Supporting Information

Tuning the Channel Size and Structure Flexibility of Metal-Organic Frameworks for Selective Adsorption of Noble Gases

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Materials and characterizations. All reagents used were purchased from Alfa Aesar, Fisher Scientific and used without purification. Powder X-ray diffraction (PXRD) patterns were performed on a Bruker D8 Advance diffractometer. Data were collected between 3° and 40° of 20 with a scan speed of 10.0 deg/min. Thermogravimetric analysis (TGA) data were recorded on a TGA550 (TA Instruments) Analyzer with a temperature ramping rate of 10 °C/min from RT to 600 °C under nitrogen atmosphere. CO₂ adsorption experiments at 195 K were performed in a dry ice-acetone bath using a volumetric gas sorption analyzer (3Flex, Miromeritics). Xe/Kr isotherms were tested on the same instrument while the temperatures were controlled by using a water bath.

Synthesis of $Zn(ox)_{0.5}(trz)$ (compound 1) and $Zn(ox)_{0.5}(atrz)$ (compound 2). The preparation was followed by a reported method with modifications. Zinc carbonate (628 mg), oxalic acid (640 mg) and 1,2,4-triazole (1.74 g) or 3-amino-1,2,3-triazole (2.1 g) were added to a binary solvent mixture of 60 mL BuOH and 60 mL H₂O in a 200 mL autoclave. The slurry was stirred for 1 hour at room temperature, and then heated at 180°C for 3 days. After being cooled to RT, the resultant powder was filtered, washed thoroughly with water and methanol and dried under air.

Column breakthrough measurements. MOF samples were packed into a stainless steel column (the steel column was 18 cm in length with 4 mm of inner and 6.4 mm outer diameter with silica wool filling the void space. The sorbent was vacuumed at 150 °C for 8 hours with a helium flow before the temperature of the column was decreased to 25 °C. The flow of He was then turned off while a gas mixture (Xe/Kr: 20/80, V/V) was sent into the column. The flow of He and sample gas mixture was measured by a Mass Flow controller to be \sim 10 ml/min. The downstream was monitored using a Hiden mass spectrometer (HPR 20). Adsorbed amounts of Xe and Kr were calculated by integrating the resulting breakthrough curves by considering dead volume times, which were measured by helium gas under the same flow rate.



Fig. S1. PXRD patterns of compound 1 along with simulated patterns based on single crystal data.



Fig. S2. PXRD patterns of compound 2 along with simulated patterns based on single crystal data.



Fig. S3. TGA data of compound 1.



Fig. S4. TGA data of compound 2.



Fig. S5. Channel segment in compound 1 (left) and 2 (right).

Isosteric Heat of Adsorption

Isosteric heat of Xe and Kr adsorption on compound **1** has been calculated using adsorption isotherms at different temperatures (278 K, 288 K, and 298 K) with virial method. The isotherms were first fitted with Virial equation.

$$\ln(p) = \ln(v) + (1/T) \sum_{i=0}^{m} a_i v^i + \sum_{j=0}^{n} b_j v^j$$

Where p is pressure, v is amount adsorbed; T is temperature and a_i , b_j are empirical parameters which are independent of temperature.

Isosteric heat of adsorption can then be calculated by the equation below.

$$Q_{st} = -R\sum_{i=0}^{m} a_i v^i$$



Fig. S6. Isosteric heat of adsorption (Q_{st}) for Xe (black) and Kr (red) on compound 1.



Fig. S7. Virial fitting of Xe adsorption isotherms on compound 1, symbols and lines represent experimental and fitted curves, respectively. Black: 278 K, red: 288 K, blue: 298 K.



Fig. S8. Virial fitting of Kr adsorption isotherms on compound **1**, symbols and lines represent experimental and fitted curves, respectively. Black: 278 K, red: 288 K, blue: 298 K.

Henry's selectivity

Henry's selectivity was calculated as the ratio of the Henry's constants of Xe and Kr at zero coverage. The adsorption isotherms of Xe and Kr at 298 K are first fitted by the Langmuir equation:

$$q = q_m bp / (1 + bp)$$

And the Henry's selectivity can be calculated as:

$$S = (q_m b)_{Xe} / (q_m b)_{Kr}$$

| | q _m | b |
|----|----------------|--------|
| Xe | 3.06331 | 0.0906 |
| Kr | 3.08118 | 0.0072 |



Fig. S9. CO₂ adsorption isotherms at 195 K for compound 1 (black) and 2 (red)



Fig. S10. Top and side view of supercell $(4 \times 2 \times 2)$ of compound 1 used for adsorption simulations.



Fig. S11. Simulations of He adsorption at 5 K (left), Xe adsorption at 298 K (middle), Kr adsorption at 298 K (right).





Fig. S12. Top and side view of supercell $(4 \times 2 \times 2)$ of compound 2 used for adsorption simulations.



Fig. S13. Adsorption loading profiles for Xe adsorption at 298 K (top) and Kr adsorption at 298 K (bottom) on compound **2**.