*Supporting information for*

# Hyper-Crosslinked Porous Organic Frameworks with Ultra-micropores for Selective Xenon Capture

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## 1. Materials and Methods:

All the organic chemicals were purchased from sigma aldrich. 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene was synthesized according to previously reported procedure[S1] with slight modification.

***Synthesis of the IISERP-POF6:***

The polymers were prepared via Fridel Craft alkylation reaction. 0.75 mmol (96 mg) naphthalene and 0.5 mmol (200 mg) tri bromide compound were dissolved in 40 ml of dry dichloromethane (DCM). Then 3.75 mmol $AlCl_3$ (500 mg) was added slowly. The mixture was gently heated at 40°C for 24 hours under $N_2$ atmosphere. After that the mixture was taken out, filtered, washed with DCM and then suspended in 20 ml 3 M HCl to dissolve unreacted $AlCl_3$. The final product was soxhletted using Dimethyl formamide (DMF) and Tetrahydrofuran (THF) mixture to eliminate oligomeric impurities yielding a yellow colored polymer (Yield ~80%). Observed elemental analysis; C: 82.65%, H: 13.82%.

***Synthesis of the IISERP-POF7:***

0.75 mmol (152 mg) pyrene and 0.5 mmol (200 mg) tri bromide compound were dissolved in 40 ml of dry dichloromethane (DCM). Then 3.75 mmol $AlCl_3$ (500 mg) was added slowly. The mixture was gently heated at 40°C for 24 hours under $N_2$ atmosphere. After that the mixture was taken out, filtered, washed with DCM and then suspended in 20 ml 3 M HCl to dissolve unreacted $AlCl_3$. The final product was soxhletted using DMF and THF mixture to eliminate oligomeric impurities yielding a brown colored polymer (Yield ~80%). Observed elemental analysis; C: 81.34%, H: 15.75%.

***Synthesis of the IISERP-POF8:***

0.75 mmol (183 mg) pyrene and 0.5 mmol (200 mg) tri bromide compound were dissolved in 40 ml of dry dichloromethane (DCM). Then 3.75 mmol $AlCl_3$ (500 mg) was added slowly. The mixture was gently heated at 40°C for 24 hours under $N_2$ atmosphere. After that the mixture was taken out, filtered, washed with DCM and then suspended in 20 ml 3 M HCl to dissolve unreacted $AlCl_3$. The final product was soxhletted using DMF and THF mixture to eliminate oligomeric impurities yielding a brown colored polymer (Yield ~80%). Observed elemental analysis; C: 86.52%, H: 12.21%.

***Gram scale synthesis of IISERP-POF6:***

As a representative of the polymers IISERP-POF6 had been synthesized in gram scale. In a typical synthesis, 7.5 mmol (1.83 g) napthalene and 5 mmol (2 g) tri bromide compound were dissolved in 300 ml of dry dichloromethane (DCM). Then 37.5 mmol $AlCl_3$ (5 g) was added slowly. The mixture was gently heated at 40°C for 36 hours under $N_2$ atmosphere. After that the mixture was taken out, filtered, washed with DCM and then suspended in 200 ml 3 M HCl to dissolve unreacted $AlCl_3$. The final product was soxhletted using DMF and THF mixture to eliminate oligomeric impurities yielding a yellow colored polymer (Yield ~75%). Observed elemental analysis; C: 79.54%, H: 16.88%.

***Stability studies in hash conditions:***

To check the stability of the polymers, they were suspended in 3M HCl, 3M NaOH, boiling water and the stability were confirmed by $N_2$ adsorption at 77 K and IR spectra.

S1: S. B. Maity and P. K. Bharadwaj, *Inorg. Chem.*, 2013, **52**, 1161−1163.

**Table S1**: Comparison of the $Xe/N_2$ selectivities of the polymers with some benchmark porous materials.

| Serial no. | Material | $Xe/N_2$ selectivity at 298K, 1bar (1Xe:99N2) | Ref. |
|---|---|---|---|
| **1** | **IISERP-POF6** | **200**[a] | **This Work** |
| **2** | **IISERP-POF7** | **180**[a] | **This Work** |
| **3** | **IISERP-POF8** | **160**[a] | **This Work** |
| 4 | Carbon-ZX | 120[a] | *Sci. Rep.* **2016**, *6*, 21295. |
| 5 | ZIF8 | ~40[a] | *Sci. Rep.* **2016**, *6*, 21295. |
| 6 | PCN-14 | 24.7[b] | *J. Phys. Chem. C* **2014**, *118*, 11685. |
| 7 | NOTT series | 18.1-21[b] | *J. Phys. Chem. C* **2014**, *118*, 11685. |
| 8 | HKUST-1 | 20.7[b] | *J. Phys. Chem. C* **2014**, *118*, 11685. |
| 9 | IRMOF series | 8.6-10.7[b] | *J. Phys. Chem. C* **2012**, *116*, 19765. |
| 10 | MOF-74 series | 5.3-18.2[b] | *J. Phys. Chem. C* **2012**, *116*, 19765. |

[a]selectivity calculated using IAST modeling. [b]Selectivity calculated from Henry's constant.

## 2. Analytical characterization:

***Powder X-ray diffraction:***

Powder X-Ray Diffraction data were recorded out Rigaku Miniflex-600 instrument and processed using PDXL software.

***Thermo gravimetric Analysis:***

Thermal analysis (thermo-gravimetric) of the polymers was carried out using NETSZCH TGA-DSC system. TGAs were performed under 20 ml/min $N_2$ gas flow (purge + protective) and the heating rate was maintained 5 K/min from 25°C to 550°C.

***IR spectroscopy:***

IR spectra were recorded using a Nicolet ID5 attenuated total reflectance IR spectrometer which operates at ambient temperature. Anhydrous KBr pellets were used to record the data.

***Field Emission Scanning Electron Microscopy:***

FE-SEM images were collected using Ultra Plus Field Emission Scanning Electron Microscope with integral charge compensator and embedded EsB and AsB detectors. Oxford X-max instruments 80 $mm^2$. (Carl Zeiss NTS, Gmbh), Imaging conditions: 2 kV, WD=2 mm, 200 kX, Inlens detector. For preparing the polymers for imaging, the samples were ground thoroughly, dispersed in methanol and were sonicated for 5 min. After that the well dispersed polymers in methanol were drop casted on silicon wafer and dried in vacuum for 12 hours.

***HR-Transmission electron microscopy (HRTEM):***

Jeol JEM220FS high-resolution transmission electron microscope (HR-TEM) equipped with a field emission source operating at 200 KeV was used for collecting the TEM images. The well dispersed sample was drop casted on a Cu grid.

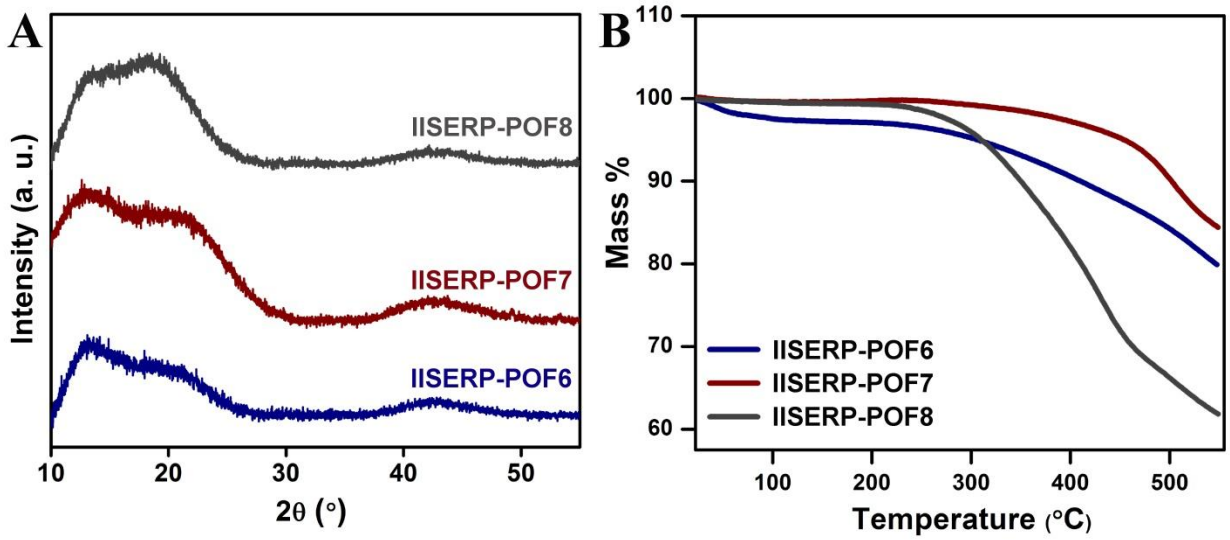


**Figure S1:** (A) Powder X-Ray Diffraction pattern of the respective polymers showing amorphous nature (B) Thermo Gravimetric Analysis (TGA) curves for the corresponding polymers showing the polymers are thermally stable up to ~200°C.

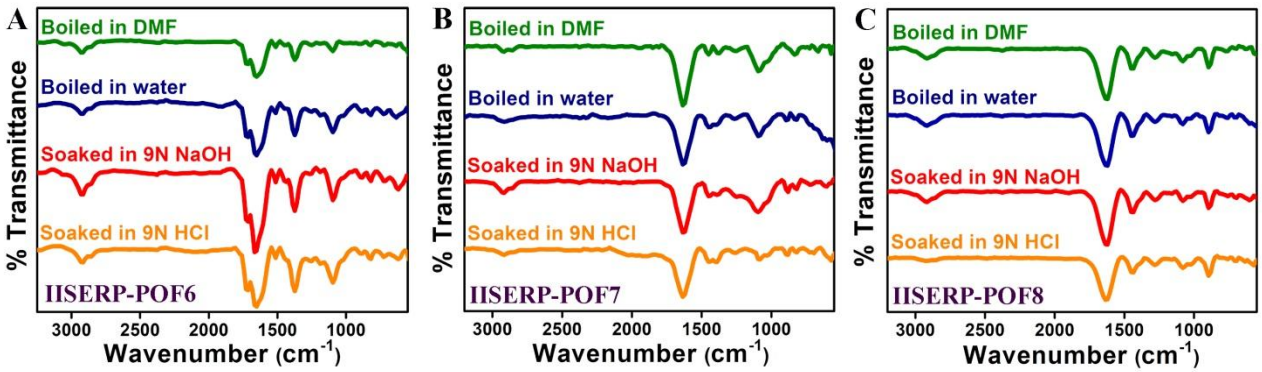


**Figure S2:** Infra-Red (IR) spectra of **POFs** treated in different chemical conditions. These spectra exemplify the stability of the polymer in different chemical environments. (*Source: Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, Applications in Coordination, Organometallic, and Bioinorganic Chemistry, 6th Edition, Kazuo Nakamoto*).

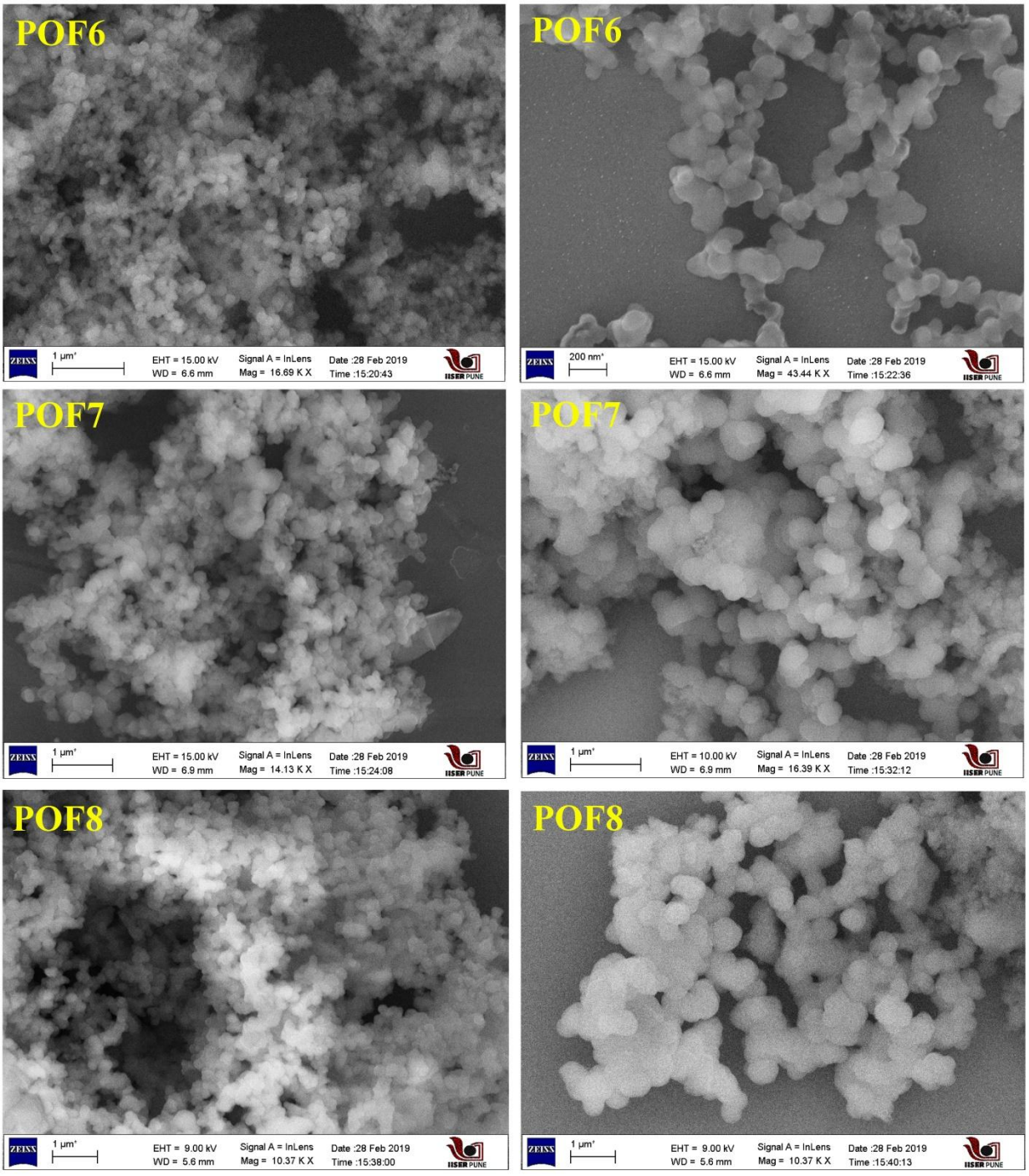


**Figure S3:** Field Emission Scanning Electron Microscopic (FESEM) images of the three polymers. The images show that all three polymers possess spherical morphology.

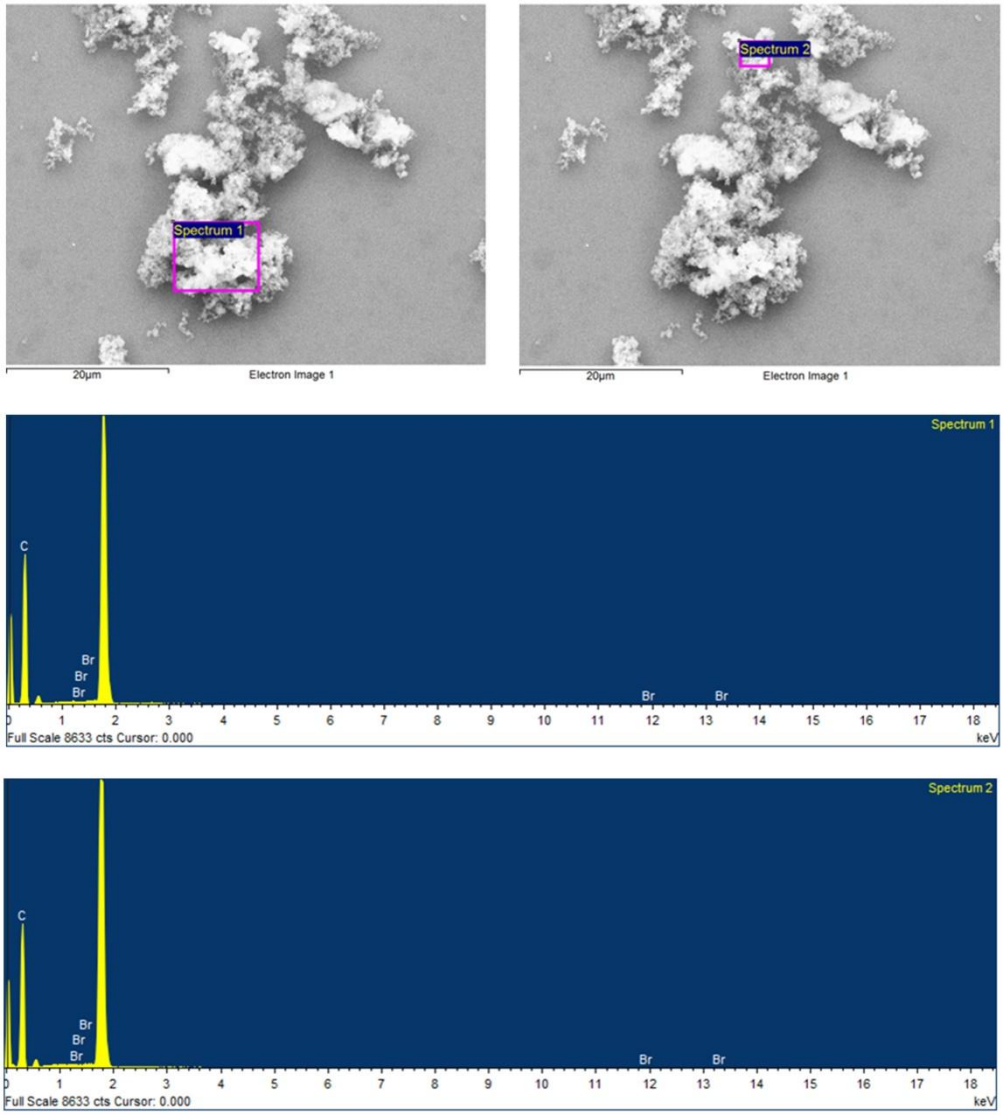


**Figure S4:** Energy Dispersive X-Ray (EDX) images of **IISERP-POF6** showing the respective elements present in the polymer.

**Table S2:** Atomic and elemental composition obtained from EDX analysis of **IISERP-POF6**.

| | **Spectrum 1** | | **Spectrum 2** | |
|---|---|---|---|---|
| **Element** | **Weight %** | **Atomic %** | **Weight %** | **Atomic %** |
| C K | 98.08 | 99.71 | 99.17 | 99.56 |
| Br L | 1.92 | 0.29 | 2.83 | 0.44 |

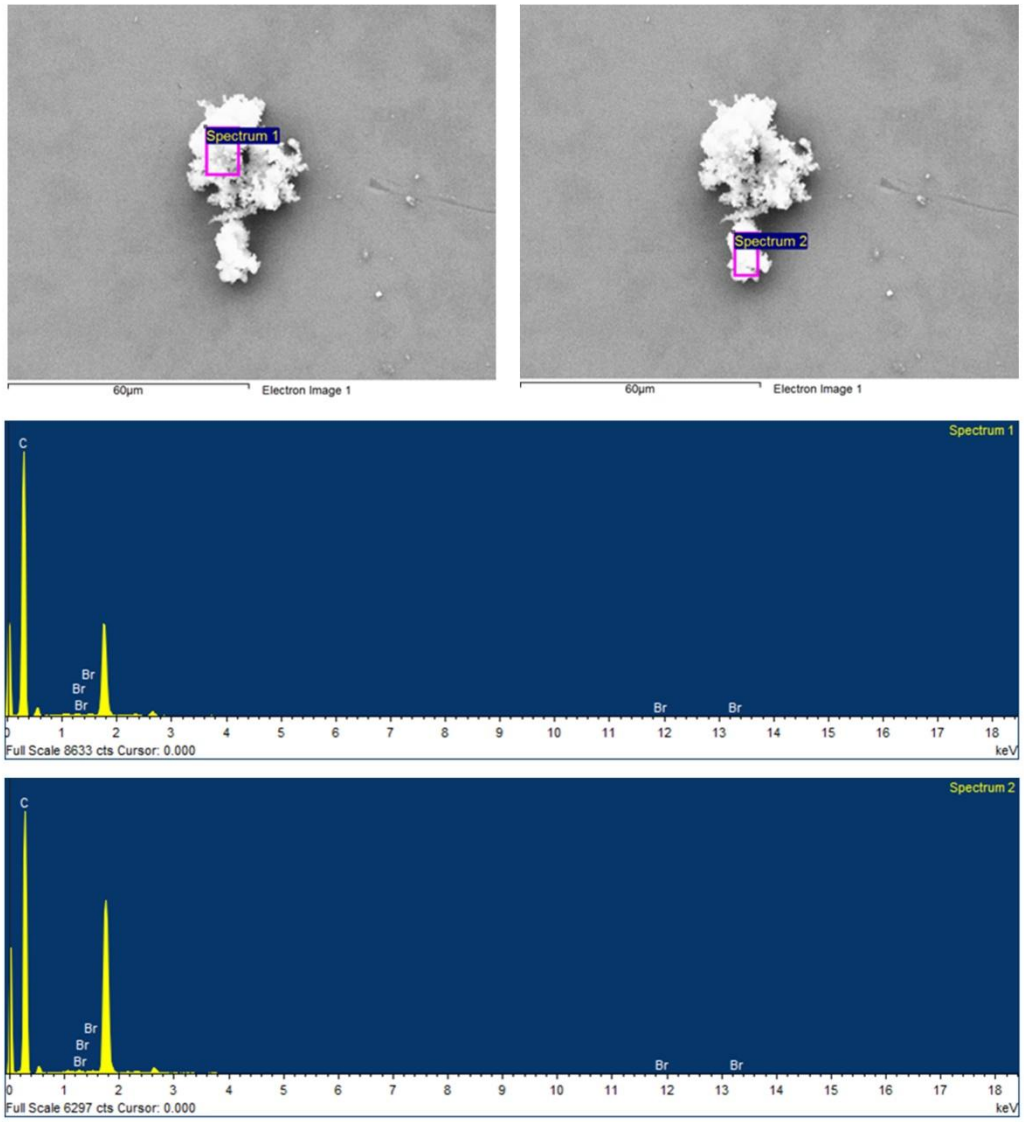


**Figure S5:** Energy Dispersive X-Ray (EDX) images of **IISERP-POF7** showing the respective elements present in the polymer.

**Table S3**: Atomic and elemental composition obtained from EDX analysis of **IISERP-POF7**.

| | **Spectrum 1** | | **Spectrum 2** | |
|---|---|---|---|---|
| **Element** | **Weight %** | **Atomic %** | **Weight %** | **Atomic %** |
| C K | 98.96 | 99.84 | 98.93 | 99.84 |
| Br L | 1.04 | 0.16 | 1.07 | 0.16 |

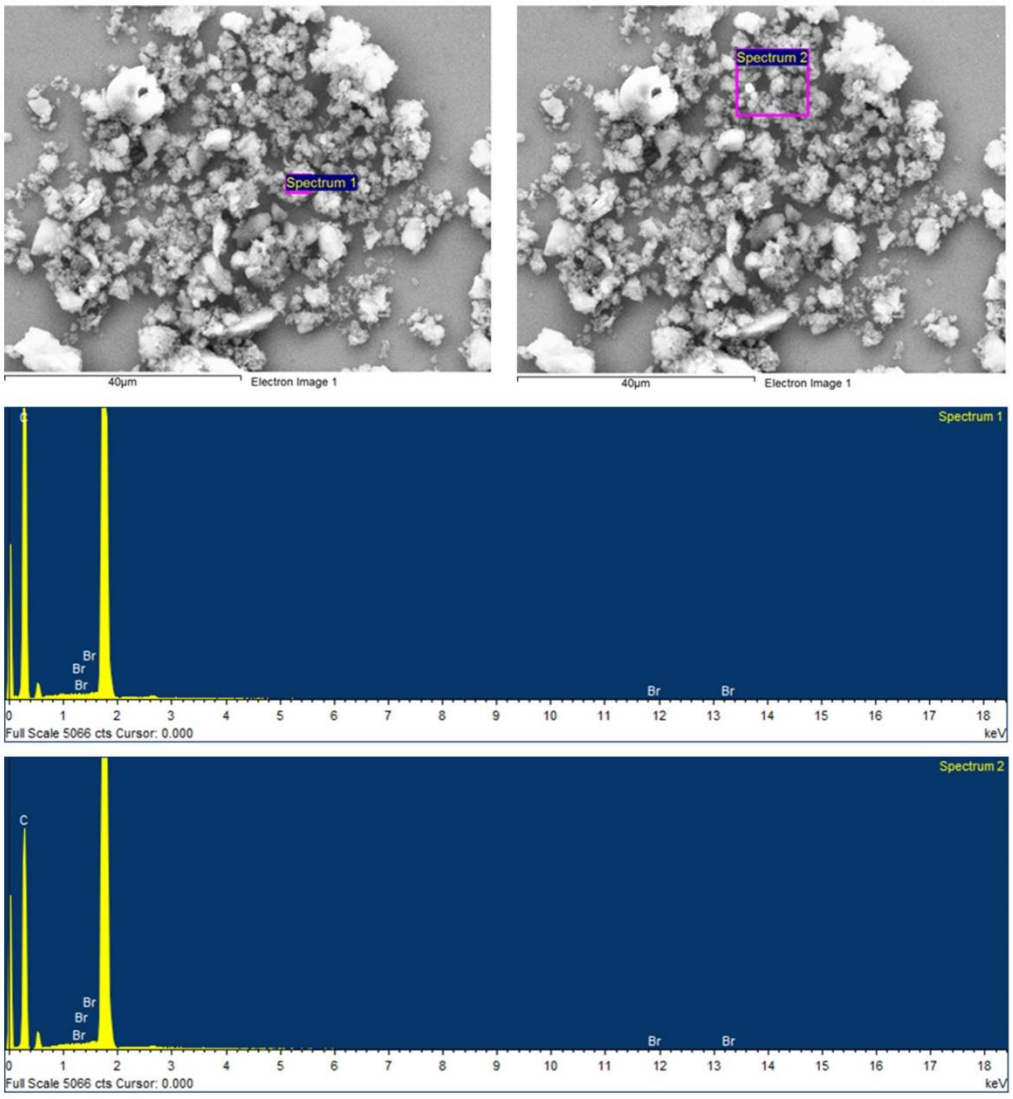


**Figure S6:** Energy Dispersive X-Ray (EDX) images of **IISERP-POF8** showing the respective elements present in the polymer.

**Table S4**: Atomic and elemental composition obtained from EDX analysis of **IISERP-POF8**.

| | **Spectrum 1** | | **Spectrum 2** | |
|---|---|---|---|---|
| **Element** | **Weight %** | **Atomic %** | **Weight %** | **Atomic %** |
| C K | 98.22 | 99.73 | 98.70 | 99.49 |
| Br L | 1.78 | 0.27 | 1.30 | 0.51 |

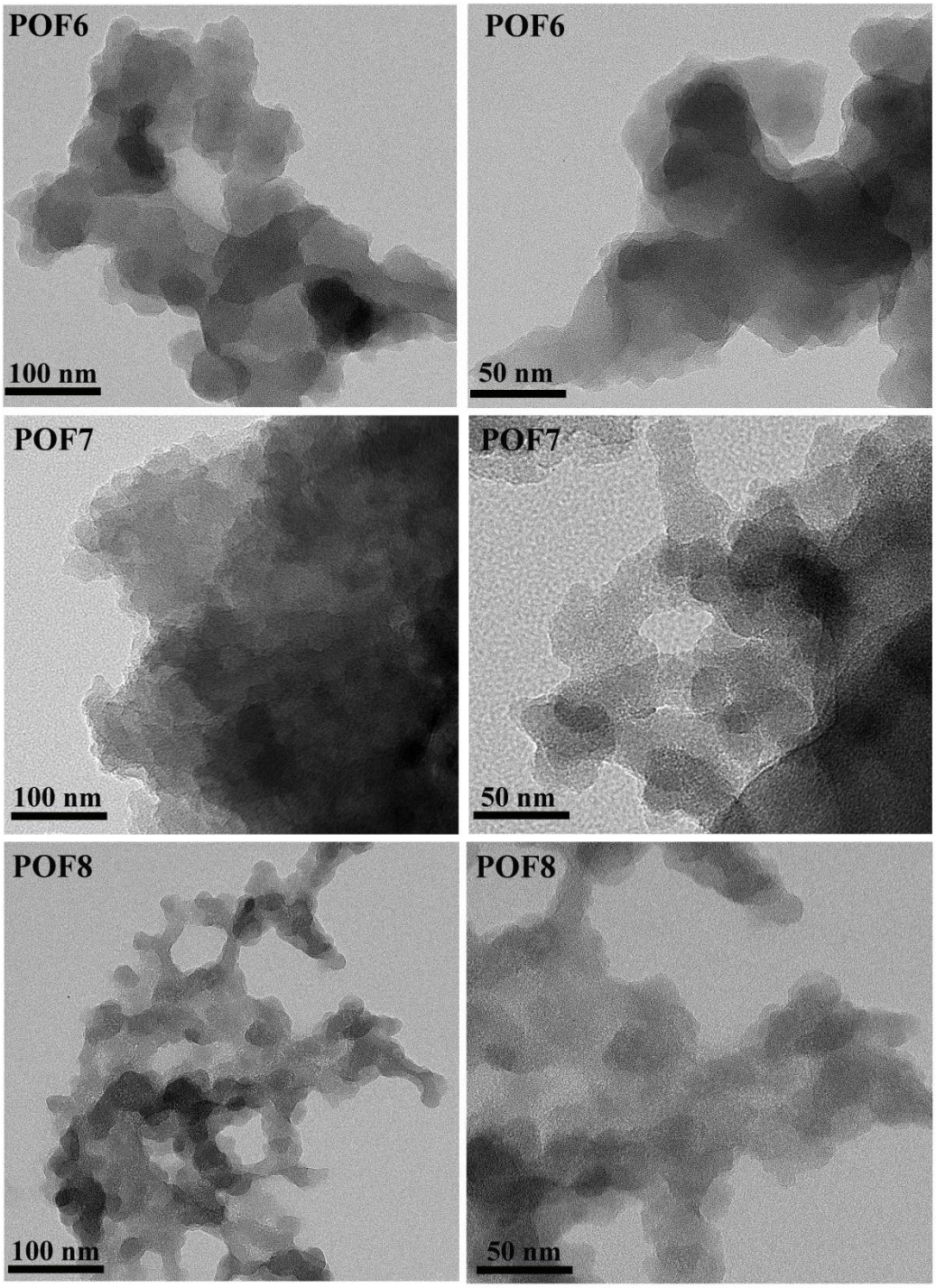


**Figure S7:** High Resolution Transmission Electron Microscopic (HRTEM) images of the three polymers. The images show that all three polymers possess spherical morphology.

## 3. Gas Adsorption Studies:

All the adsorptions were carried out using a 3-FLEX pore and surface area analyser, Micromeritics and few cases 'Autosorb IQ', Quantachrome.

***Langmuir fits:***

In most 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.[S2] Utilizing this routine circumvents some of the problems associated with favoring either high or low pressure regions when linearizing the Langmuir equation 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)

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

***Virial analysis:***

The Xe & Kr adsorption data for the polymers were measured from 0- 1bar at 278, 288 and 298 K and were fitted by the following virial equation.

*ln(P) = ln(Va)+(A0+A1*Va +A2*Va^2 ...+ A6*Va^6)/T+(B0+B1*Va)*

Where P is pressure, Va is amount adsorbed, T is temperature, and A0, A1, A2 …, A4 and B0, B1 are temperature independent empirical parameters.

**Table S5:** Fitted Virial parameters for Xe.

| Parameters | IISERP-POF6 | IISERP-POF7 | IISERP-POF8 |
|---|---|---|---|
| A0 | -3208.061845 | -3200.490362 | -3243.346928 |
| A1 | 619.2541303 | 718.1017016 | 501.8488689 |
| A2 | -270.7945347 | -328.0339082 | -198.7313009 |
| A3 | 59.84408912 | 81.72084534 | 45.48335781 |
| A4 | 0 | -0.459100703 | 0 |
| B0 | 15.22197341 | 15.12487157 | 15.5214489 |
| B1 | 0 | -0.038330415 | 0 |

**Table S6:** Fitted Virial parameters for Kr.

| Parameters | IISERP-POF6 | IISERP-POF7 | IISERP-POF8 |
|---|---|---|---|
| A0 | -2697.304481 | -2651.063435 | -2187.629647 |
| A1 | -204.0152665 | 192.5161732 | -237.3467145 |
| B0 | 16.29700252 | 16.0864836 | 14.48544663 |
| B1 | 1.280113504 | 0 | 1.442828328 |

***Ideal Adsorption Solution Theory (IAST):***

IAST calculations were employed as described by Prausnitz et al.[S3] The equation that is involved in selectivity calculations has been given below.

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

***IAST fitting parameters:***

**Table S7:** Fitted IAST parameters for Xe/Kr (20Xe:80Kr composition) selectivity at 298 K and 288 K for **IISERP-POF6**.

| Constants | Gas A | | Gas B | |
|---|---|---|---|---|
| | 288 K | 298 K | 288 K | 298 K |
| qA1 | 3.849746839 | 3.082682691 | 2.536684261 | 2.324022715 |
| qA2 | 0 | 0 | 0 | 0 |
| kA1 | 0.008437009 | 0.006507509 | 0.000457617 | 0.000416795 |
| kA1 | 0 | 0 | 0 | 0 |
| nA1 | 0.678442665 | 0.731527453 | 0.992821604 | 0.954831647 |
| nA1 | 0 | 0 | 0 | 0 |
| HA1 | 0.032480347 | 0.020060586 | 0.001160829 | 0.000968641 |
| HA1 | 0 | 0 | 0 | 0 |

**Table S8:** Fitted IAST parameters for Xe/Kr (20Xe:80Kr composition) selectivity at 298 K and 288 K for **IISERP-POF7**.

| Constants | Gas A | | Gas B | |
|---|---|---|---|---|
| | 288 K | 298 K | 288 K | 298 K |
| qA1 | 3.849746839 | 3.082682691 | 2.536684261 | 2.324022715 |
| qA2 | 0 | 0 | 0 | 0 |
| kA1 | 0.008437009 | 0.006507509 | 0.000457617 | 0.000416795 |
| kA1 | 0 | 0 | 0 | 0 |
| nA1 | 0.678442665 | 0.731527453 | 0.992821604 | 0.954831647 |
| nA1 | 0 | 0 | 0 | 0 |
| HA1 | 0.032480347 | 0.020060586 | 0.001160829 | 0.000968641 |
| HA1 | 0 | 0 | 0 | 0 |

**Table S9:** Fitted IAST parameters for Xe/Kr (20Xe:80Kr composition) selectivity at 298 K and 288 K for **IISERP-POF8**.

| Constants | Gas A | | Gas B | |
|---|---|---|---|---|
| | 288 K | 298 K | 288 K | 298 K |
| qA1 | 4.048261507 | 3.49427188 | 2.539073057 | 2.32658096 |
| qA2 | 0 | 0 | 0 | 0 |
| kA1 | 0.005828481 | 0.004462894 | 0.000397678 | 0.000356362 |
| kA1 | 0 | 0 | 0 | 0 |
| nA1 | 0.748253836 | 0.780912786 | 1.00583943 | 0.984825712 |
| nA1 | 0 | 0 | 0 | 0 |
| HA1 | 0.023595216 | 0.015594564 | 0.001009733 | 0.000829105 |
| HA1 | 0 | 0 | 0 | 0 |

**Table S10:** Fitted IAST parameters for $Xe/N_2$ ($1Xe:99N_2$ composition) selectivity at 298 K for all the polymers.

| Constants | Gas A | | | Gas B | | |
|---|---|---|---|---|---|---|
| | POF6 | POF7 | POF8 | POF6 | POF7 | POF8 |
| qA1 | 3.584327049 | 3.083585995 | 3.454944772 | 0.067818734 | 0.081464087 | 0.083108822 |
| qA2 | 0 | 0 | 0 | 0 | 0 | 0 |
| kA1 | 0.005114634 | 0.006541535 | 0.004416721 | 0.000332957 | 0.000284879 | 0.000244613 |
| kA1 | 0 | 0 | 0 | 0 | 0 | 0 |
| nA1 | 0.748628779 | 0.730605945 | 0.785567598 | 1.317373312 | 1.318282045 | 1.318445365 |
| nA1 | 0 | 0 | 0 | 0 | 0 | 0 |
| HA1 | 0.018332521 | 0.020171385 | 0.015259528 | 2.25807E-05 | 2.32074E-05 | 2.03295E-05 |
| HA1 | 0 | 0 | 0 | 0 | 0 | 0 |

**Table S11:** Fitted IAST parameters for $Xe/CO_2$ ($1Xe:99CO_2$ composition) selectivity at 298 K for all the polymers.

| Constants | Gas A | | | Gas B | | |
|---|---|---|---|---|---|---|
| | POF6 | POF7 | POF8 | POF6 | POF7 | POF8 |
| qA1 | 3.584327049 | 3.08117948 | 3.454944772 | 5.502305792 | 4.950602554 | 5.058374449 |
| qA2 | 0 | 0 | 0 | 0 | 0 | 0 |
| kA1 | 0.005114634 | 0.006461629 | 0.004416721 | 0.000599257 | 0.001373547 | 0.00075008 |
| kA1 | 0 | 0 | 0 | 0 | 0 | 0 |
| nA1 | 0.748628779 | 0.732785981 | 0.785567598 | 0.966857085 | 0.821108768 | 0.932937072 |
| nA1 | 0 | 0 | 0 | 0 | 0 | 0 |
| HA1 | 0.018332521 | 0.019909438 | 0.015259528 | 0.003297297 | 0.006799885 | 0.003794186 |
| HA1 | 0 | 0 | 0 | 0 | 0 | 0 |

S2: Saleh, M.; Lee, H. M.; Kemp, K. C.; Kim, K. S. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7325.
S3: Myers, A. L.; Prausnitz, J. M. *AIChE J.* **1965**, *11*, 121.

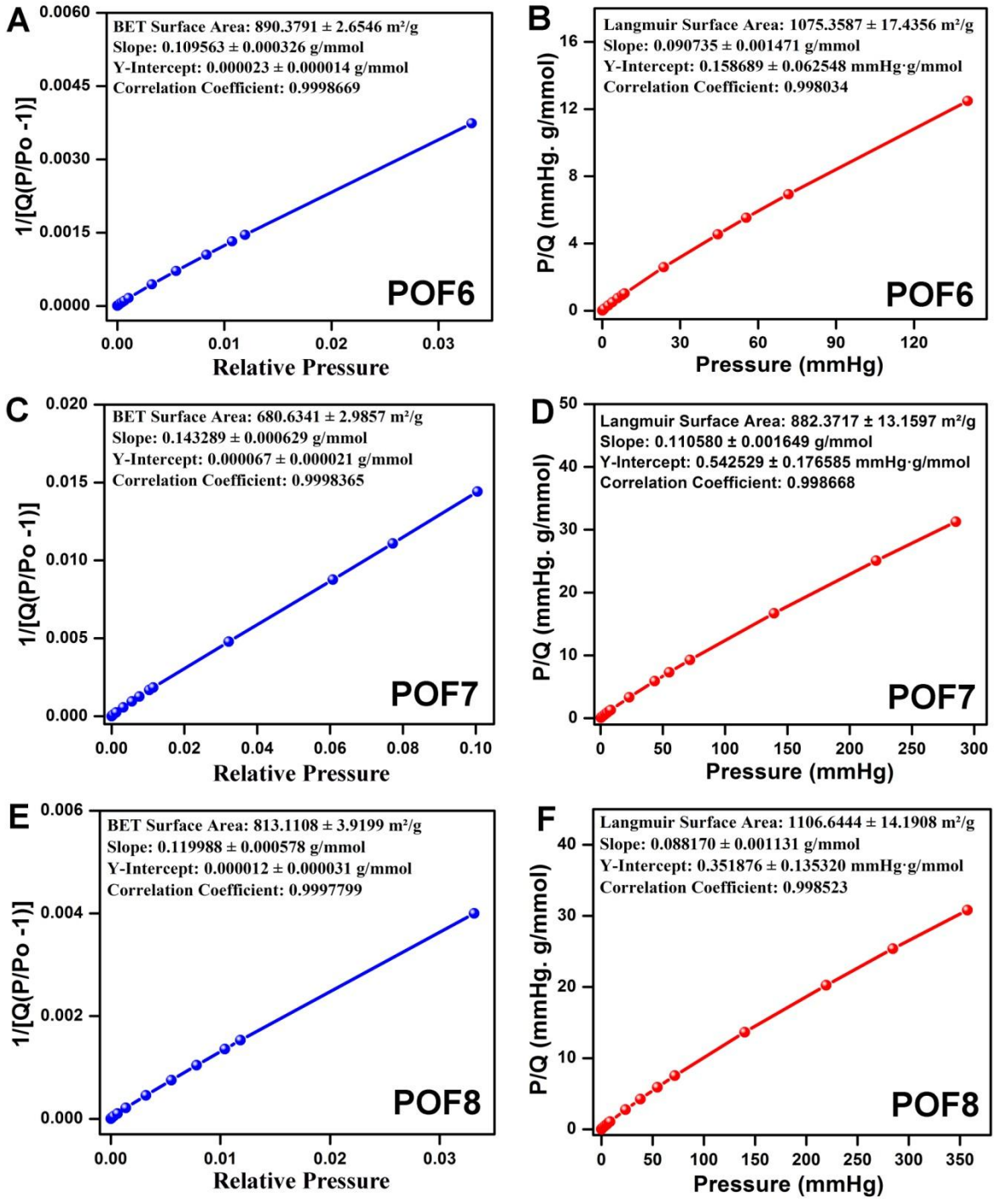


**Figure S8:** BET, Langmuir fits and surface area reports obtained from $N_2$ 77 K adsorption isotherms for the polymers.

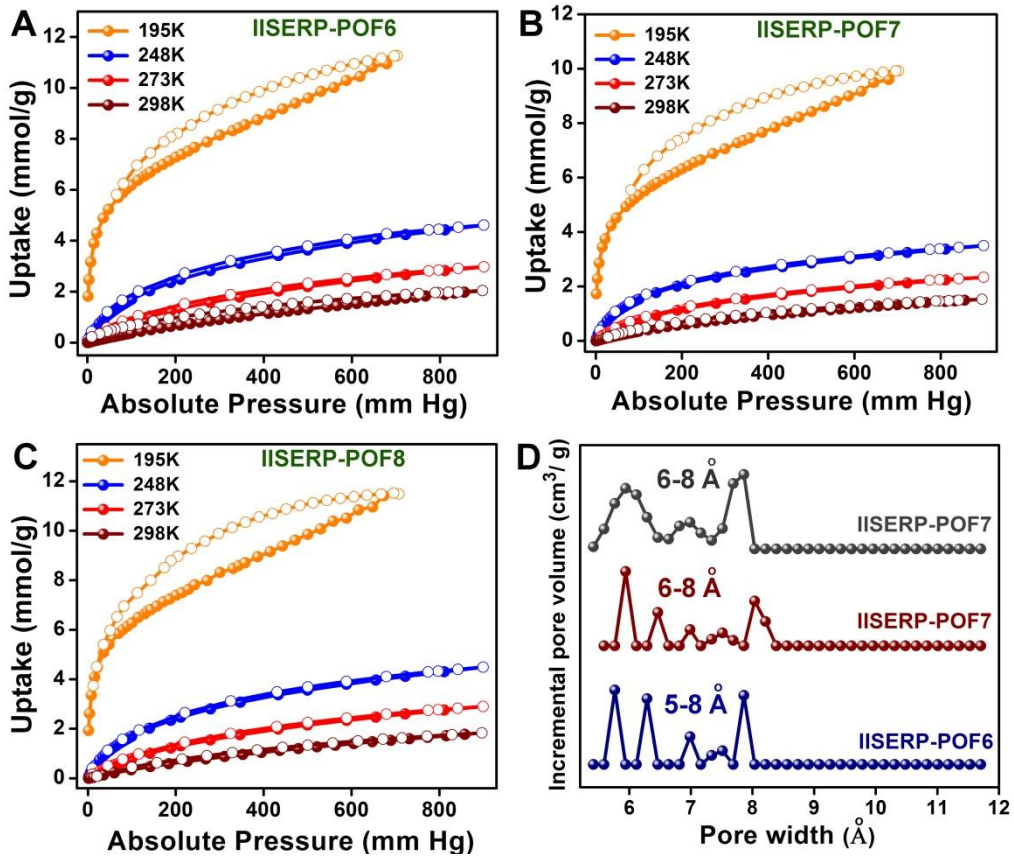


**Figure S9:** (A, B, C) $CO_2$ isotherms of the polymers at different temperatures. (D) Pore size distribution obtained from NLDFT fit using $CO_2$ isotherm at 273K.

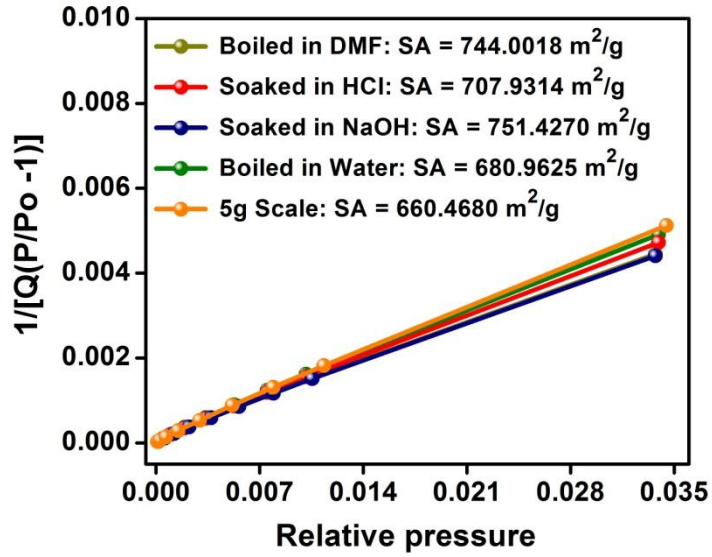


**Figure S10:** BET plots for **IISERP-POF6** treated in different chemical environments.

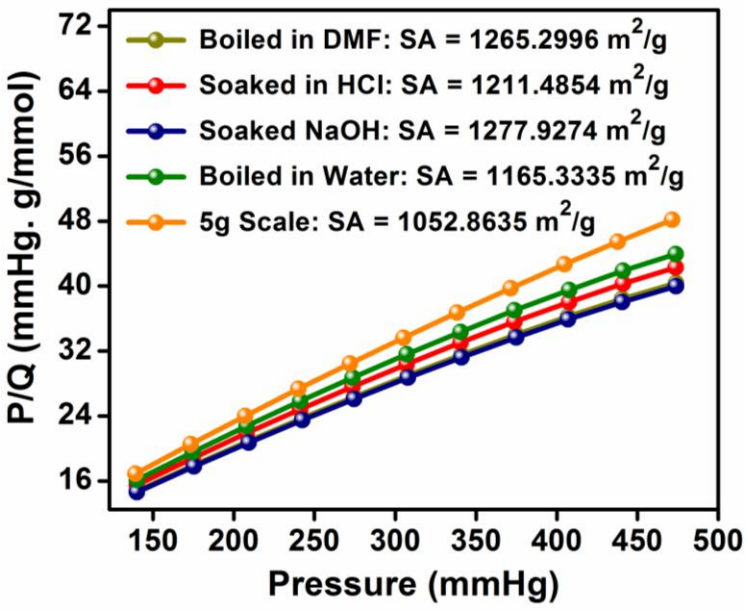


**Figure S11:** Langmuir plots for **IISERP-POF6** treated in different chemical environments.

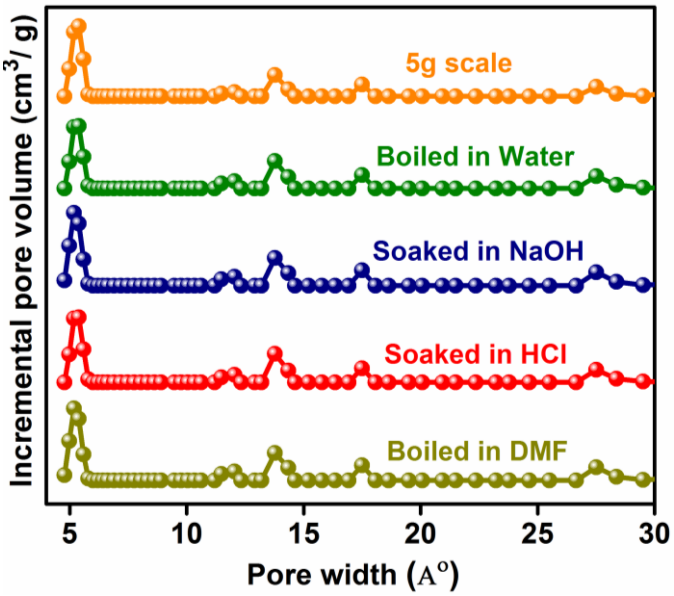


**Figure S12:** NLDFT pore size distribution plots for **IISERP-POF6** treated in different chemical environments.

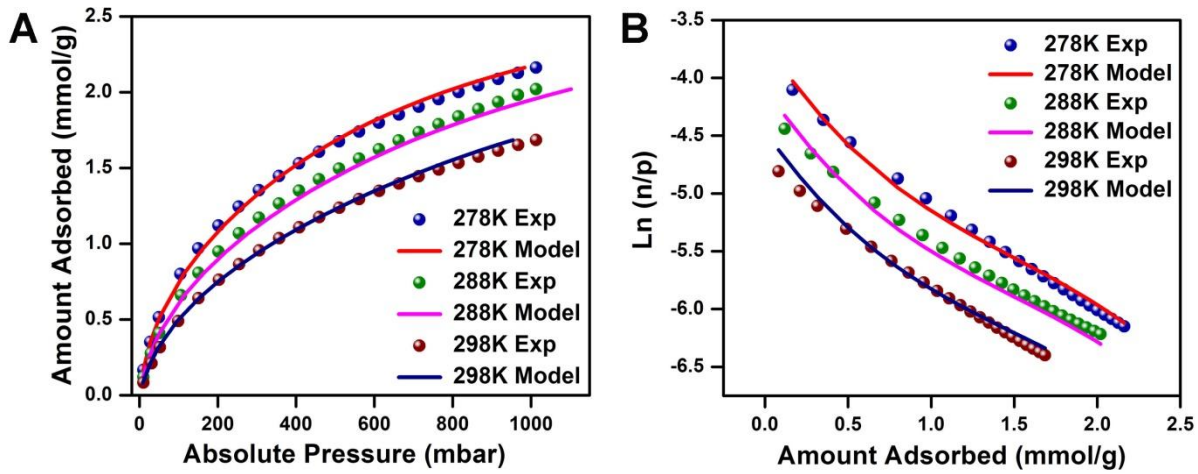


**Figure S13:** (A) Comparison of experimental Xe isotherms with the isotherms calculated from virial model for **IISERP-POF6** at three different temperatures, 278 K, 288 K, and 298 K. (B) Virial plots for Xe adsorption at three different temperatures, 278 K, 288 K, and 298 K.

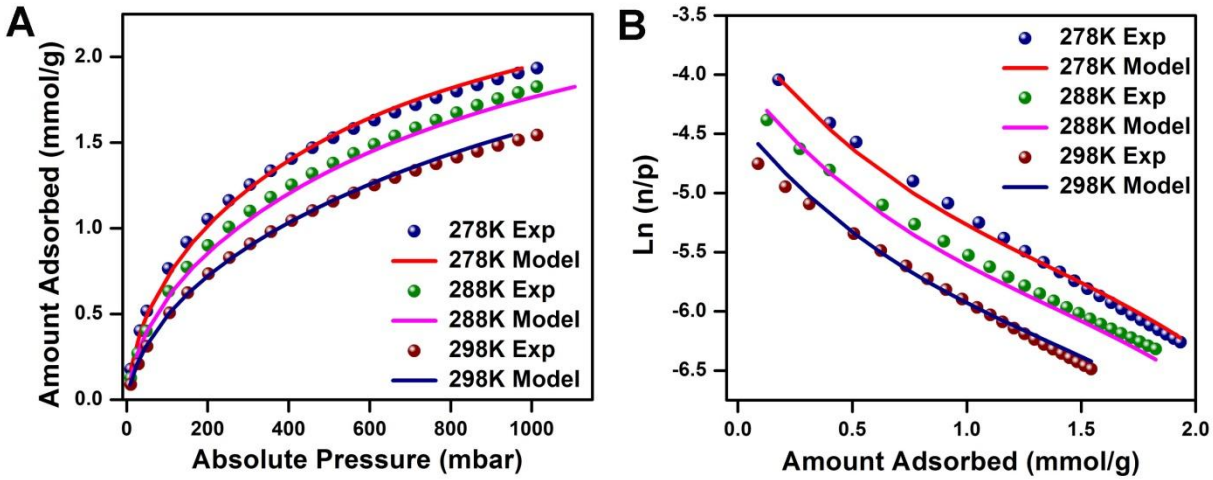


**Figure S14:** (A) Comparison of experimental Xe isotherms with the isotherms calculated from virial model for **IISERP-POF7** at three different temperatures, 278 K, 288 K, and 298 K. (B) Virial plots for Xe adsorption at three different temperatures, 278 K, 288 K, and 298 K.

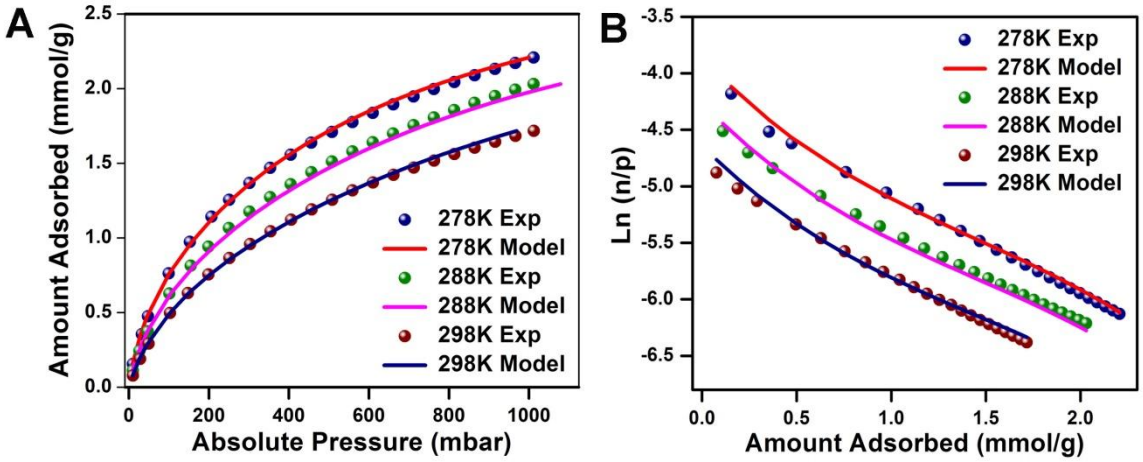


**Figure S15:** (A) Comparison of experimental Xe isotherms with the isotherms calculated from virial model for **IISERP-POF8** at three different temperatures, 278 K, 288 K, and 298 K. (B) Virial plots for Xe adsorption at three different temperatures, 278 K, 288 K, and 298 K.

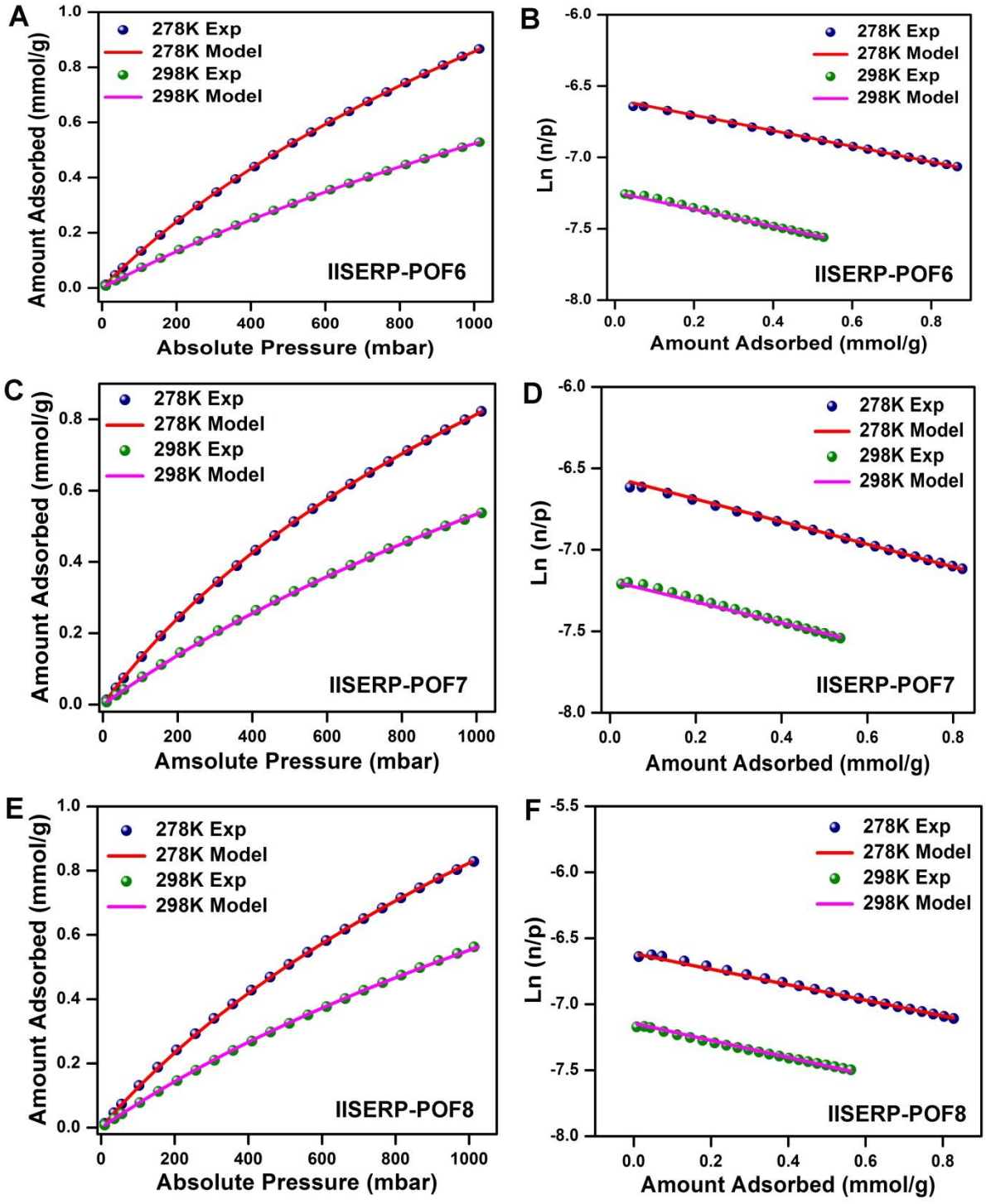


**Figure S16:** Virial model fitting using Kr adsorption isotherms at two different temperatures, 278 K and 298 K.

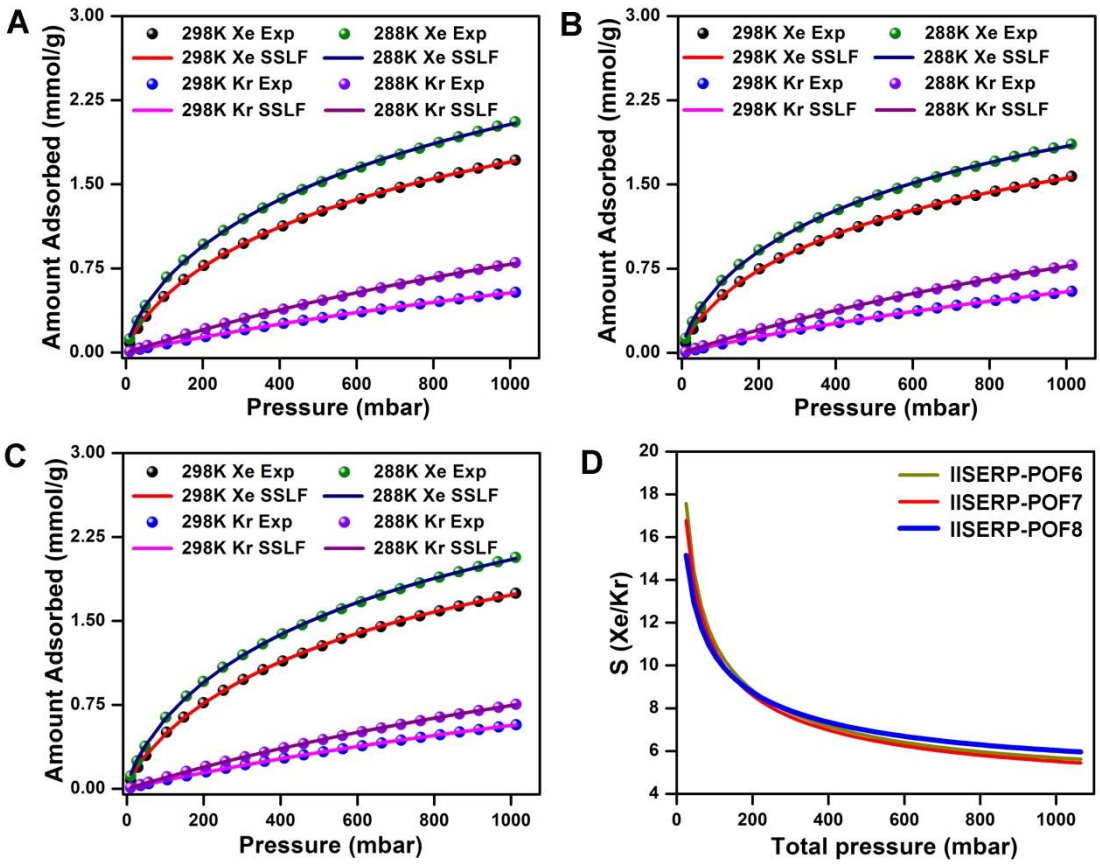


**Figure S17**: (A, B, C) IAST fits for Xe and Kr at different temperatures, 288 K and 298 K. **(A: IISERP-POF6; B: IISERP-POF7; IISERP-POF8)** (D) Xe/Kr selectivity at 288 K.

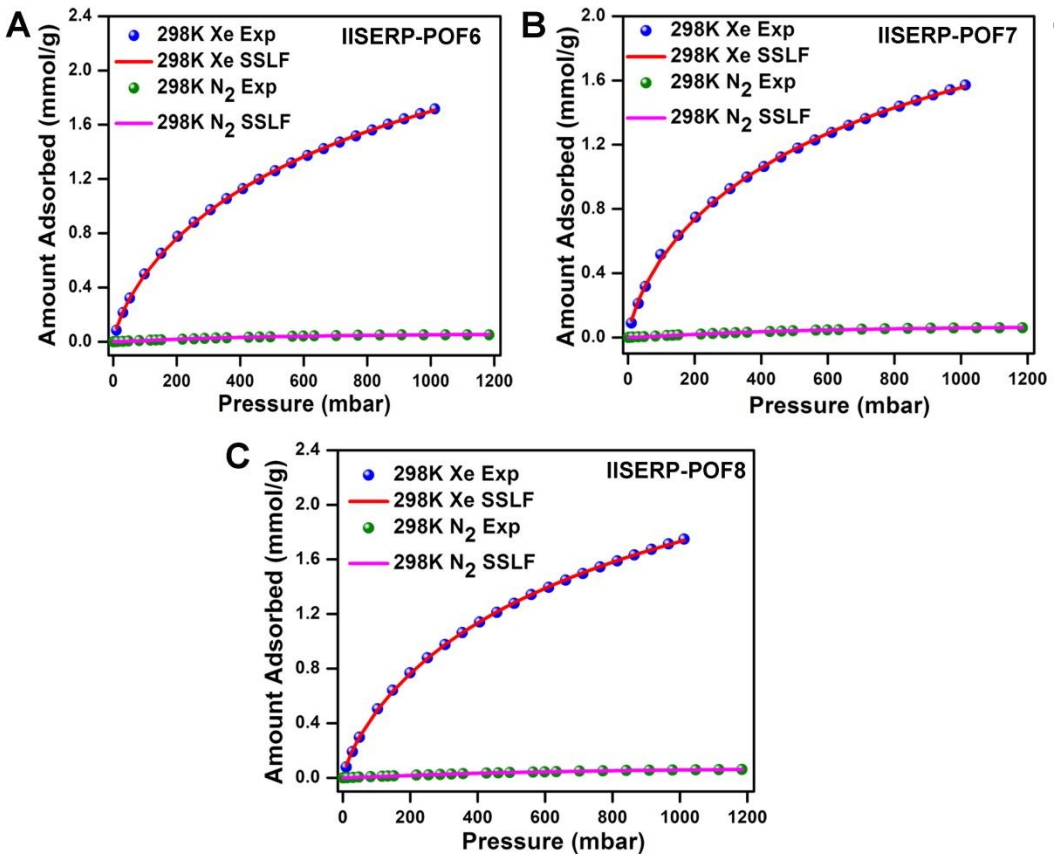


**Figure S18:** IAST fitting for Xe and $N_2$ at 298 K.

## **Breakthrough studies:**

For the breakthrough measurements, ~0.250 g of pre-activated (160°C under vacuum) sample of the POF was packed in a 6.35 cm long and 0.5-cm diameter column. This was further activated at 50°C under flowing helium overnight. Pressurization of the 0.25" (6.35 mm) diameter column packed with POF was accomplished with a syringe pump (Teledyne ISCO) directly connected to the system through a series of 0.07 mm (ID) segments of tubing (PEEK) and valves. System pressure was maintained by coordinated adjustments to the syringe pump flow rate and the needle metering valve (Tescom). An inline pressure transducer was used to verify column pressure. The column was cooled to room temperature and a premixed mixture of Xe and Kr was introduced with a flow rate of 20 ml/min at a total pressure of 15 psi (1.02 atm). Effluent gas chemistry was tracked with a Stanford Research residual gas analyzer (RGA). Masses (a.m.u.) corresponding to Xe (131), Kr (84) and He (4) were monitored throughout the experiments. The flow rate (20 ml/min) through the needle metering valve created a sampling pressure of $5 \times 10^{-5}$ torr to $3.0 \times 10^{-4}$ Torr in the RGA and was maintained throughout the experiments. Indications of Xe and Kr breaking through the column were indicated by an increase in the pressure for masses 131 and 84 respectively.