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Xe Adsorption and Separation under Nuclear Reprocessing Condition by microporous metal organic frameworks with a V shaped Linker

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1. Synthesis of frameworks **1-3**

Synthesis of frameworks 1-3 were achieved by slight modification of the literature procedure under solvothermal conditions using Teflon lined stainless steel Parr autoclaves. Starting materials include cadmium nitrate tetrahydrate [$Cd(NO_3)_2{\cdot}4H_2O$, 98%, Sigma-Aldrich], sodium hydroxide [NaOH], strontium nitrate [$Sr(NO_3)_2$], 4, 4'-sulfonyldibenzoic acid [4,4'-SDB, 98%, Sigma-Aldrich], ethanol [95%] and were used without purification.

Initial synthesis of framework **1** follows literature procedure. In a typical synthesis, 1 mmol of $Cd(NO_3)_2{\cdot}4H_2O$ (0.31 gram) and 1 mmol of 4,4'-SDB (0.32 gram) were added in 15 ml of 95% ethanol and stirred for approximately 1 hour. The resultant solution were then heated at 180ºC for 3 days, forming needle shaped crystals as product. The product so formed were washed with ethanol (3x, 50 ml each) and dried in air overnight. The phase purity was determined by powder XRD and TG analysis. The scale-up synthesis was carried out to get high-quality sample for breakthrough analysis. In a typical synthesis, 3.231 gram of $Cd(NO_3)_2$ was mixed with 2.716 gram of 4,4'-SDB in 150 ml ethanol and stirred for 2 hours to achieve homogeneity. The resultant solution was heated at 180ºC for 3 days, followed by washing by ethanol and overnight air dry. The crystalline powder product (1.05 gram) was characterized by powder XRD, and found to be phase pure.

For framework **2**, we followed the synthetic procedure from Lin and coworkers for initial synthesis. For a typical synthesis, 0.04 gram of NaOH, 0.062 gram of 4,4'-SDB were mixed with DMF/ethanol/water (7/2/1 ml) and heated at 120ºC for 3 days. The crystalline product was washed with 95% ethanol and dried in air overnight. The phase purity of framework **2** was confirmed by powder XRD and TG analysis. We later synthesized framework **2** using a modified procedure. In a typical synthesis, 0.045 gram of NaOH and 0.07 gram of 4,4'-SDB in 15 ml 95% ethanol and stirred for 2 hours to achieve homogeneity. The resultant solution was heated at 180ºC for 3 days, followed by product filtration, washing with ethanol (2x, 25 ml) and air drying. For scale-up work, a linear increase in reactant amount was carried out. In a typical reaction, 0.61 gram of 4,4'-SDB and 0.4 gram of NaOH was added to a mixed solution of DMF/ethanol/water (70/20/10 ml) and heated at 120ºC for 2 days. The resultant product was filtered, washed with ethanol and dried in air overnight. The phase purity was confirmed by powder XRD.

framework **3** was synthesized using a modified procedure from literature. In a typical synthesis, 0.33 gram of $Sr(NO_3)_2$ and 0.12 gram of 4,4'-SDB in a mixed solvent (7 ml ethanol and 3 ml water) and stirred for 2 hours to achieve homogeneity. The resultant solution was heated at 150ºC for 3 days, followed by filtration and washing with ethanol (3x, 25 ml). The resultant crystalline product was dried in air and characterized by powder XRD and TG analysis.

2. Activation and adsorption studies on frameworks **1-3**

frameworks **1-3** were activated as a function of temperature (373 K, 423 K, 473 K, 523 K, 563 K) and pure component Xe and Kr isotherms were collected at 298K and up to 1 bar using a Quantachrome Autosorb iQ_2 gas-adsorption instrument. Based on the adsorption data, 473 K was chosen as the final activation temperature for frameworks **1-3**. Heats of adsorption (Q*st*) data of Xe and Kr for frameworks **1-3** was calculated using Clausius Clapeyron equation based on temperature dependent (278 K, 288 K and 298 K) adsorption curves.

3. Breakthrough Experiment

Based on the single component isotherm data of frameworks **1-3**, framework **1** was selected for breakthrough experiment under nuclear reprocessing conditions (400 ppm Xe, 40 ppm Kr, balance air). 1.05 gram of framework **1** was loaded in a column with a diameter of 10 mm and length of 100 mm. The powder sample was packed between layers of glass-wool to ensure packing efficiency. The material was activated at 373 K for 12 hours under constant He flow (5 ml/min). Once the activation was complete, the experimental gas mixture (400 ppm Xe, 40 ppm Kr, balance air) was introduced into the sample bed at a constant flow rate of 5ml/min. The inlet and outlet pressure was monitored by pressure gauge and kept constant at 1 bar during the breakthrough analysis. Both the He flow and the experimental gas mixture flow rate were controlled by a syringe pump (Teledyne ISCO). 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 line pressure at 1bar. Effluent gas chemistry was tracked with a Stanford Research residual gas analyzer (RGA). Masses (a.m.u.) corresponding to N_2 (28), O_2 (32), Kr (84) and Xe (131). Indications of Xe and Kr breaking through the column were indicated by an increase in the pressure for masses 131 and 84 respectively. Similarly, for the 1000 ppm Kr mixture, breakthrough was recognized by an increase in the pressure for mass 84. The experimental gas mixtures (400 ppm Xe, 40 ppm Kr, balance air and 1000 ppm Kr, balance dry air respectively, also termed as simulated off-gas stream) were purchased from Advanced Specialty Gases (Reno, NV).

The equilibrium breakthrough capacity for framework **1'** was calculated as

$$\text{Breakthrough/equilibrium capacity (q in mmol/kg)} = \frac{Cvt}{MTg} \times 10^6$$

Where C is the partial pressure of the gas in inlet feed, v is flow rate in ml/min, t is time in minute, M is ideal gas constant, T is temperature in K and g is the weight of the adsorbent in gram

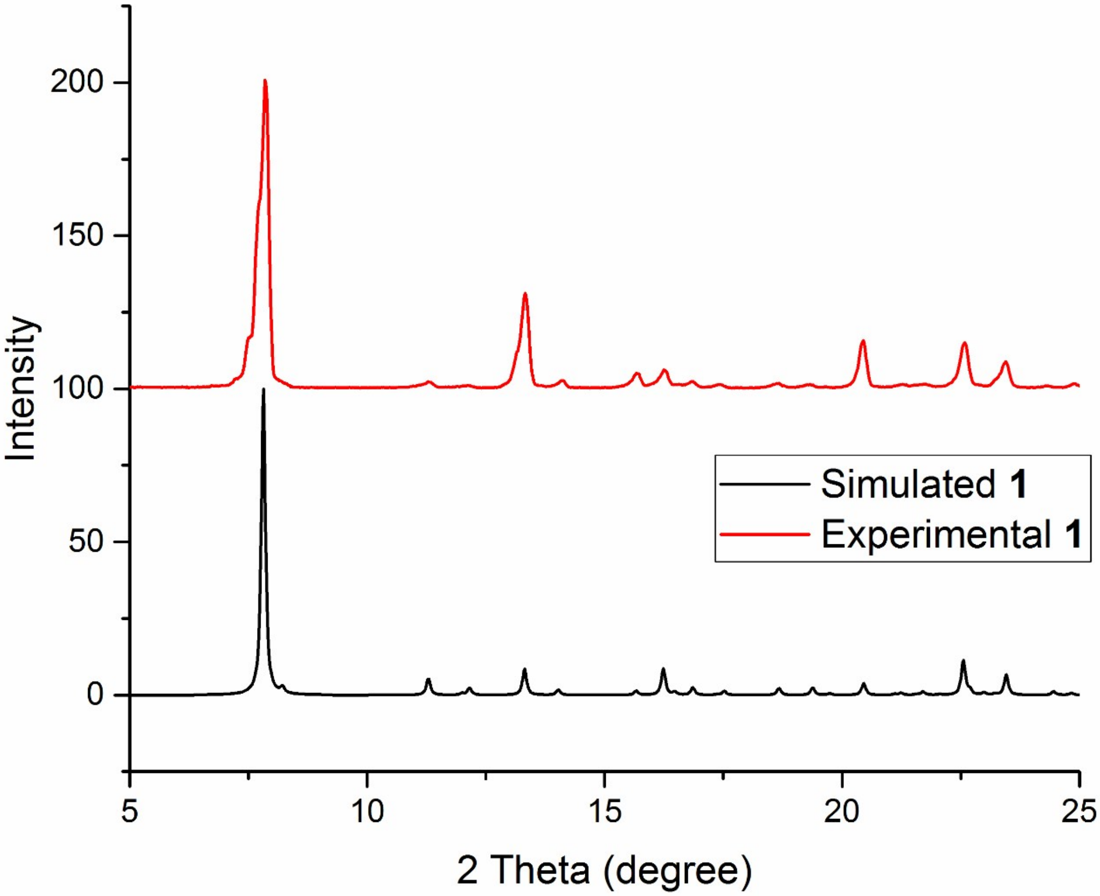

Figure S1. Simulated (bottom) and experimental (top) powder pattern of framework **1**

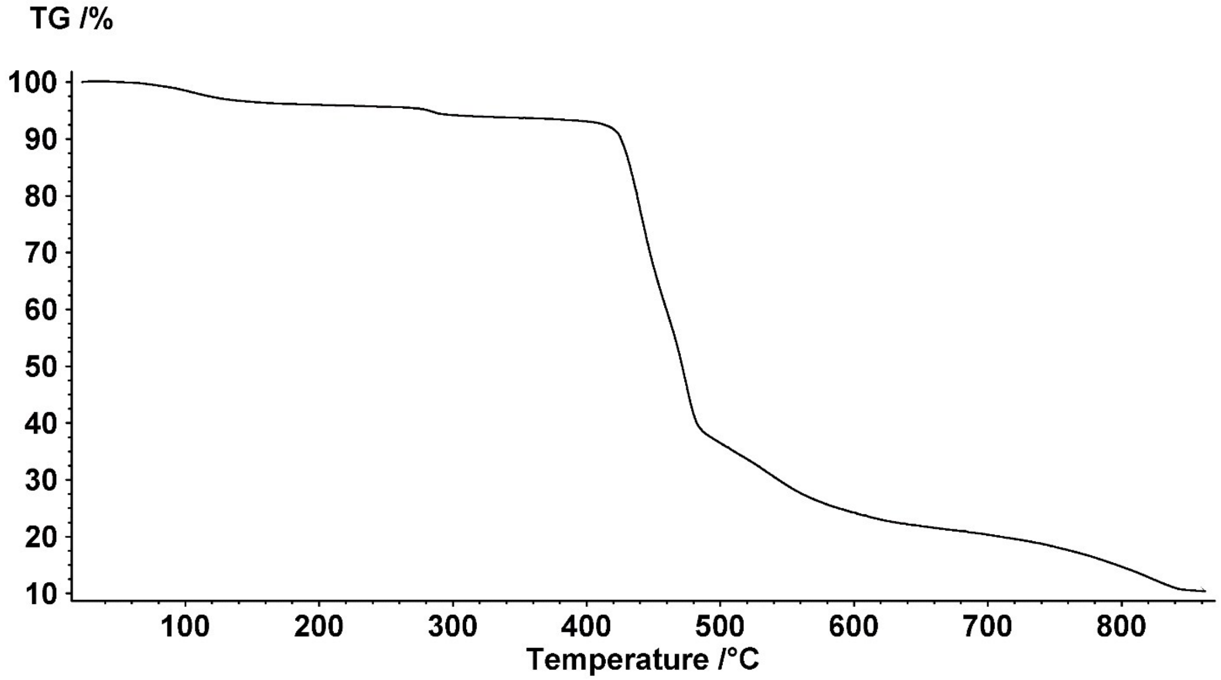

Figure S2. Thermogravimetric (TG) pattern of framework **1** under N_2 atmosphere.

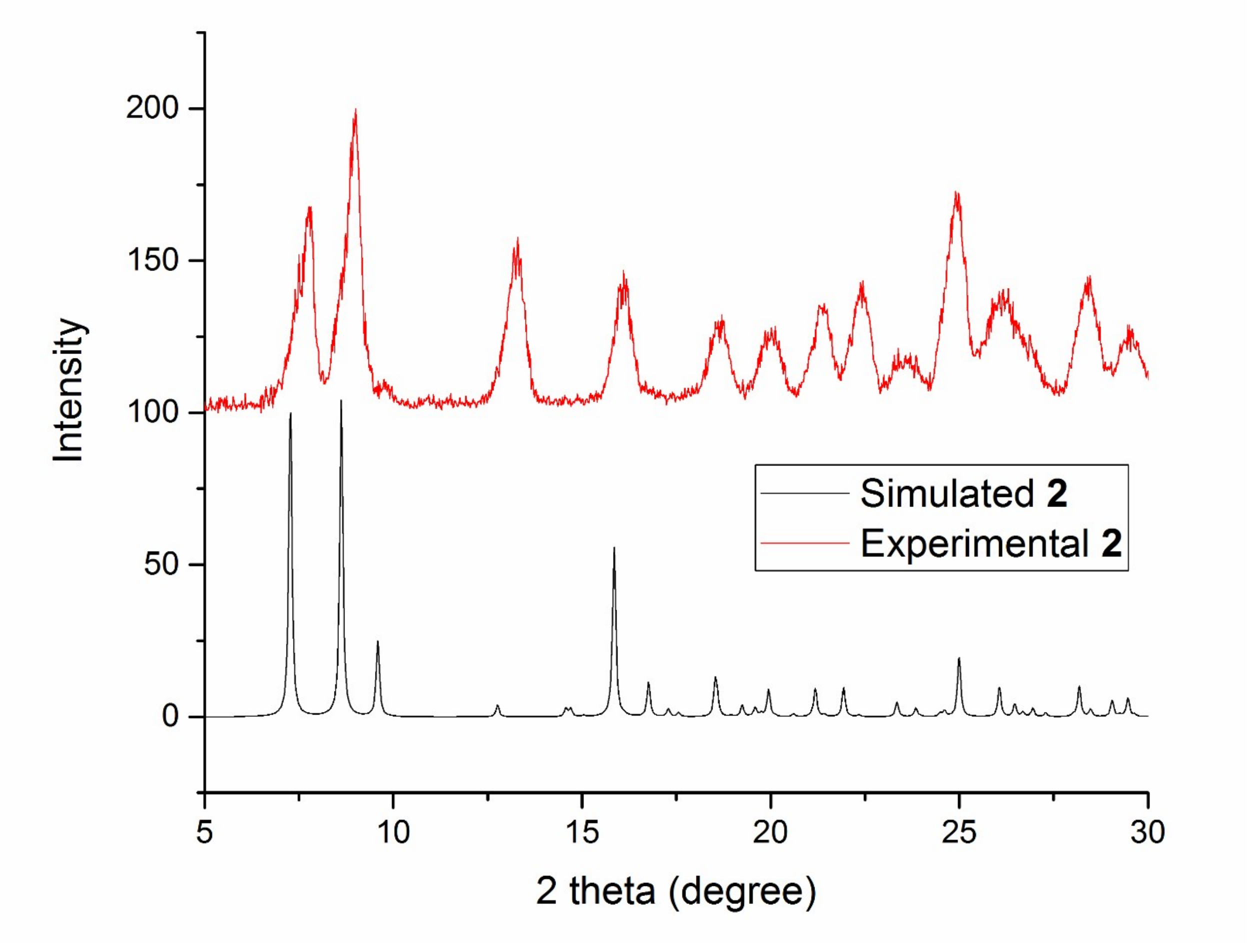

Figure S3. Simulated (bottom) and experimental (top) powder pattern of framework **2**

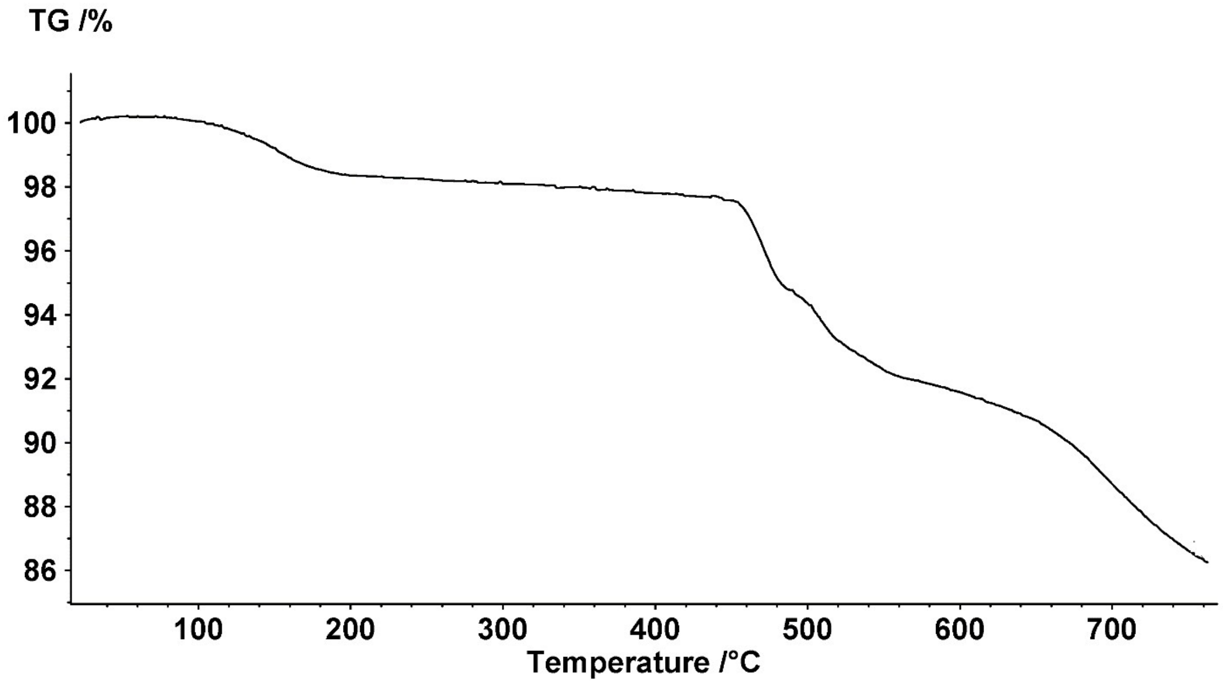

Figure S4. Thermogravimetric (TG) pattern of framework **2** under N_2 atmosphere.

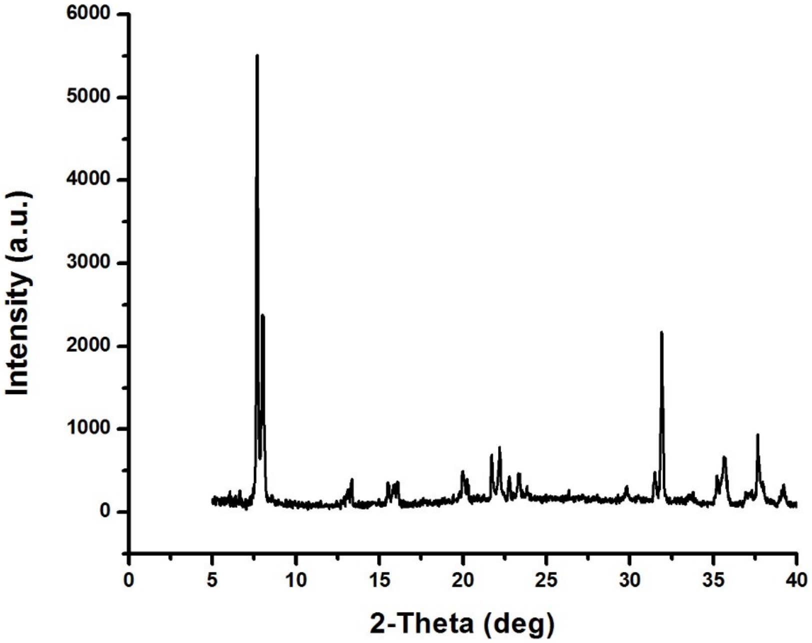

Figure S5. Experimental powder pattern of framework **3**

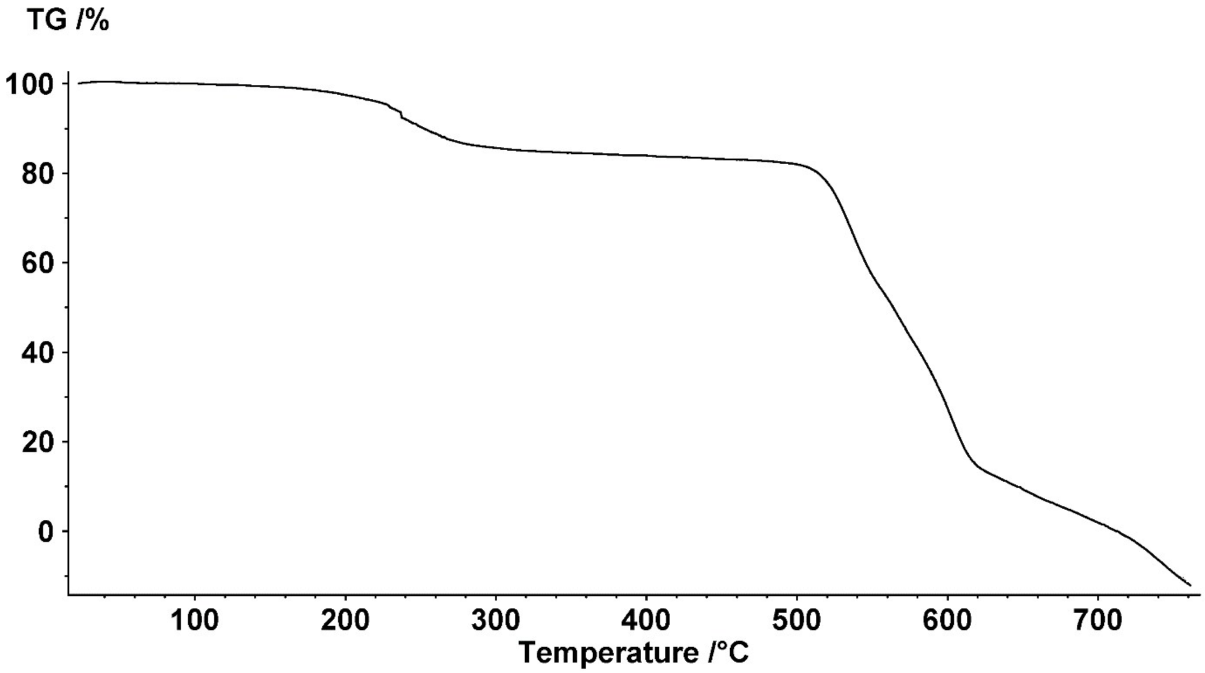

Figure S6. Thermogravimetric (TG) pattern of framework **3** under N_2 atmosphere.

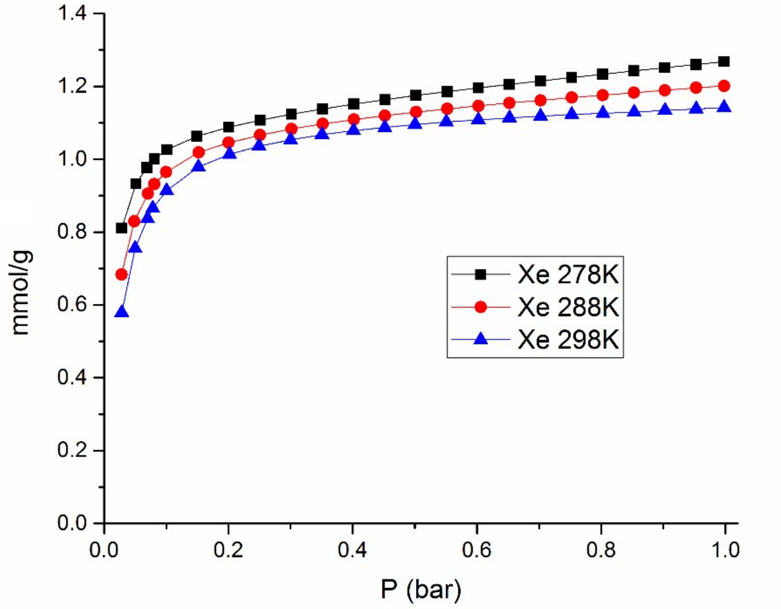

Figure S7. Xe adsorption in framework **1'** as a function of adsorption temperature (black -278K, red- 288K, blue- 298K)

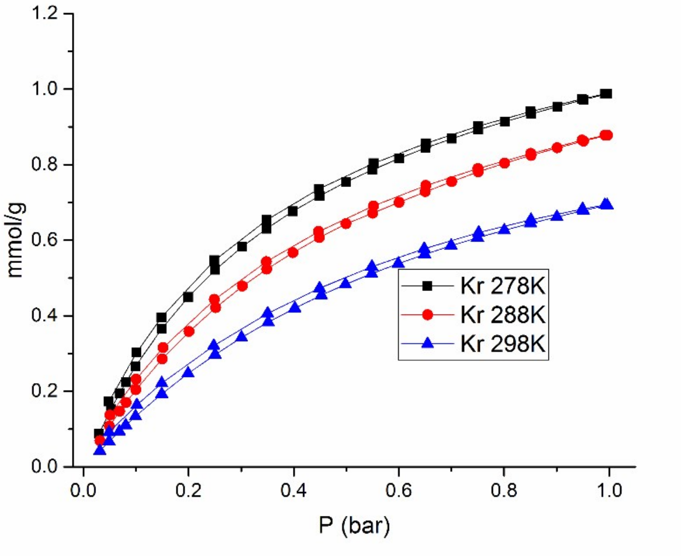

Figure S8. Kr adsorption in framework **1’** as a function of adsorption temperature (black -278K, red- 288K, blue- 298K)

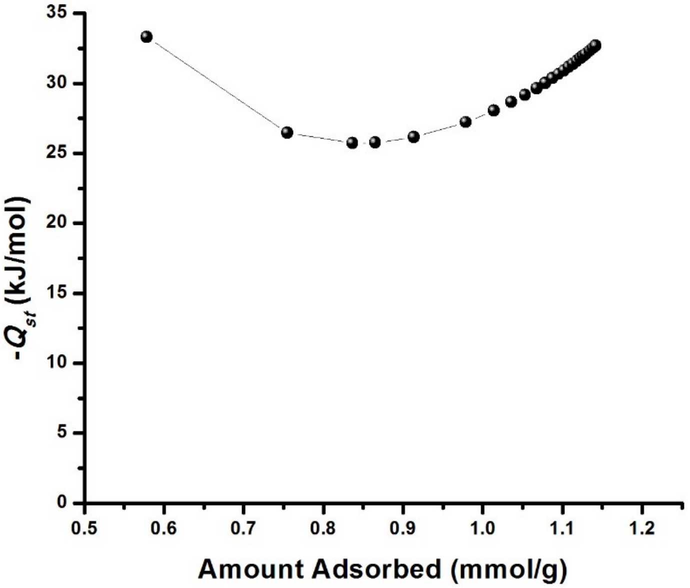

Figure. S9. Xe Heats of Adsorption (Q*st*) of framework **1’** as a function of gas loading

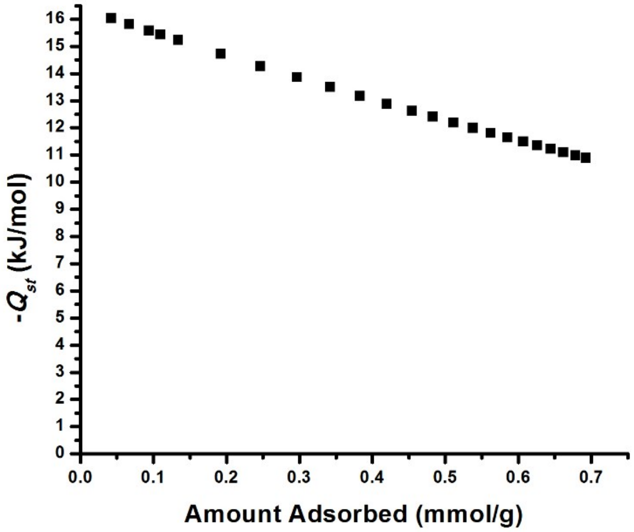

Figure. S10. Kr Heats of Adsorption (Q*st*) of framework **1'** as a function of gas loading

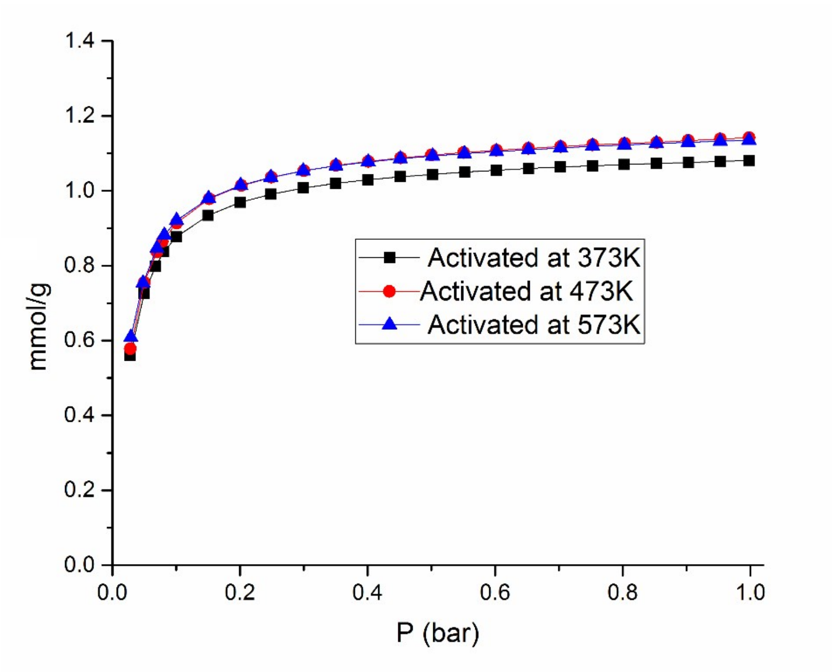

Figure S11. Xe adsorption in framework **1'** as a function of activation temperature (black -373K, red- 473K, blue- 573K)

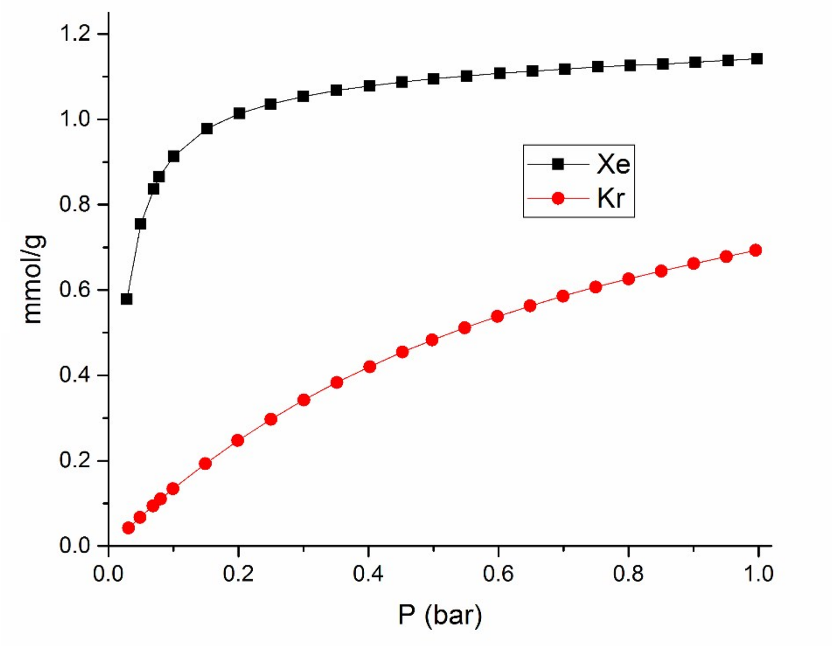

Figure S12. Comparison between Xe (black) and Kr (red) adsorption in framework **1'** at 298K.

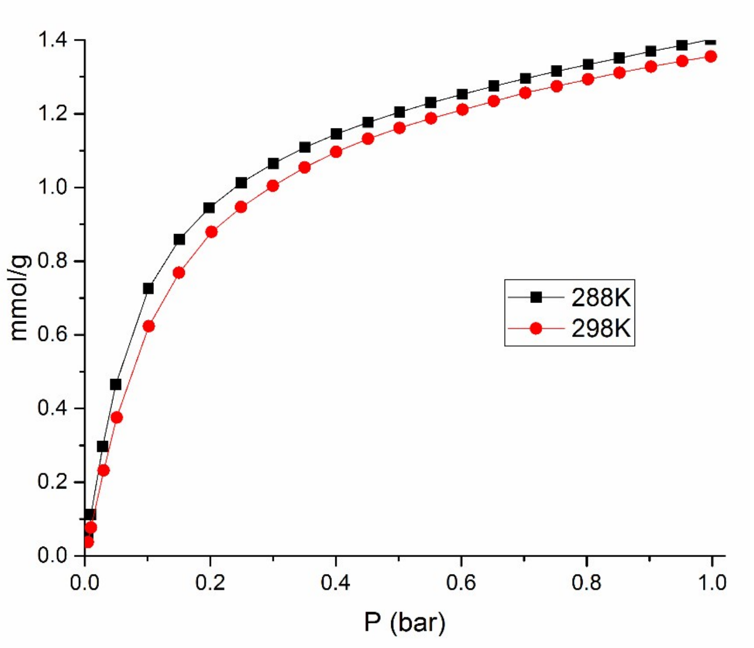

Figure S13. Xe adsorption in framework **2'** as a function of adsorption temperature (black - 288K, red- 298K)

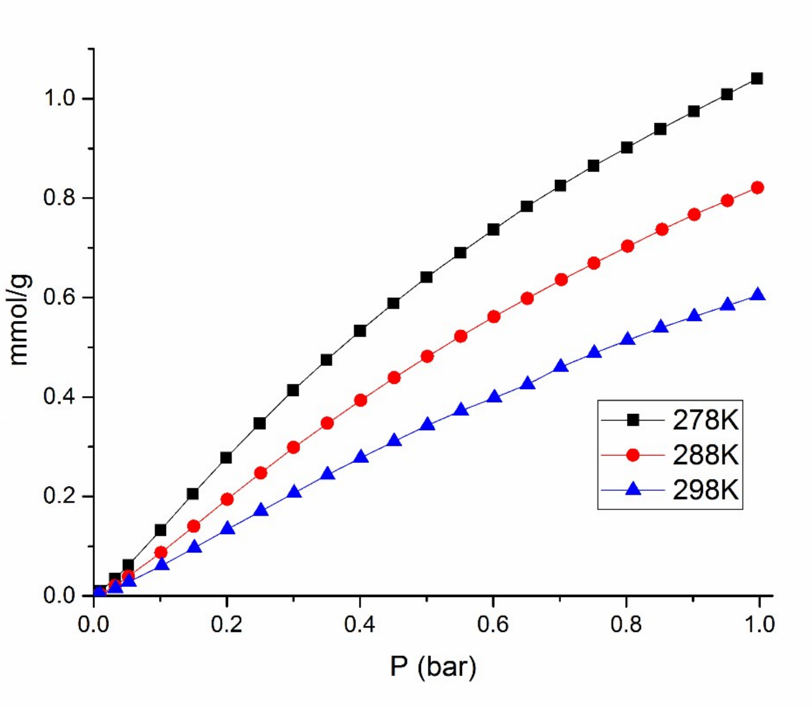

Figure S14. Kr adsorption in framework **2’** as a function of adsorption temperature (black - 278K, red- 288K, blue- 298K)

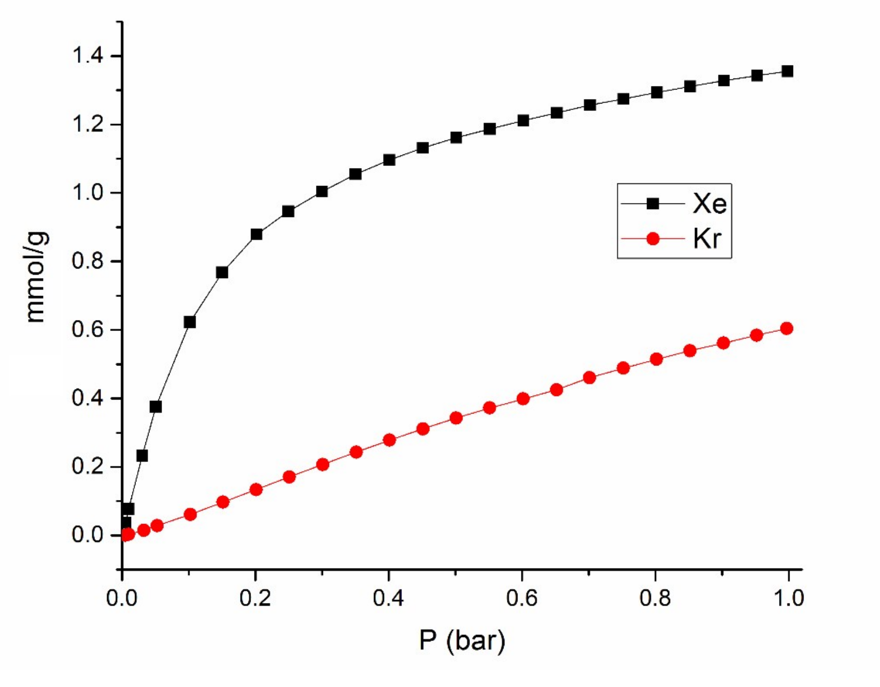

Figure S15. Comparison between Xe (black) and Kr (red) adsorption in framework **2’** at 298K

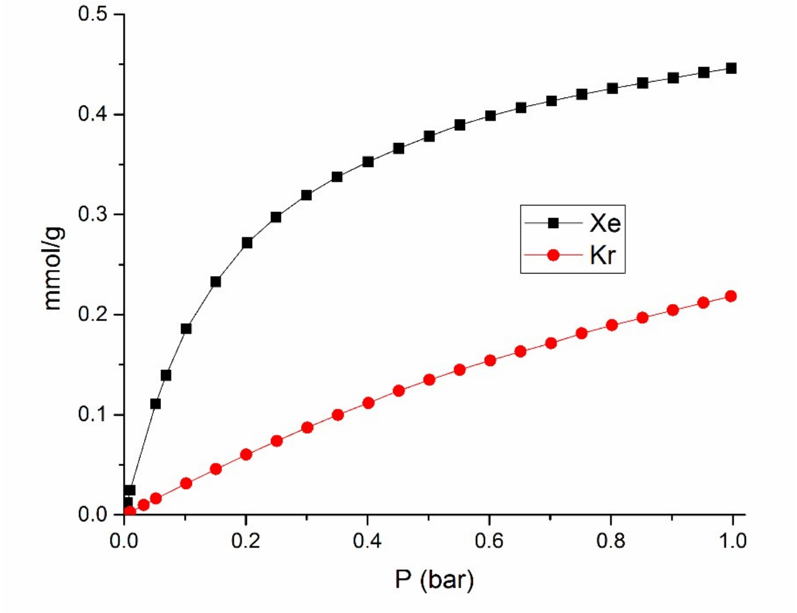

Figure S16. Comparison between Xe (black) and Kr (red) adsorption in framework **3’** at room temperature.