Electronic Supplementary Information

Benzothiazole- and Benzoxazole-Linked Porous Polymers for Carbon Dioxide Storage and Separation

Mohammad Gulam Rabbani,*[a] Timur Islamoglu[b] and Hani M. El-Kaderi*[b]

[a] Prof. M. G. Rabbani*
Department of Chemistry
University of Wisconsin-Platteville
1 University Plaza, Platteville, WI 53818-3099
Fax: (+1)(608) 342-1559
E-mail: rabbanim@uwplatt.edu

[b] Dr. Timur Islamoglu, Prof. H. M. El-Kaderi*
Department of Chemistry
Virginia Commonwealth University
W. Main St., Richmond, VA 23284-2006, US
Fax: (+1)(804) 828-8599
E-mail: helkaderi@vcu.edu

*To whom correspondence should be addressed. E-Mail: rabbanim@uwplatt.edu

and helkaderi@vcu.edu

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***Section S1**: Characterization of BTLPs & BOLPs*

Figure S1: TGA traces of BTLPs and BOLPs under nitrogen atmosphere.

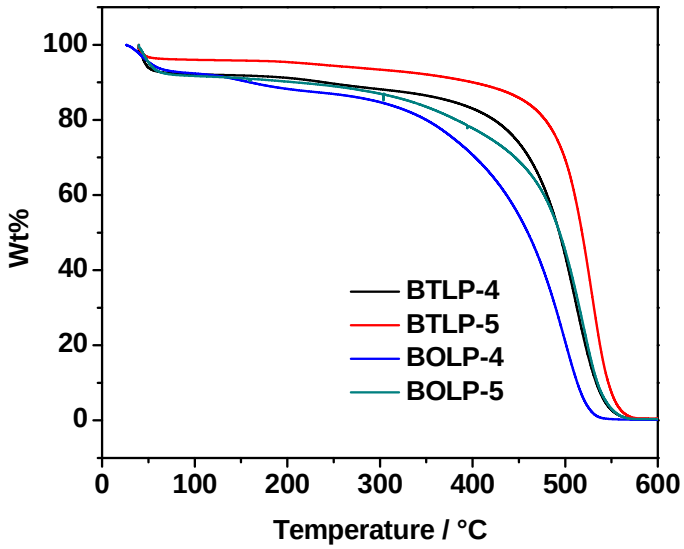


Figure S2: PXRD- pattern for BTLPs and BOLPs indicating their amorphous nature.

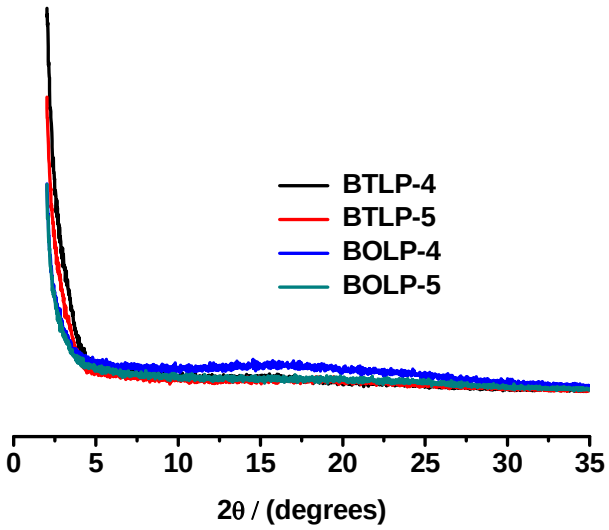
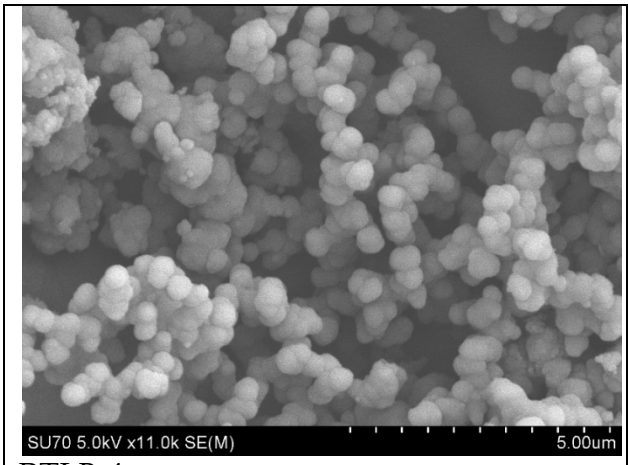
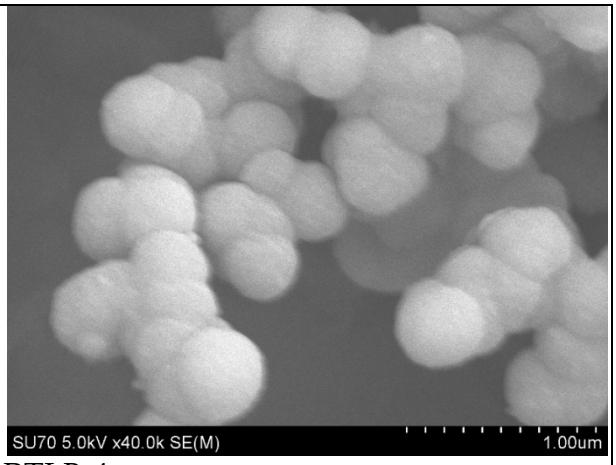


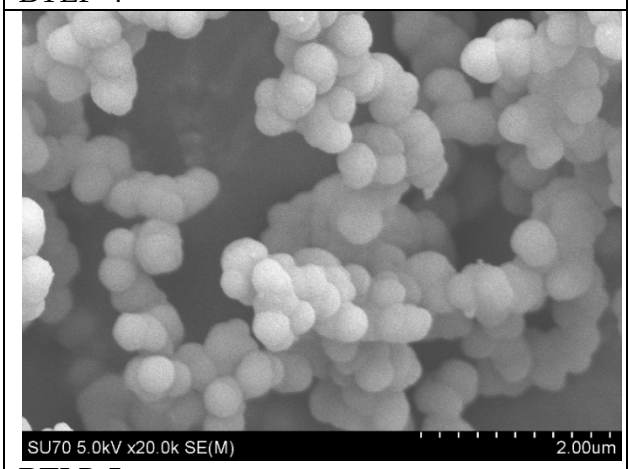
Figure S3: SEM images of BTLPs and BOLPs.



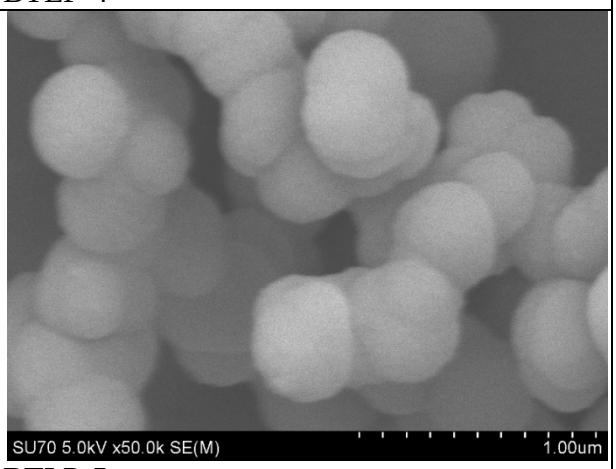
BTLP-4



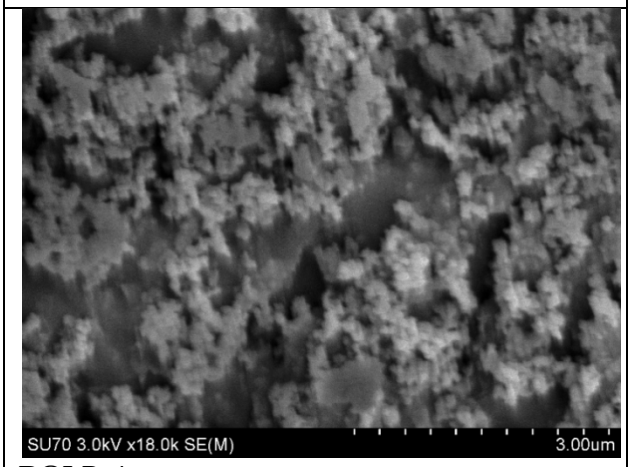
BTLP-4



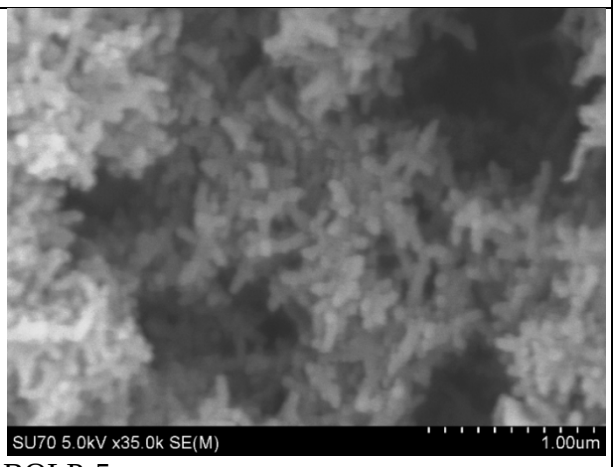
BTLP-5



BTLP-5



BOLP-4



BOLP-5

Figure S4: Attenuated Total Reflectance-Infrared (ATR-FTIR) spectra (600-4000 cm^{-1}) of starting monomers and BTLPs and BOLPs.

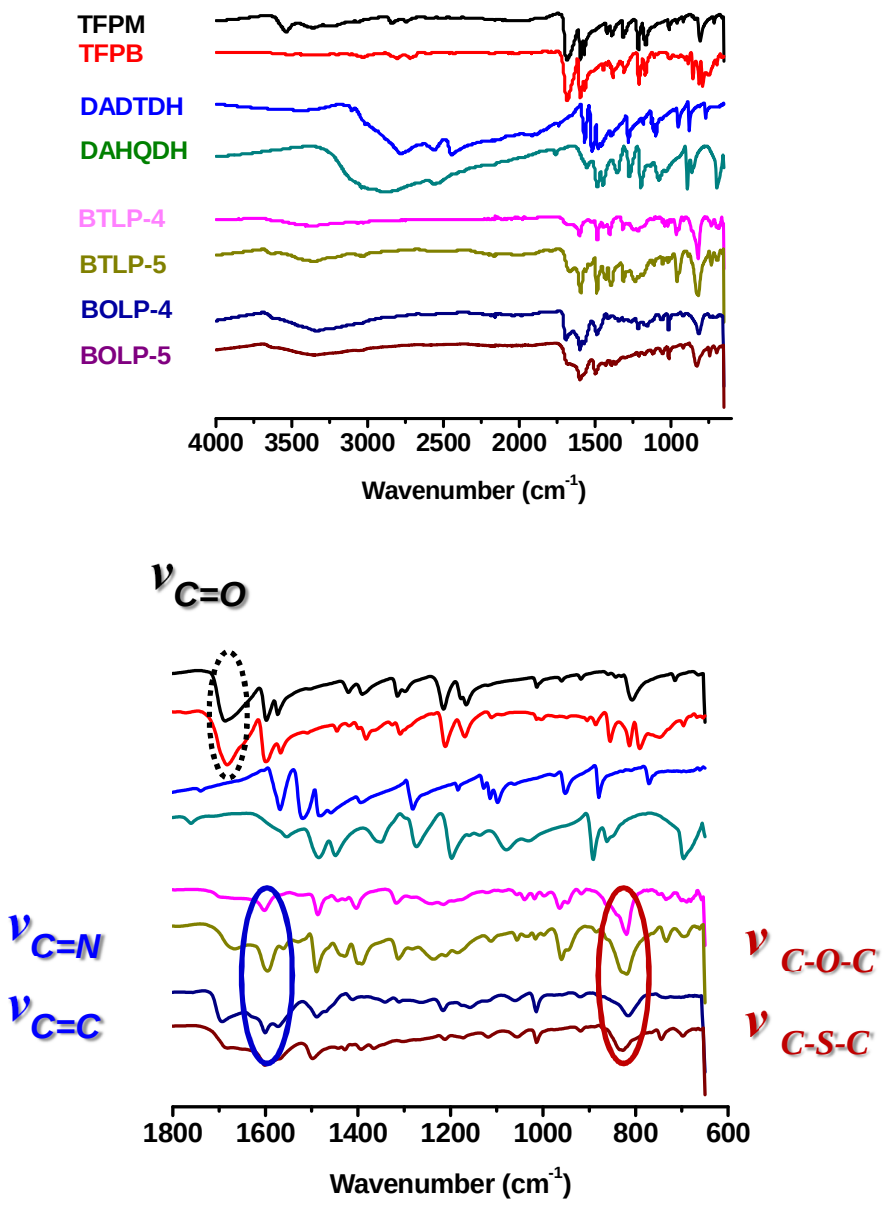
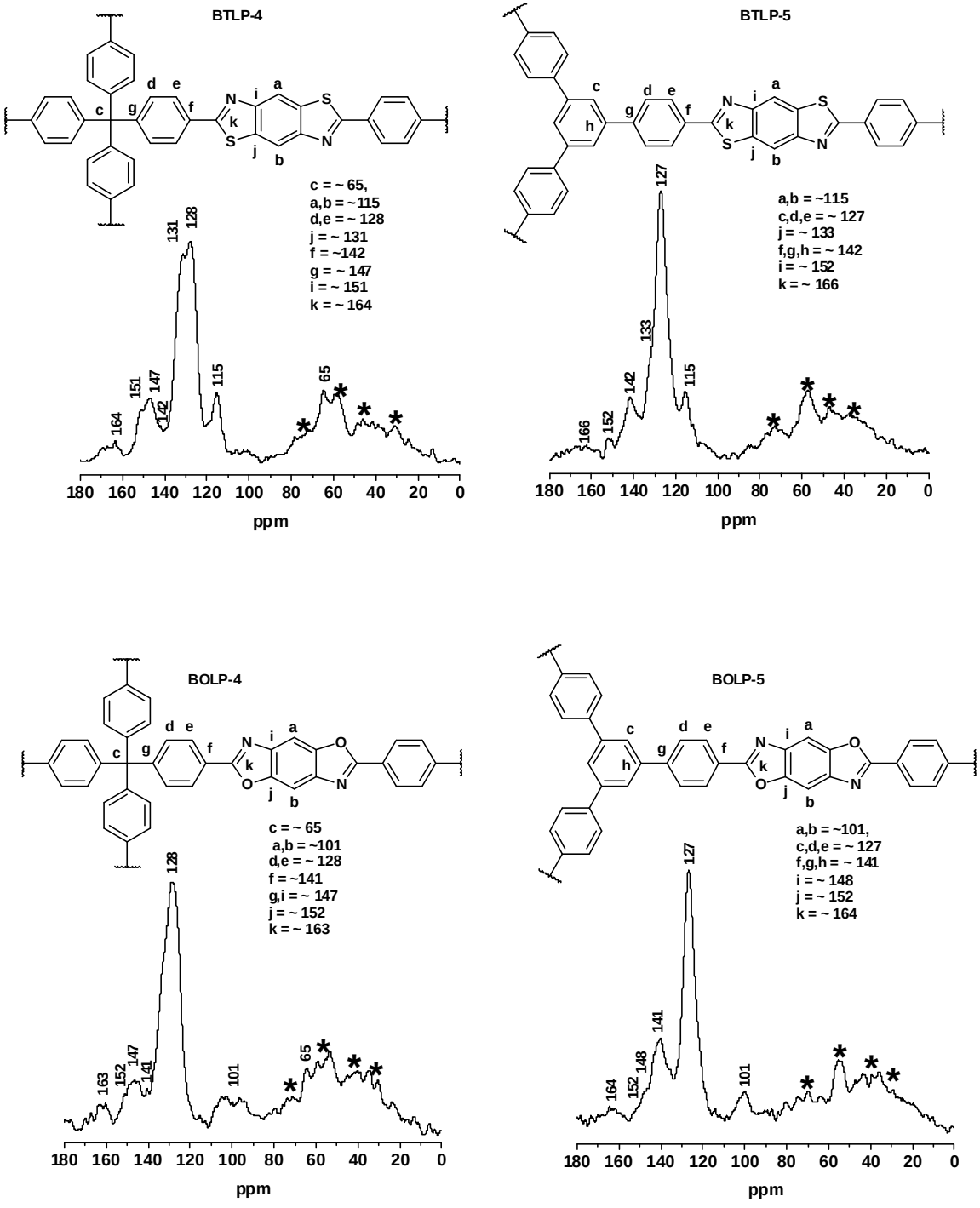


Figure S5: Solid state ^{13}C CP-MAS NMR spectrum of BTLPs and BOLPs.



Section S2: *Low-Pressure (0 –1 bar) Gas Adsorption Measurements for BTLPs and BOLPs*

Low-pressure gas sorption experiments were performed for Ar, N_2, CO_2 and CH_4. The surface properties, for example, surface areas, pore size distributions, pore volume etc. were evaluated from Ar (87 K) adsorption isotherms. Gas storage and selective adsorption properties were evaluated by measuring the adsorption isotherms for CO_2 (273 K and 298 K), CH_4 (273 K and 298 K) and N_2 (273 K and 298 K). The binding affinity (isosteric heats of adsorption) for CO_2, and CH_4 was evaluated from single-component adsorption isotherms using virial equation.

Table S1. Porosity of BTLPs and BOLPs

Polymers	BET	Langmuir (0.1-0.3)	Fitting Error % [a]	PSD (Å) [a]	PV [b]
BTLP-4	1011	1388	0.119	7.55	0.53 (0.54)
BTLP-5	705	1030	0.136	7.93	0.41 (0.42)
BOLP-4	698	1185	0.678	8.68	0.54 (0.58)
BOLP-5	759	1125	0.408	8.30	0.52 (0.56)

[a] Fitting and pore size distribution (PSD) were calculated using zeolites/silica (spher./cylindr. pores, NLDFT ads.) model.

[b]: Pore volume at P/Po = 0.80 (values in parenthesis are at 0.85).

Figure S6. BET and Langmuir Plots for BTLPs and BOLPs. Pressure range to calculate BET surface areas are selected using Micropore BET Assistant on Quantachrome ASiQWin 3.0 software package which picks the data points satisfy the BET consistency rule.

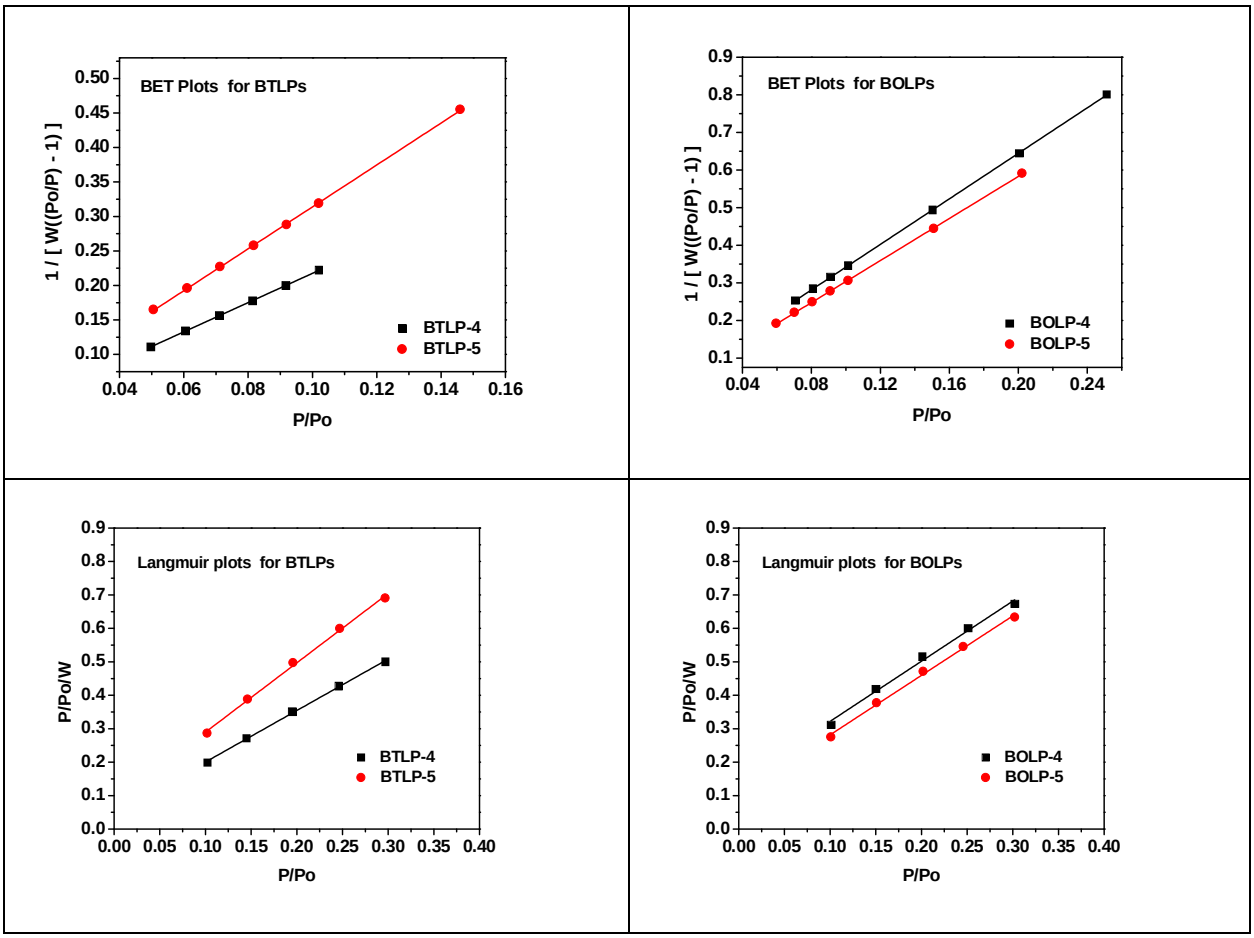


Figure S7. Fittings and pore size distributions for BTLPs and BOLPs.

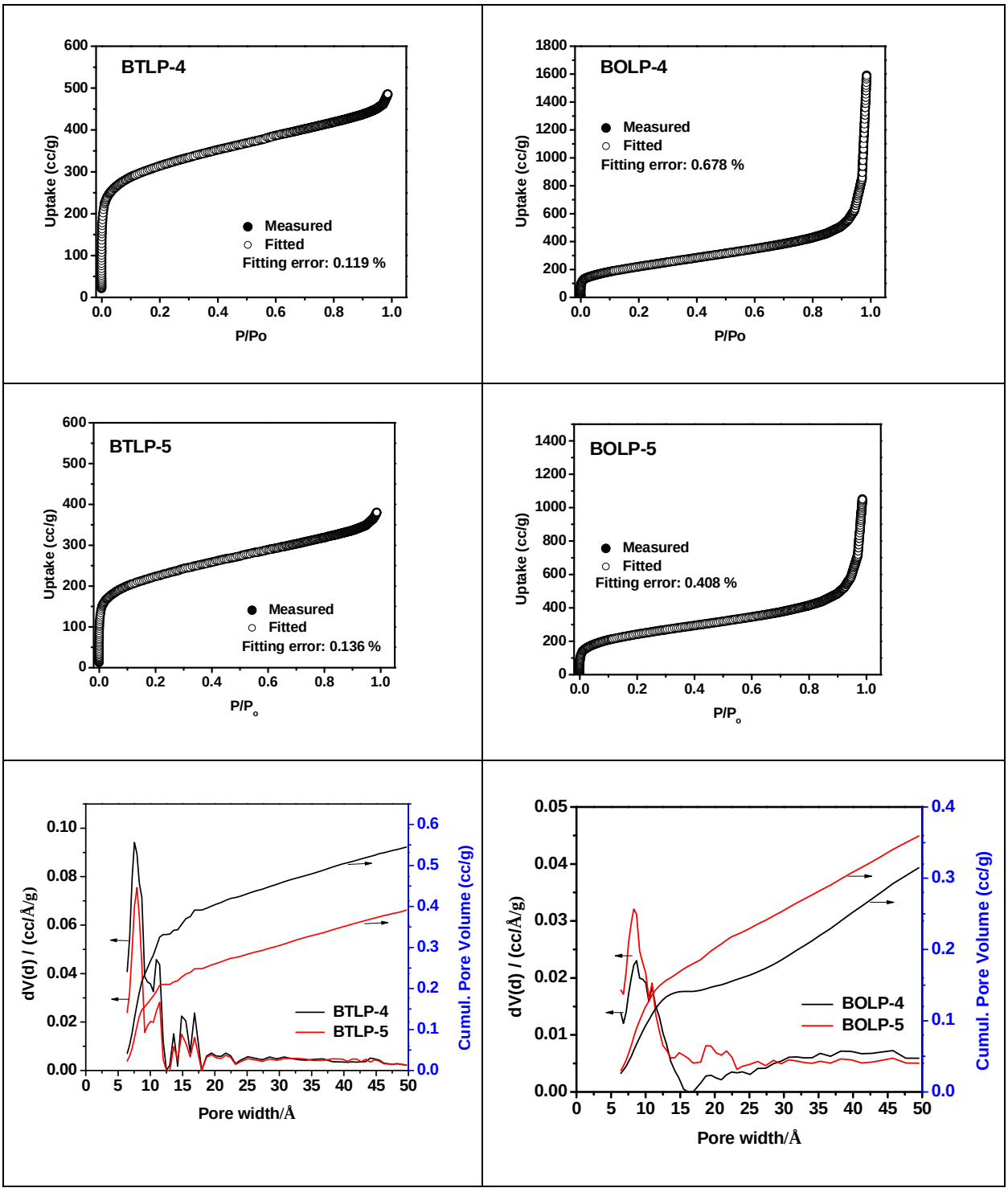


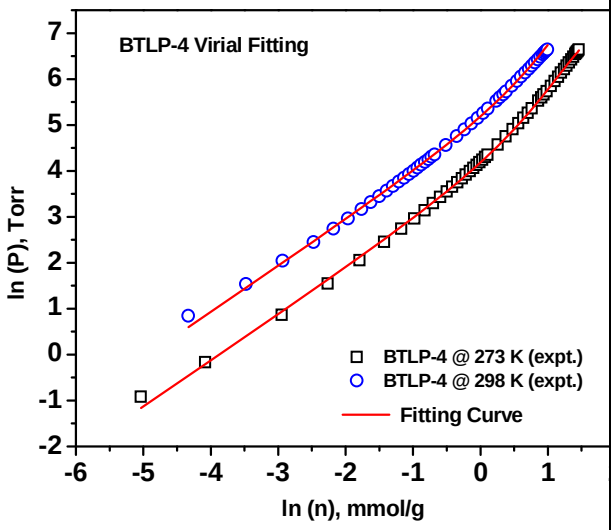
Figure S8. Low-pressure CO_2 gas uptakes and the isosteric heat of adsorptions for BTLPs.

Virial Equation Parameters for BTLP-4

A0=-3437.4115	B0=16.46058479
A1=203.432742	B1=-0.466390189
A2=-30.054856	B2=0.155615323
A3=-2.5779277	

Virial Equation Parameters for BTLP-5

A0=-3499.9639	B0=17.02307099
A1=321.019852	B1=-0.72262873
A2=-4.3237413	B2=0.041695927
A3=-3.5340697	



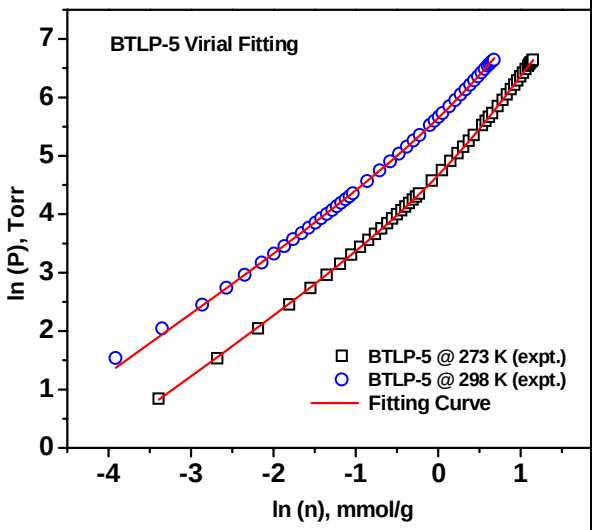


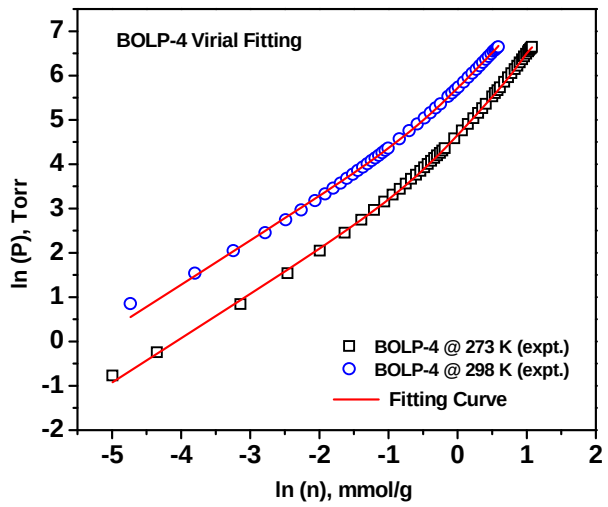
Figure S9. Low-pressure CO_2 gas uptakes and the isosteric heat of adsorptions for BOLPs.

Virial Equation Parameters for BOLP-4

A0=-4041.9523	B0=18.58652087
A1=410.067008	B1=-1.386200835
A2=180.918853	B2=0.34315757
A3=-179.84508	
A4=33.7299725	
A5=5.32880514	
A6=-1.744536	

Virial Equation Parameters for BOLP-5

A0=-3940.107	B0=18.50745779
A1=423.874694	B1=-1.578341259
A2=287.204053	B2=0.371136128
A3=-316.6096	
A4=107.209265	
A5=-13.187666	



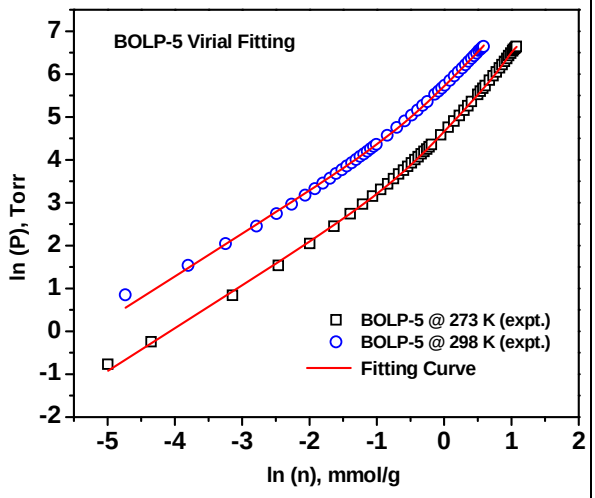


Figure S10. CO_2 uptakes (at 273K and 1 bar) vs surface areas plot for BTLPs, BOLPs, BILPs and BBO-COFs (from Table 1).

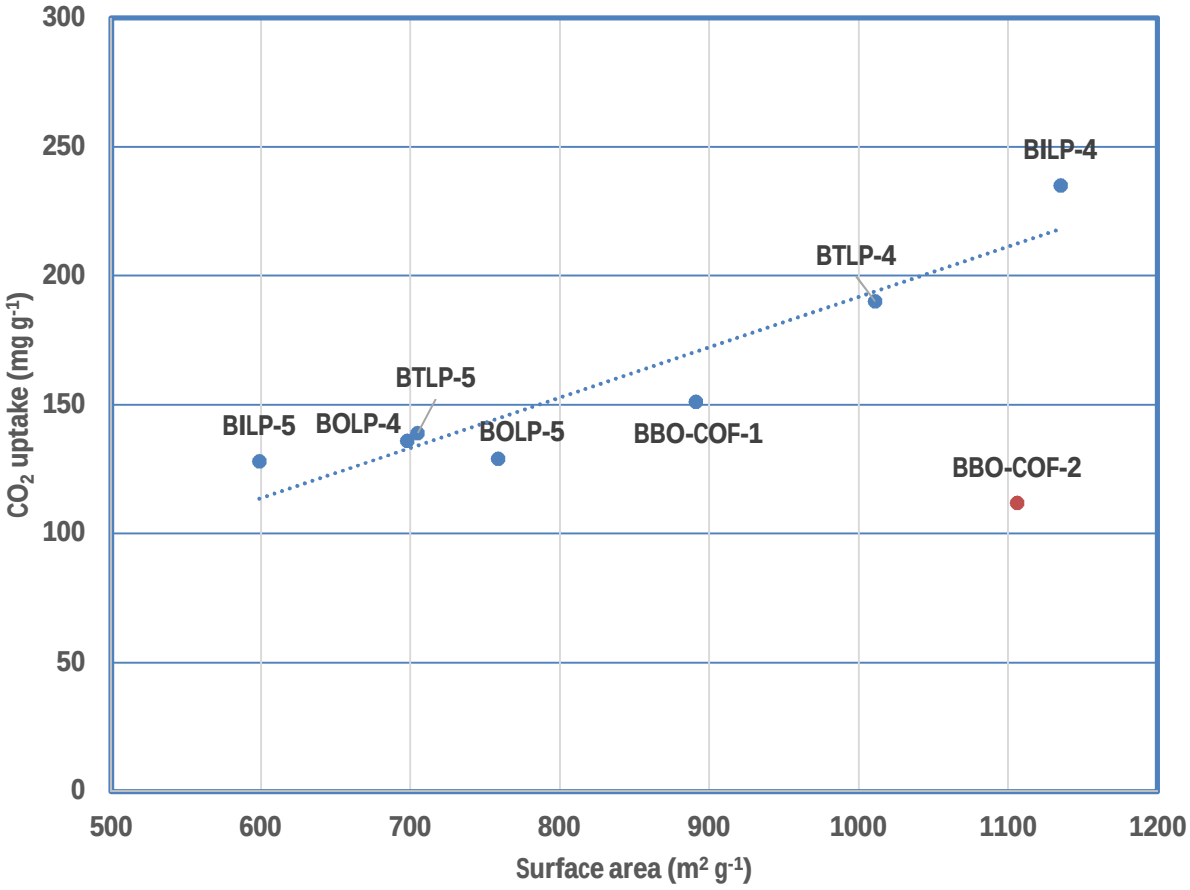
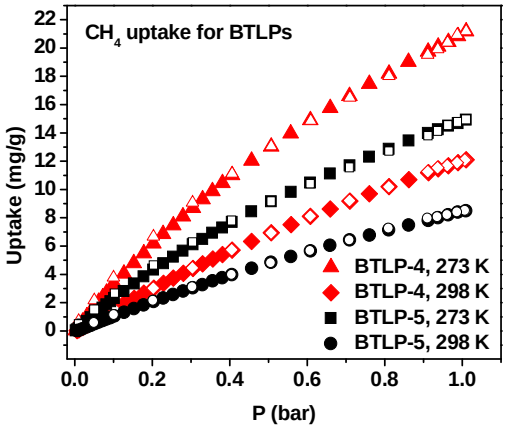
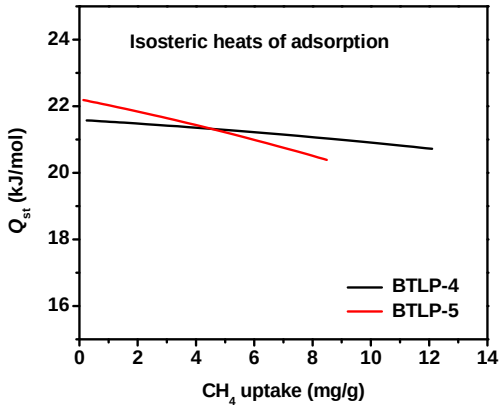


Figure S11. Low-pressure CH_4 gas uptakes and the isosteric heat of adsorptions for BTLPs. Q_{st} is calculated from Virial equation where isotherms collected at 273 and 298 K were fitted. Pressure is Torr and uptake is mmol/g.



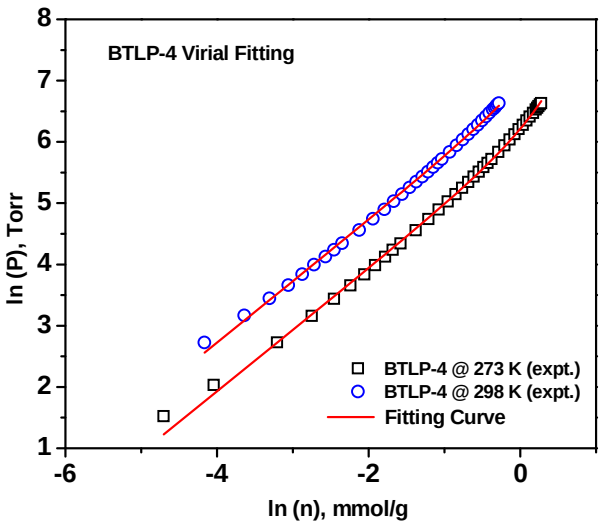


Virial Equation Parameters for BTLP-4

A0=-2596.41522	B0=15.43765681
A1=98.33602377	B1=-0.266744261
A2=52.85392084	

Virial Equation Parameters for BTLP-5

A0=-2671.29443	B0=22.74994966
A1=339.5642231	B1=-1.297028644
A2=140.6936928	B2=0.019997378



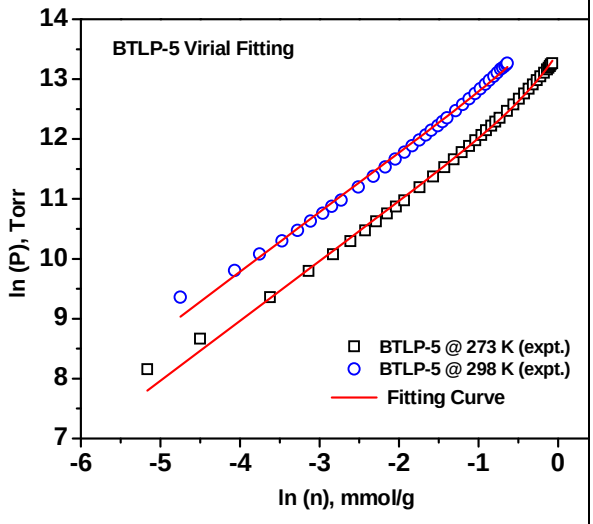
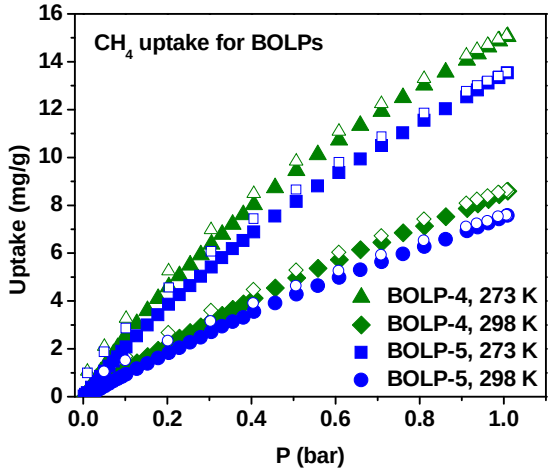
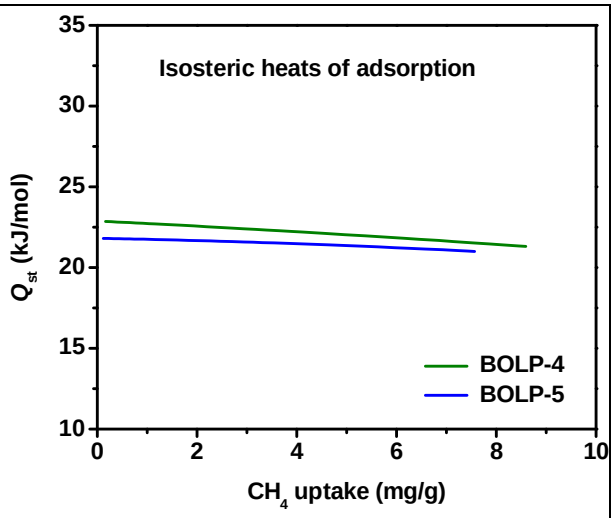


Figure S12. Low-pressure CH_4 gas uptakes and the isosteric heat of adsorptions for BOLPs. Q_{st} is calculated from Virial equation where isotherms collected at 273 and 298 K were fitted. Pressure is Torr and uptake is mmol/g.



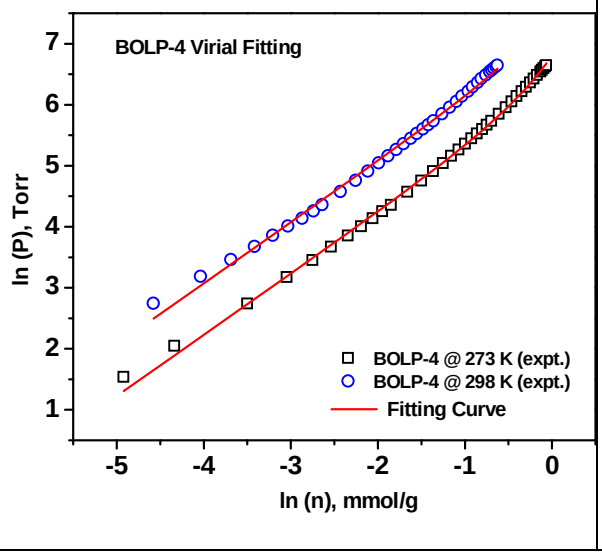


Virial Equation Parameters for BOLP-4

A0=-2751.9567	B0=16.30616766
A1=290.164472	B1=-0.912239836
A2=116.388496	

Virial Equation Parameters for BOLP-5

A0=-2623.9551	B0=16.0857293
A1=116.249015	B1=-0.561845267
A2=193.688156	



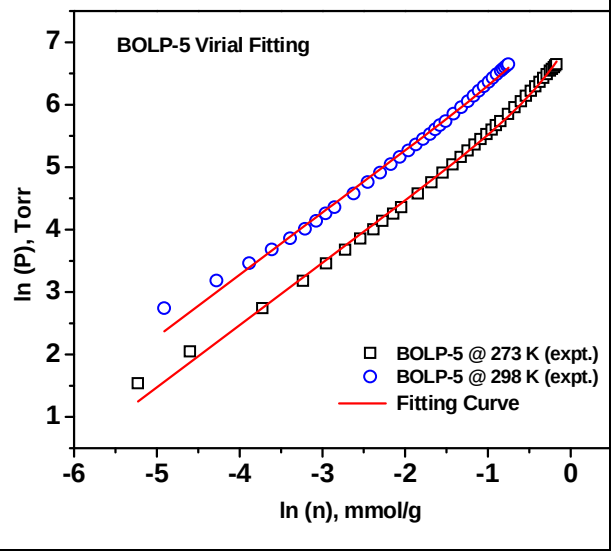


Figure S13. Selectivity for BTLPs

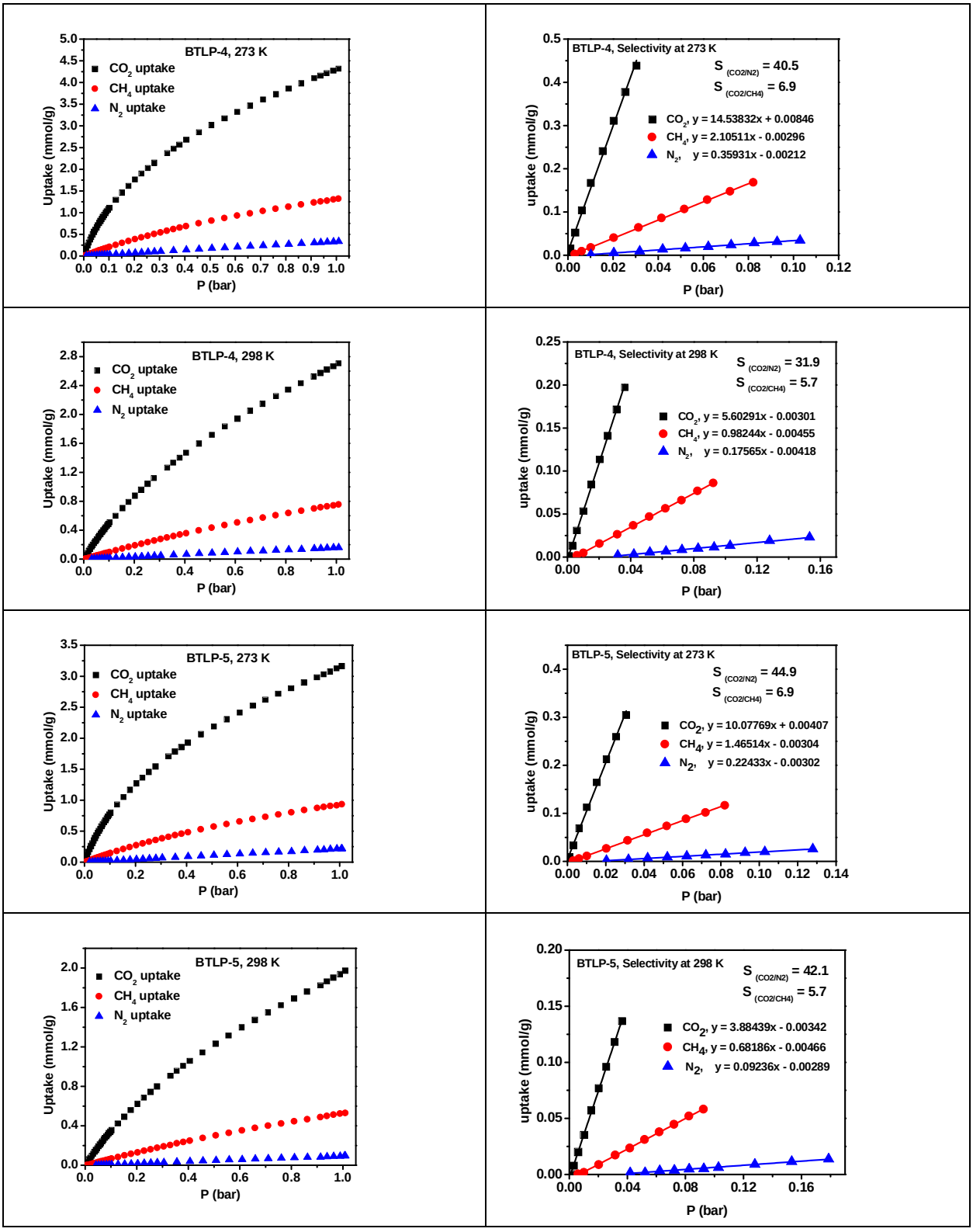
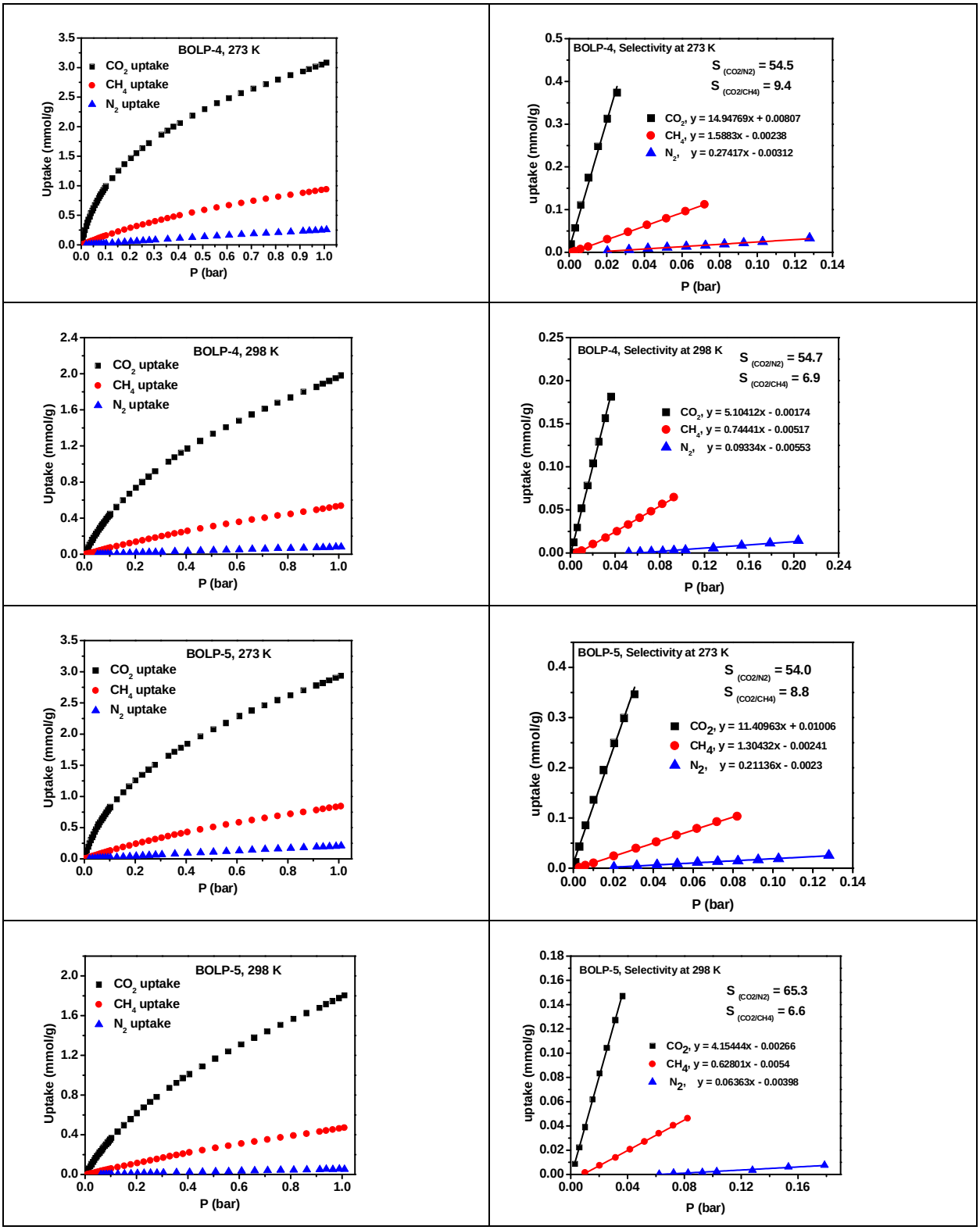


Figure S14. Selectivity for BOLPs



In order to calculate selecitivities by IAST, the pure component isotherms of CO_2 were fitted with the dualsite Langmuir (DSL) isotherm model with a temperature dependent parameter. CH_4 and N_2 isotherms were fitted to single site Lagmuir isotherms. Fitting parameters were used to calculate IAST selectivities. Details about the calculations were explained previously.

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

$$q = q_A + q_B = \frac{q_{sat,A} * (b_A * \exp\left(\frac{E_A}{R*T}\right) * p}{1 + b_A * \exp\left(\frac{E_A}{R*T}\right) * p} + \frac{q_{sat,B} * (b_B * \exp\left(\frac{E_B}{R*T}\right) * p}{1 + b_B * \exp\left(\frac{E_B}{R*T}\right) * p}$$

where, q is total molar loading; q_{sat} is saturation loading, mol kg^{-1}; p is total system pressure, Pa; R is ideal gas constant, 8.314 J mol^{-1} K^{-1}; b is Langmuir constant, Pa^{-1}; T is absolute temperature,K. Subscripts A and B refers to site A and site B, respectively.

Figure S15. Dual site or single site Langmuir fitting plots for BOLP-4 at 273 (blue square) and 298 K (red circles) for CO_2 (top), CH_4 (middle) and N_2 (bottom).

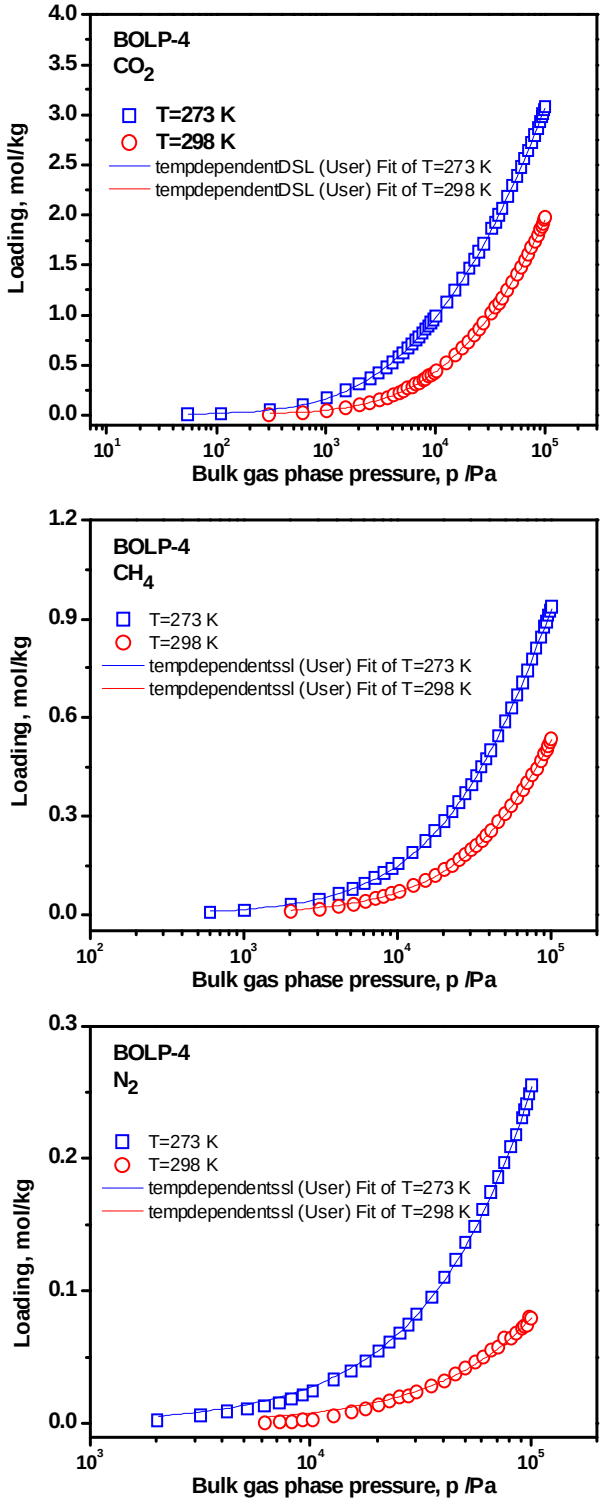


Figure S16. Dual site or single site Langmuir fitting plots for BOLP-5 at 273 (blue square) and 298 K (red circles) for CO_2 (top), CH_4 (middle) and N_2 (bottom).

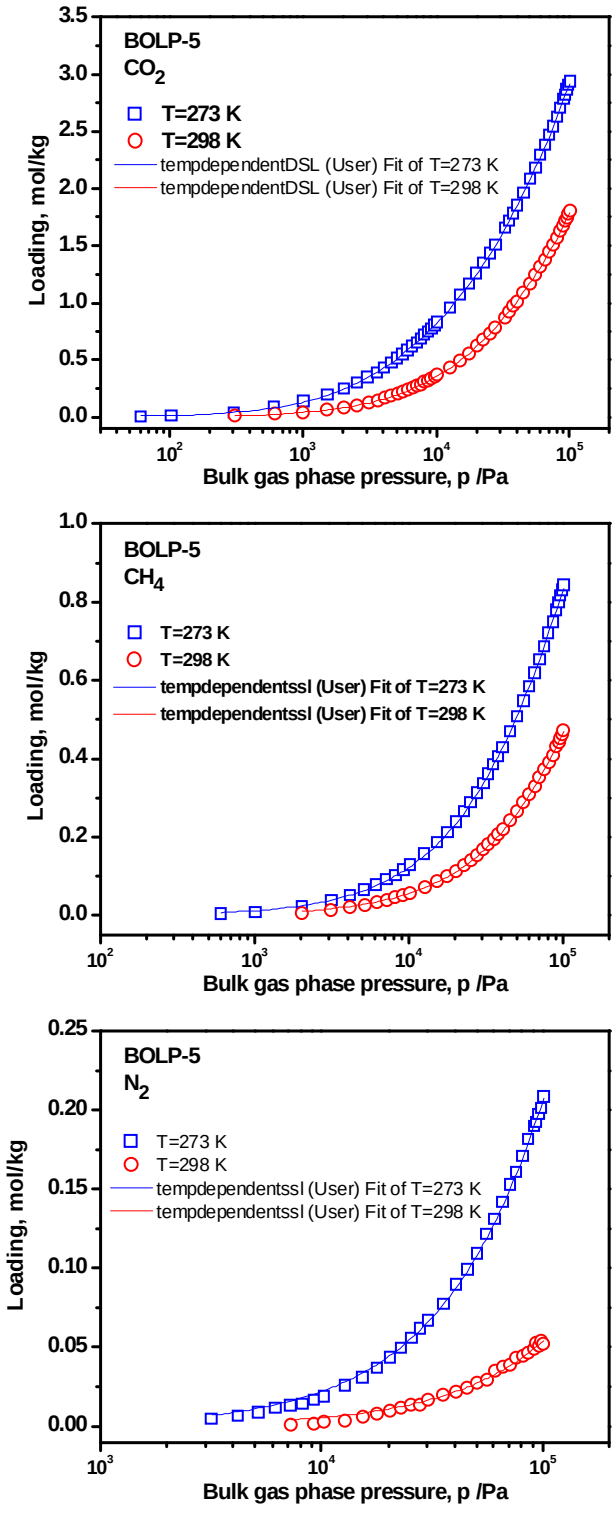


Figure S17. Dual site or single site Langmuir fitting plots for BTLP-4 at 273 (blue square) and 298 K (red circles) for CO_2 (top), CH_4 (middle) and N_2 (bottom).

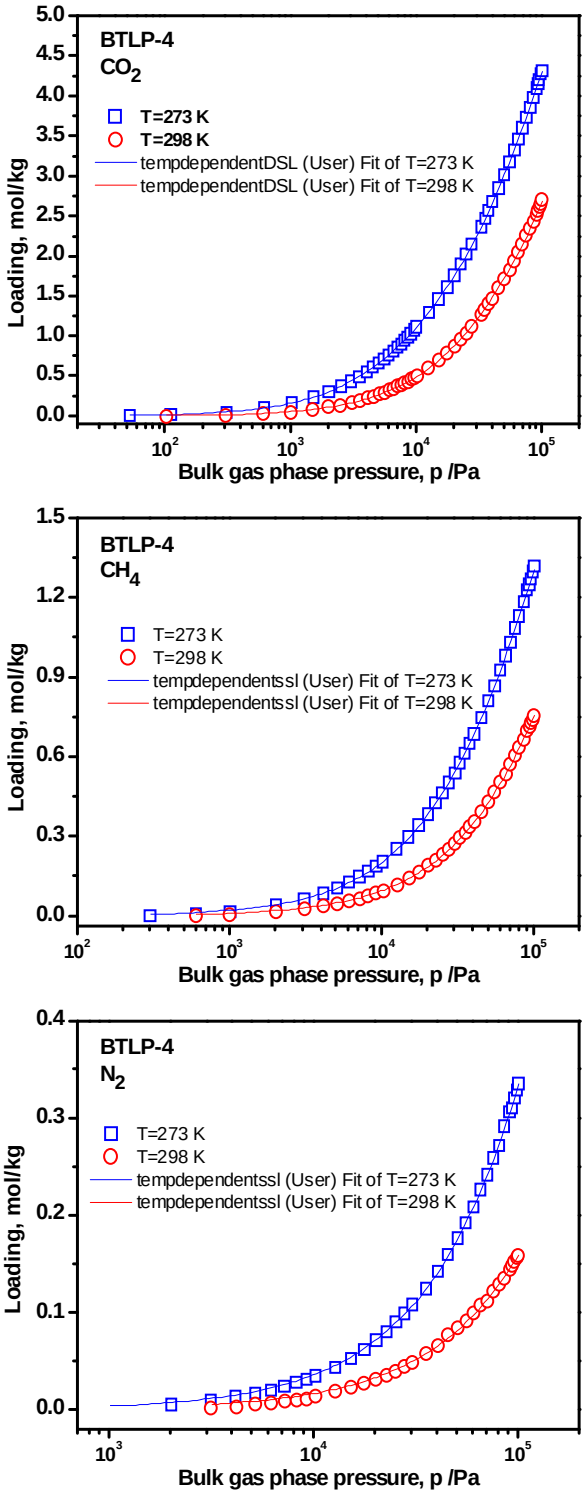


Figure S18. Dual site or single site Langmuir fitting plots for BTLP-5 at 273 (blue square) and 298 K (red circles) for CO_2 (top), CH_4 (middle) and N_2 (bottom).