{BILP-14}@n\text{CO}_2]$ are the total energies of BILP-15 and BILP-14 interacting with n number of CO₂ molecules. $E[\text{BILP-15}]$, $E[\text{BILP-14}]$ and $E[\text{CO}_2]$ are the total energies of BILP-15, BILP-14 and the CO₂ molecule respectively.

Figure S1. CO₂ interactions with BILP-14

(a)



(b)



(c)

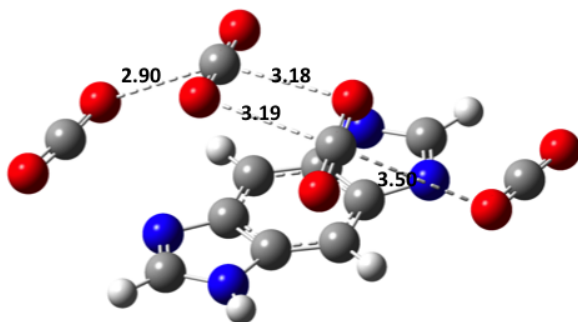
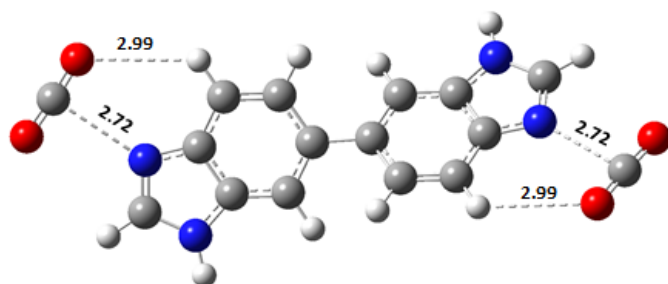
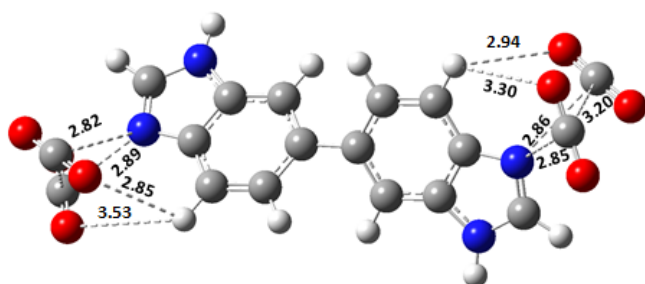


Figure S2. CO₂ interactions with BILP-15

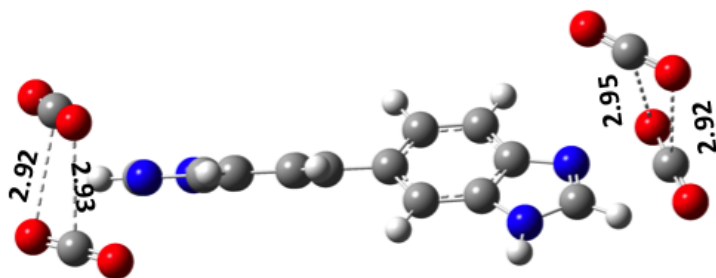
(a)



(b)



(c)



Section S2: Synthesis of the aryl-aldehyde and BILPs.

Synthesis of 1,2,4,5-Tetrakis-(4-formylphenyl)benzene (TFPB)

A mixture of 1,2,4,5-Tetrabromobenzene (1.5 g, 3.85 mmol), 4-formylphenylboronic acid (3.4 g, 22.7 mmol), palladium tetrakis(triphenylphosphine) (0.12 g, 0.10 mmol, 5.2 mol%), and potassium carbonate (4.2 g, 30.4 mmol) in dry 1,4-Dioxane (50 mL) was stirred under nitrogen for 3 days at 90 °C. The white suspension reaction mixture was poured into a slurry ice containing 80 mL concentrated hydrochloric acid. The solid product was filtered and washed with water and 2 M HCl three times. The final product was obtained after extraction of the crude product with chloroform (4 × 50 mL). The extracted organic layer was dried over MgSO₄, filtered and evaporated under reduced pressure. The resultant solid was recrystallized from hot ethylacetate to afford (TFPB) as a yellowish powder (1.3 g, 68%). Anal. Calcd for C₃₄H₂₂O₄: C, 82.58%; H, 4.48%; O, 12.94% Found: C, 82.27%; H, 4.59%; O, 13.00%. ¹H NMR (300 MHz, CDCl₃, δ (ppm)): (s, 4H, formyl H), (s, 4H, Ar H), (d, 8H, Ar H) and (d, 8H, Ar H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm) 191.0, 146.0, 140.0, 136.0, 133.0, 130.0, 131.0.

Synthesis of BILP-14.

A 100 ml Schlenk flask was charged with (60 mg, 0.211 mmol) of 1,2,4,5-Benzenetetramine tetrahydrochloride salt and 30 mL of anhydrous DMF. The solution was cooled to around -30 °C and a solution of 1,2,4,5-tetrakis(4-formylphenyl)benzene (50 mg, 0.10 mmol) in 25 mL anhydrous DMF was added dropwise to the pervious charged solution. Temperature was maintained around -30 °C until yellowish brown solid product formation completed and then raised to RT and kept for overnight. The flask containing the reaction mixture was flashed with air for 15 minutes and capped. The reaction

mixture was then heated in an oven at 130 °C (0.5 °C/min) for 3 days to afford a fluffy brownish polymer which was isolated by filtration over a glass frit. The product was immersed in DMF (20 ml overnight) and then in (20 ml) acetone. The product was dried under vacuum at 120 °C and 1.0×10^{-5} Torr for 20 hours to give BILP-14 as a brown fluffy solid (56 mg, 73%). Anal. Calcd for $C_{46}H_{26}N_8 \cdot 4H_2O$: C, 72.44%; H, 3.41%; N, 14.70 %. Found: C, 71.82%; H, 4.98%; N, 13.11%.

Synthesis of BILP-15.

This polymer was synthesized according to the polymerization conditions mentioned for BILP-14 above using 3,3'-Diaminobenzidine tetrahydrochloride hydrate (65 mg, 0.181 mmol) and 1,2,4,5-tetrakis(4-formylphenyl)benzene (40 mg, 0.081 mmol). The 3,3'-Diaminobenzidine tetrahydrochloride hydrate was used in excess due to the presence of 10% hydrate in the building block. After activation the final product BILP-15 was obtained as a brownish fluffy solid (60 mg, 81%). Anal. Calcd for $C_{58}H_{34}N_8 \cdot 4H_2O$: C, 76.15%; H, 4.60%; N, 12.25%. Found: C, 75.90%; H, 4.66%; N, 12.60%.

Section 3: Characterization of BILPs

Characterizations of aryl-aldehyde starting material and BILPs.

^1H and ^{13}C NMR spectral characterization of starting building units

Figure S3. ^1H NMR for 1,2,4,5-tetrakis(4-formylphenyl)benzene (TFPB) in CDCl_3 .

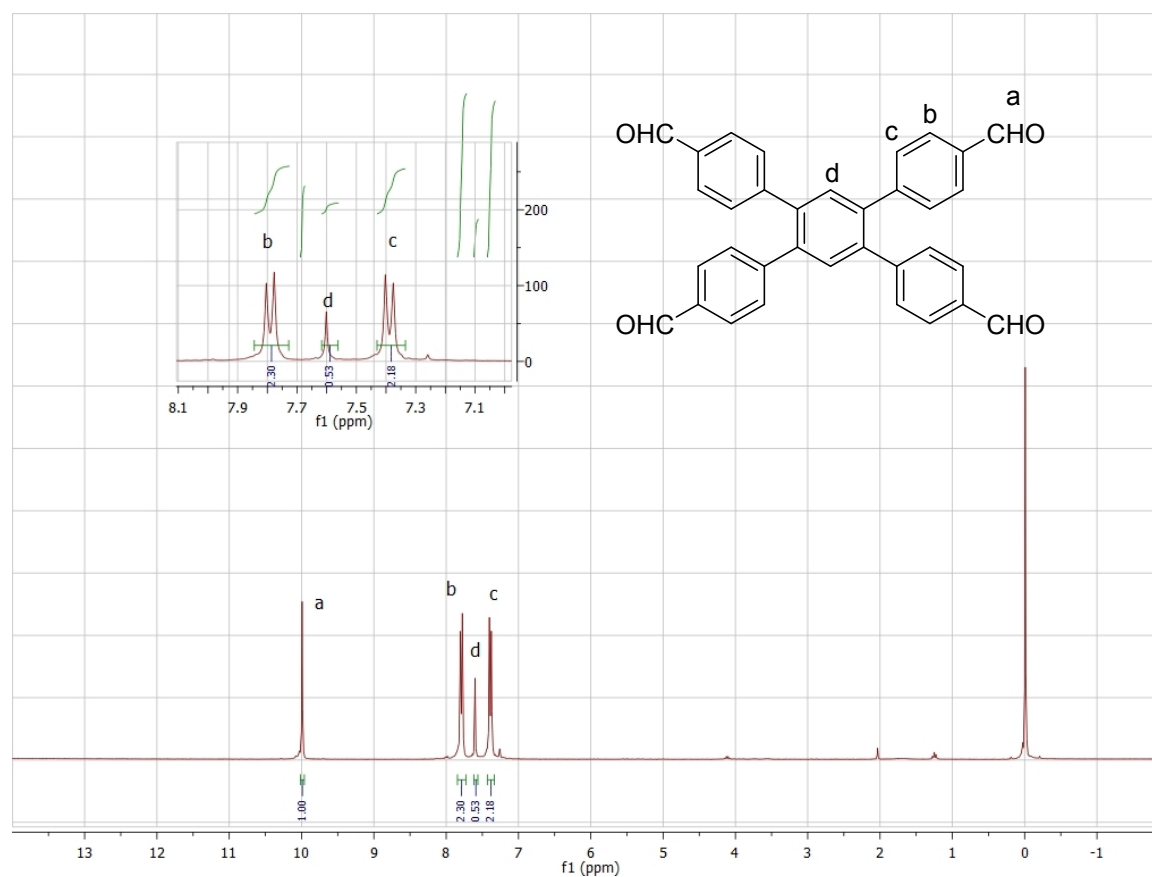


Figure S4. ^{13}C -NMR for 1,2,4,5-tetrakis(4-formylphenyl)benzene (TFPB) in CDCl_3 .

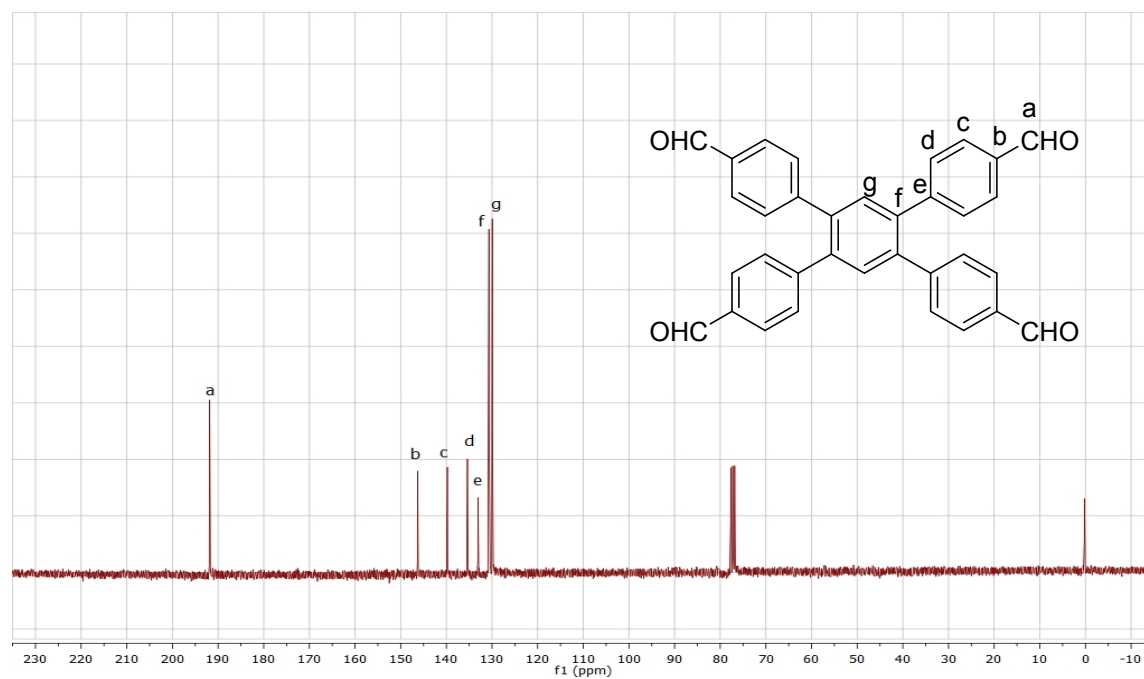


Figure S5: SEM images of BILP-14 (A) and BILP-15 (B).

The samples were prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminum sample holder. The samples were then coated with platinum at 1×10^{-5} mbar of pressure in a nitrogen atmosphere for 90 seconds before imaging. Images were taken on a Hitachi SU-70 Scanning Electron Microscope.

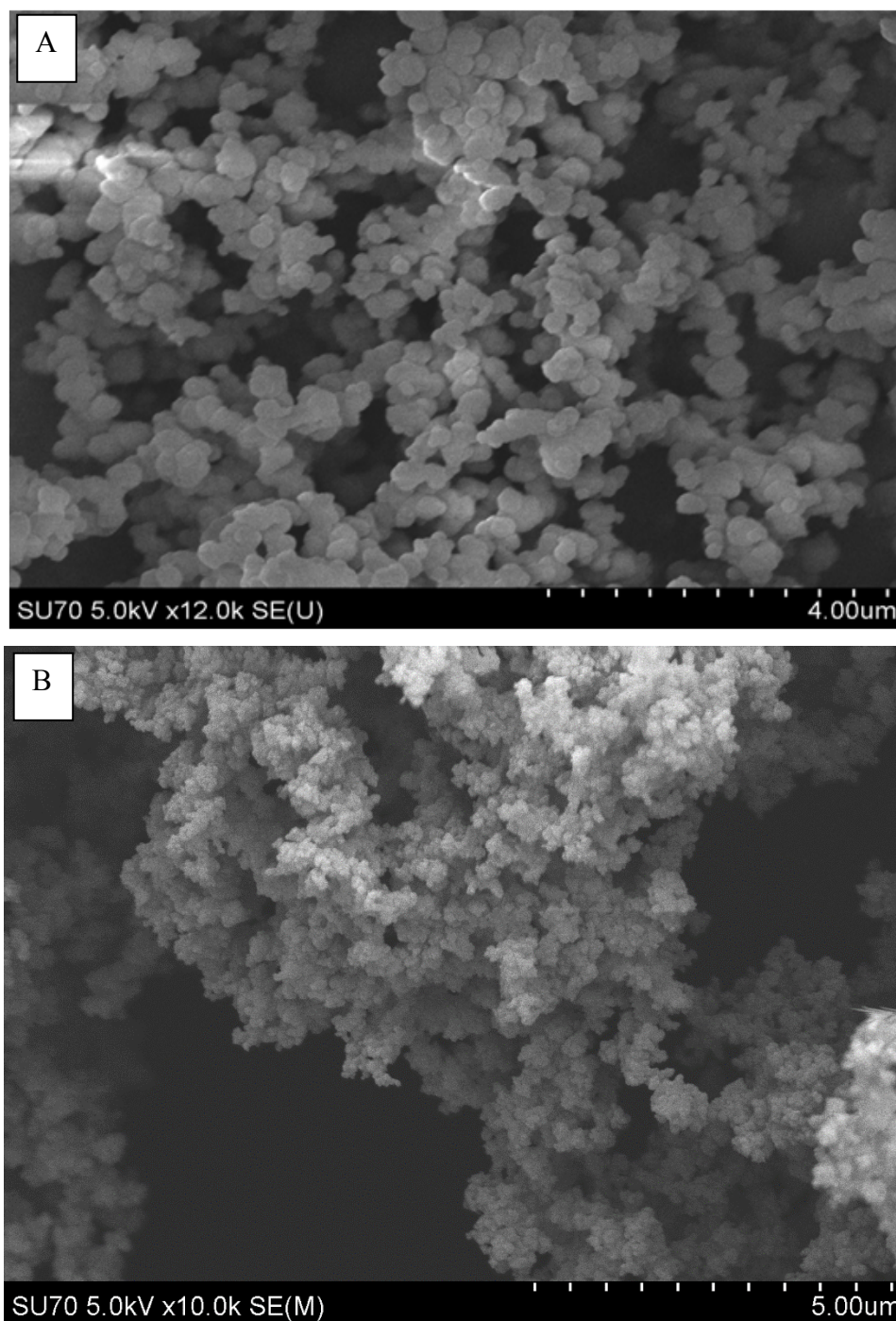


Figure S6: Thermal gravimetric profiles of BILP-14 and BILP-15, measured under N₂. Thermogravimetric analysis (TGA) was carried out using a TA Instruments Q-5000IR series thermal gravimetric analyzer with samples held in 50 μ L platinum pans under inert N₂ air (heating rate 5 $^{\circ}$ C/min).

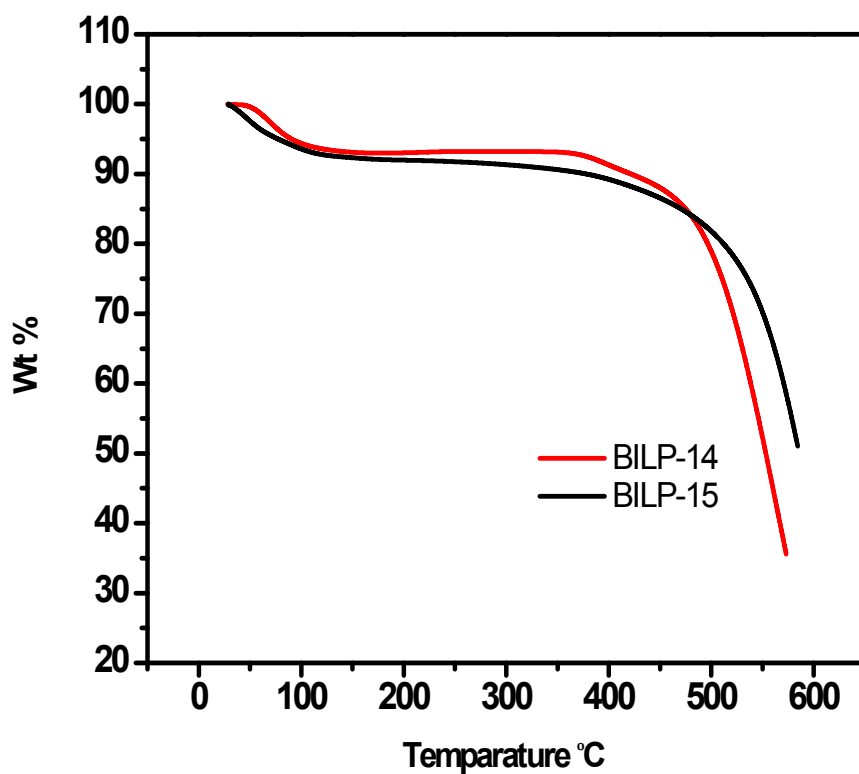


Figure S7: FT-IR spectra of BILP-14 and BILP-15 and their aryl-aldehydes starting building units.

The region from 2000-400 cm^{-1} is expanded to show the characteristic vibrations of imidazole ring and the consumption of the aldehyde C=O functional group. The vibrations at 1620, 1480 and 1435 cm^{-1} are attributed to the skeleton of the imidazole ring. The vibration band at 1700 cm^{-1} corresponds to the carbonyl of the aldehyde building block, which disappeared completely upon condensation. The stretching at around 3425 cm^{-1} and 3220 cm^{-1} are assigned to free N-H and hydrogen bonded N-H or O-H respectively. The new band at 1640 cm^{-1} band is due to the N-H bending and the bands ranging from 2750-3030 cm^{-1} are due to aromatic CH stretching.

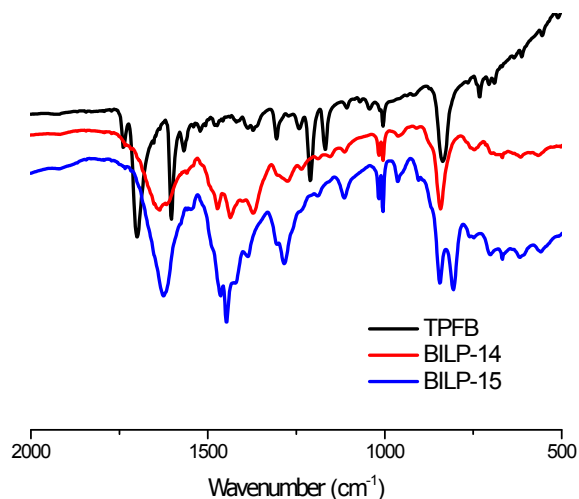
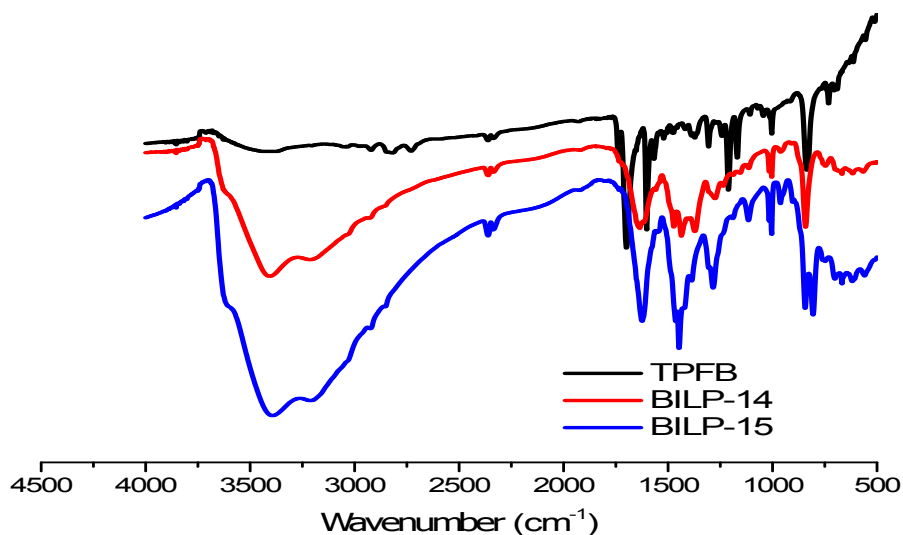


Figure S8: Solid-state ^{13}C CP-MAS NMR spectra of BILP-14 and BILP-15.

^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectra for solid samples were taken at Spectral Data Services, Inc. Spectra were obtained with samples on a Tecmag-based NMR spectrometer, operating at a H-1 frequency of 363 MHz, using a contact time of 1 ms and a delay of three seconds for the CPMAS experiment; samples were spun at 7.0 kHz

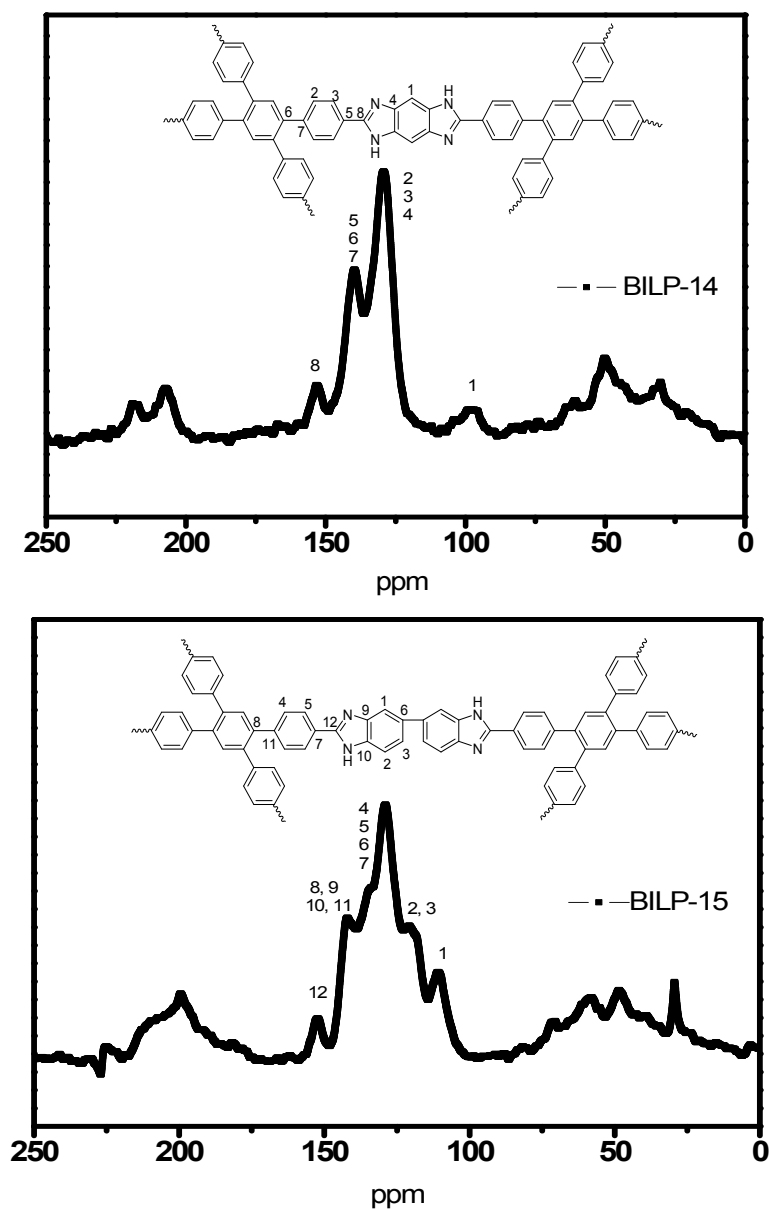
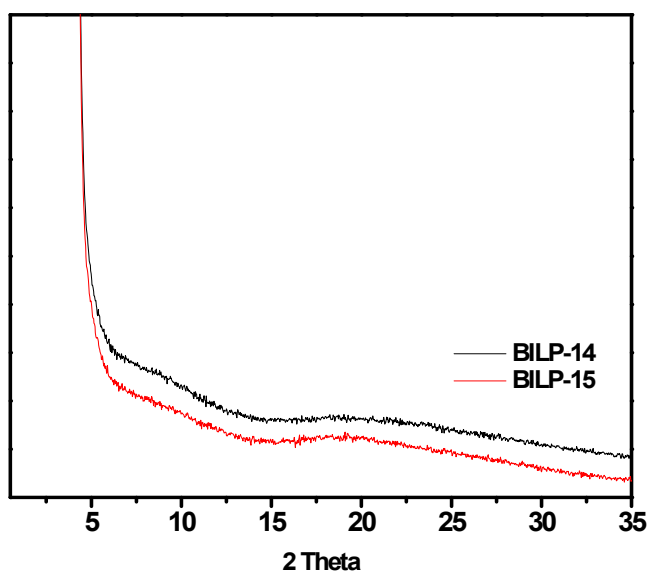


Figure S9: XRD profiles for BILP-14 and BILP-15 show the amorphous pattern of the polymers.

Powder X-ray diffraction data were collected on a Panalytical X'pert pro multipurpose diffractometer (MPD). Samples were mounted on a sample holder and measured using Cu K α radiation with a 2θ range of 1.5-35.



Section 3: Low-Pressure (0 – 1.0 bar) Gas Adsorption Measurements for BILPs.

Activation of BILPs for gas adsorption measurements: A sample was loaded into a 9 mm large bulb cell (from Quantachrome) of known weight and then hooked up to MasterPrep. The sample was degassed at 120 °C for 20 hours. The degassed sample was weighed precisely and then transferred back to the analyzer. The temperatures for adsorption measurements was controlled by using refrigerated bath of liquid nitrogen (77 K) or liquid argon (87 K), and temperature controlled water bath (273 K and 298 K). Adsorption measurements were performed on an Autosorb-1 C (Quantachrome) volumetric analyzer using adsorbates of UHP grade.

Figure S10: Pore Size Distribution calculated from the Ar adsorption isotherms by the Non-Local Density Functional Theory (NLDFT) method using a cylindrical pore model. The filled symbols are adsorption points and the empty symbols are desorption points.

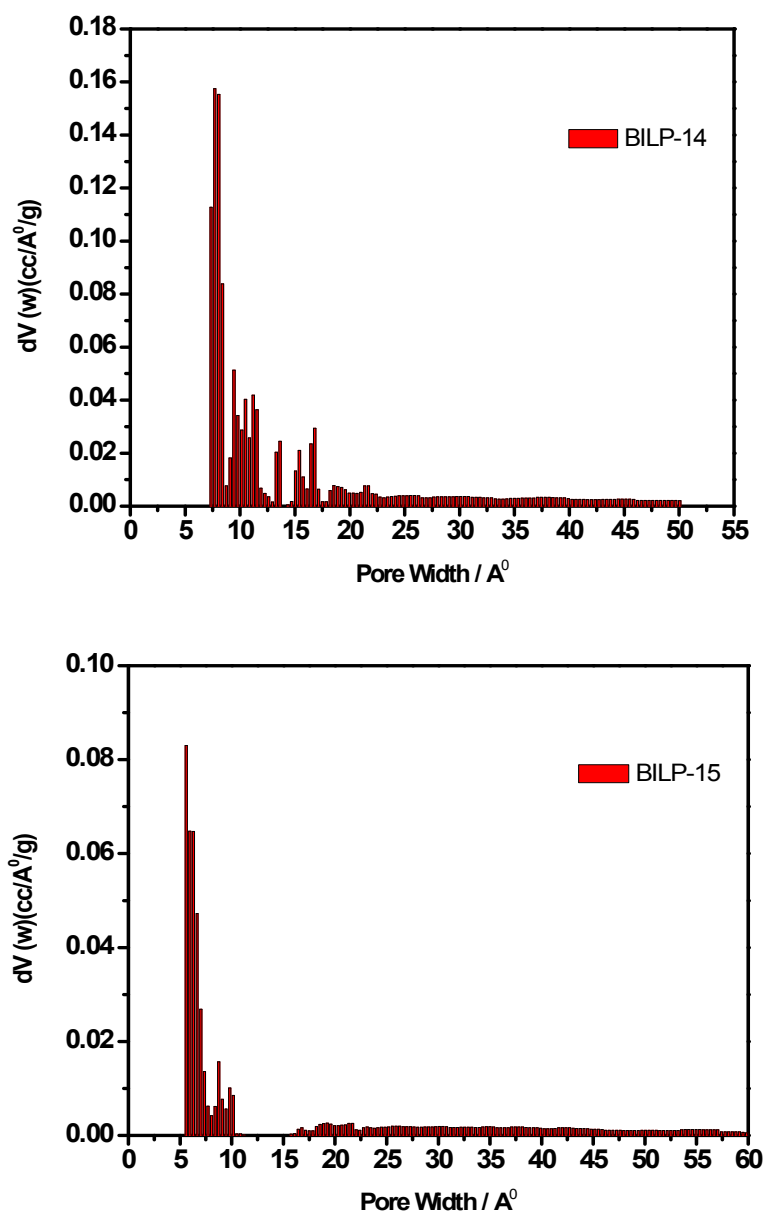


Figure S11: Experimental Ar adsorption isotherm (filled circles) for BILP-14, BILP-15 measured at 87 K. The calculated NLDFT isotherm is overlaid as open circle and the BET plots for BILP-14, BILP-15 calculated from the Ar adsorption isotherm at 87 K. The model was applied from $P/P_0 = 0.05$ -0.16. The correlation factor is indicated. (W = Weight of gas absorbed at a relative pressure P/P_0).

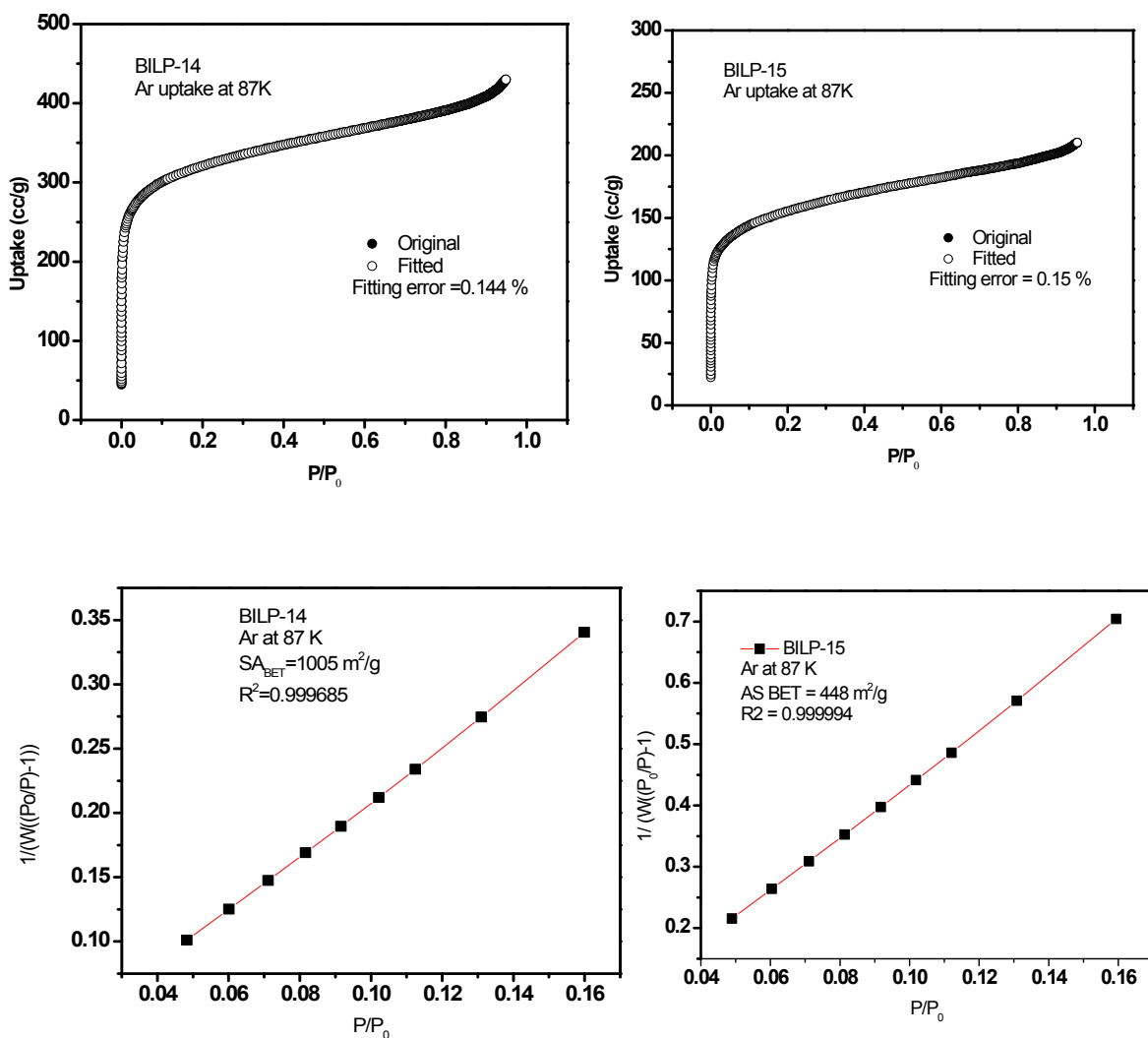


Figure S12: Methane and Carbon dioxide uptake isotherms for BILP-14 and BILP-15 at 273 K, 288 K and 298 K. Adsorption filled, desorption (empty).

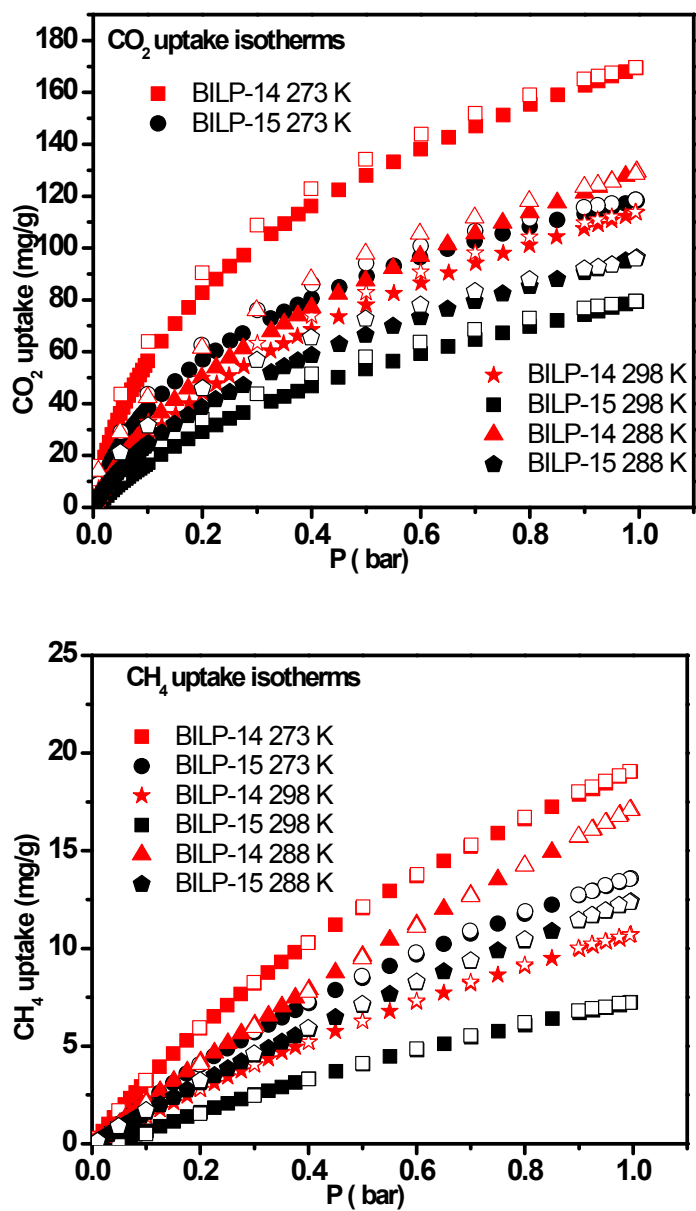


Figure S13: Virial analysis of CH₄ and CO₂ adsorption data at 273, 298, and 288 K for BILP-14 and BILP-15.

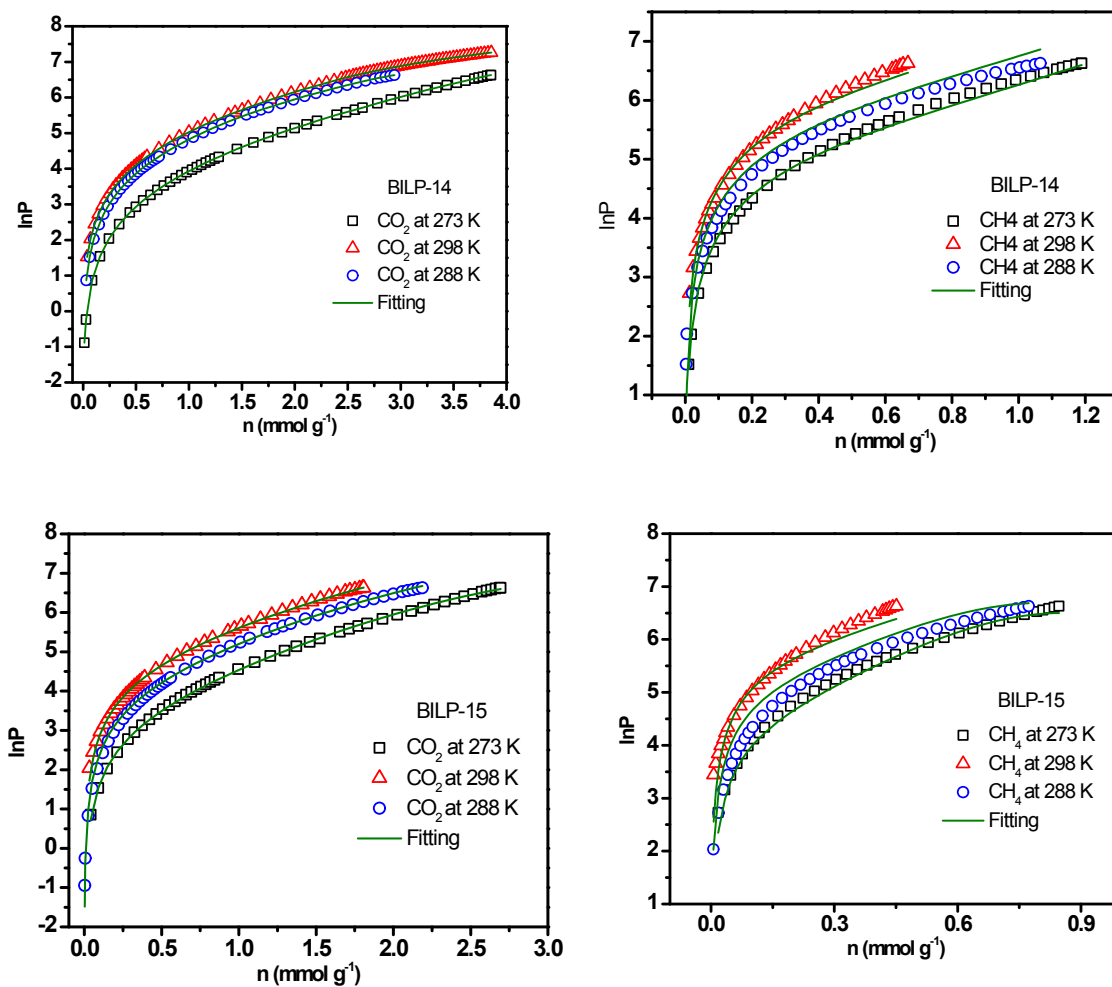
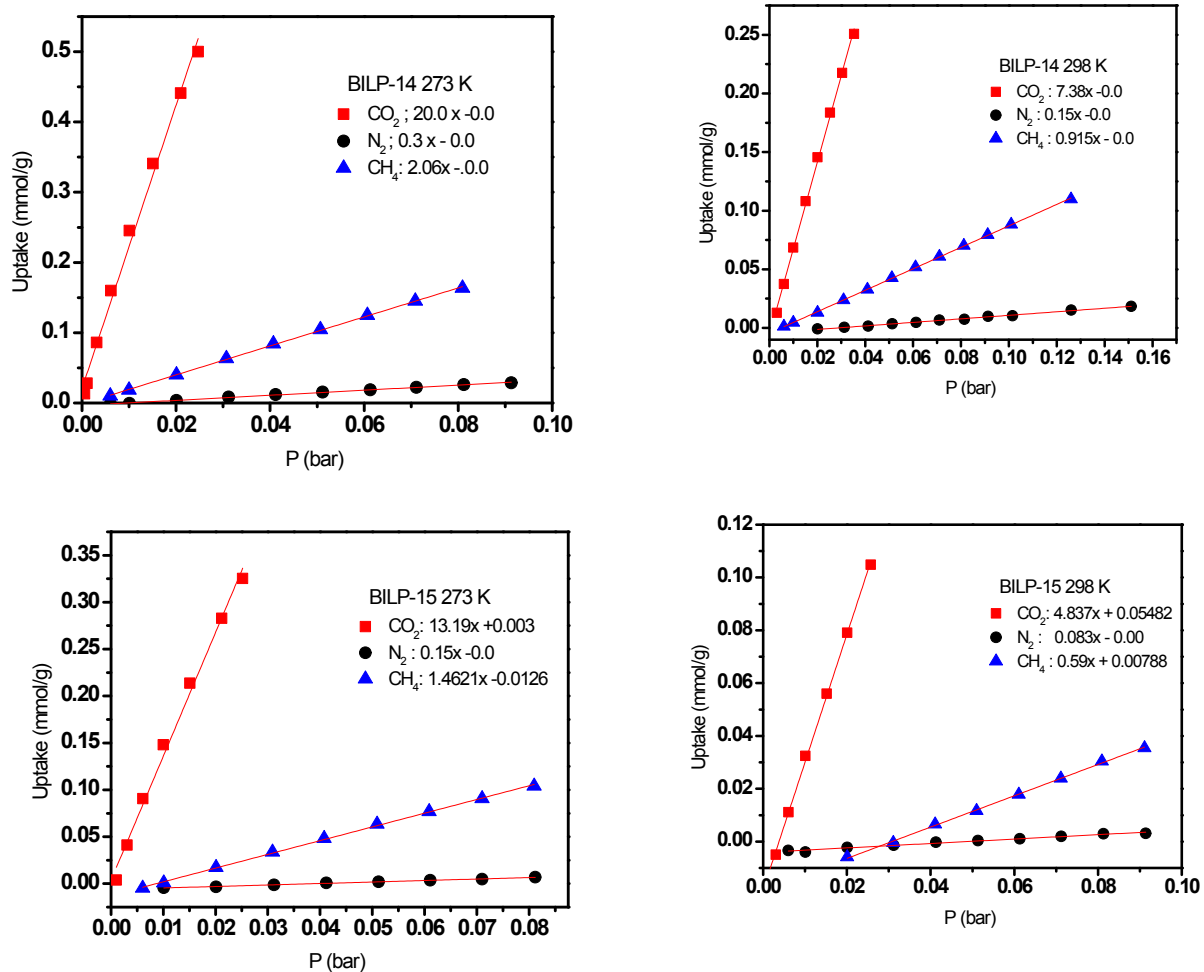


Figure S14: Adsorption selectivity of CO₂ over N₂ and CH₄ for BILP-14 and BILP-15 from initial slope calculations.



Ideal adsorbed solution theory

The pure component isotherms of CO₂ measured at 273 and 298 K were fitted with the dual-site Langmuir (DSL) model

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

with T-dependent parameters b_A and b_B

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right), \quad b_B = b_{B0} \exp\left(\frac{E_B}{RT}\right)$$

where, q is molar loading of adsorbate (mol kg⁻¹), q_{sat} is saturation loading (mol kg⁻¹), b is parameter in the pure component Langmuir isotherm (Pa⁻¹), p is bulk gas phase pressure (Pa), $-E$ is heat of adsorption (J mol⁻¹), R is ideal gas constant (8.314 J mol⁻¹ K⁻¹), T is absolute temperature (K), subscripts A and B refers to site A and site B , respectively.

Since the pure component isotherms of CH₄ and N₂ do not show any inflection characteristic they were fitted with the single-site Langmuir (SSL) model

$$q = q_{sat,A} \frac{b_A p}{1 + b_A p}$$

with T-dependent parameter b_A

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right)$$

Pure-component isotherm fitting parameters were then used for calculating Ideal Adsorbed Solution Theory (IAST)¹ binary-gas adsorption selectivities, S_{ads} , defined as

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

Figure S15: IAST selectivities of CO₂/ CH₄ for 50/50 (A), and CO₂/ N₂ 10/90 (B) binary mixtures at 298 K for BILP-14 and BILP-15.

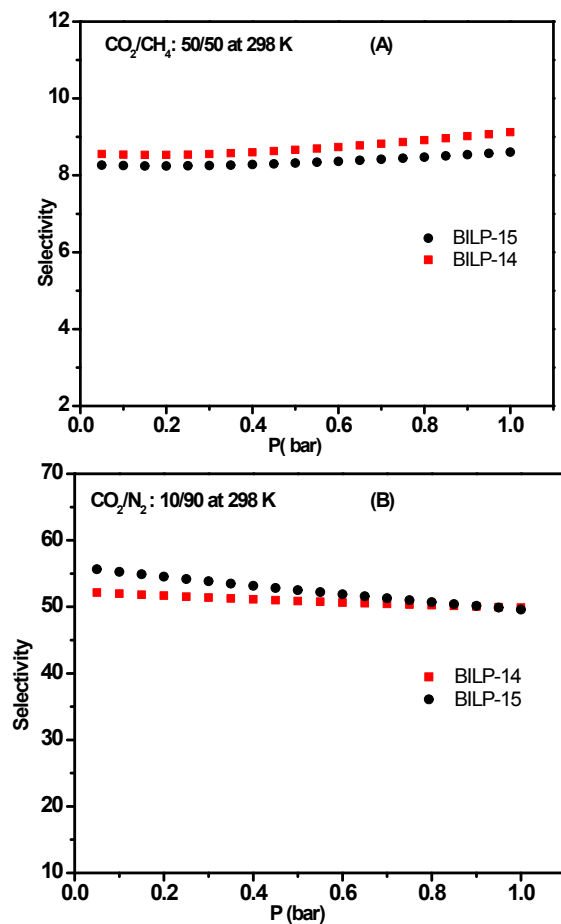


Table 1S. Initial slope selectivity of BILP-14 and BILP-15 at 273 K (298 K), and the IAST selectivity of BILP-14 and BILP-15 at 298 K for the binary mixtures of (CO₂/N₂: 10:90) and (CO₂/CH₄: 50:50).

BILP	Selectivity			
	Initial slope at 273 K(298 K)		IAST at 298 K	
	CO ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /N ₂ (10:90)	CO ₂ /CH ₄ (50:50)
BILP-14	56 (49)	10 (9)	52	8.6
BILP-15	83 (63)	9 (8)	56	8.3