Supporting Information

A flexible zinc tetrazolate framework with breathing behaviour on xenon adsorption and selective adsorption of xenon over other noble gases

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Table S1. Crystal data and structure refinement for **[Zn(mtz)₂]**

	[Zn(mtz)₂]
chemical formula	$C_{16}H_{24}N_{32}Zn4$
formula weight	926.15
temperature (K)	293(2)
wavelength (Å)	0.71073
crystal system	monoclinic
space group	Pc
a (Å)	19.2148(14)
b (Å)	13.3436(8)
c (Å)	10.6713(5)
α (º)	90.00
β (º)	95.038(6)
γ (º)	90.00
V (Å³)	2725.5(3)
Z	2
density (calculated g/cm⁻³)	1.129
absorbance coefficient (mm⁻¹)	1.781
F(000)	928
crystal size (mm³)	0.36×0.33×0.32
goodness of fit on F_2	1.007
R_{int}	0.0407
R1, wR2 ($I>2\sigma(I)$)[a]	0.0486, 0.1270
R1, wR2 (all data)[a]	0.0780, 0.1374

[a]$R1 = \Sigma(|F_o| - |F_c|) /\Sigma|F_o|$; $wR2 =|\Sigma w(|F_o|-|F_c|^2) /\Sigma wF_o^2]^{1/2}$
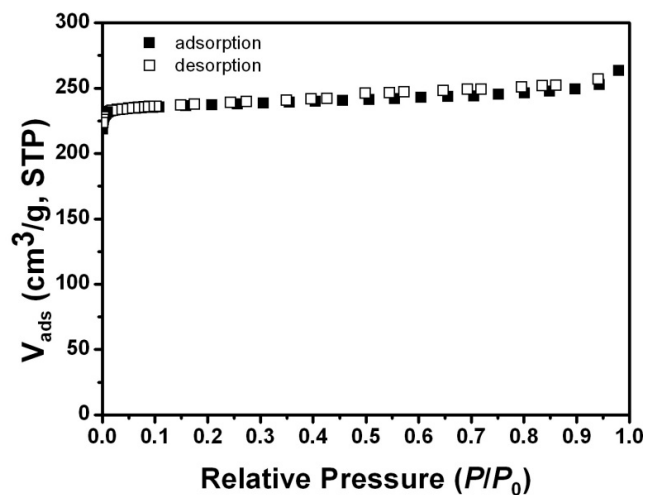
Figure S1. The N_2 sorption isotherm for **[Zn(mtz)$_2$]** at 77K. The BET and Langmuir surface area were calculated to be 710.5 m^2 g^{-1} and 1046.6 m^2 g^{-1}, respectively. And the corresponding pore volume is 0.407 cm^{3}g^{-1}.
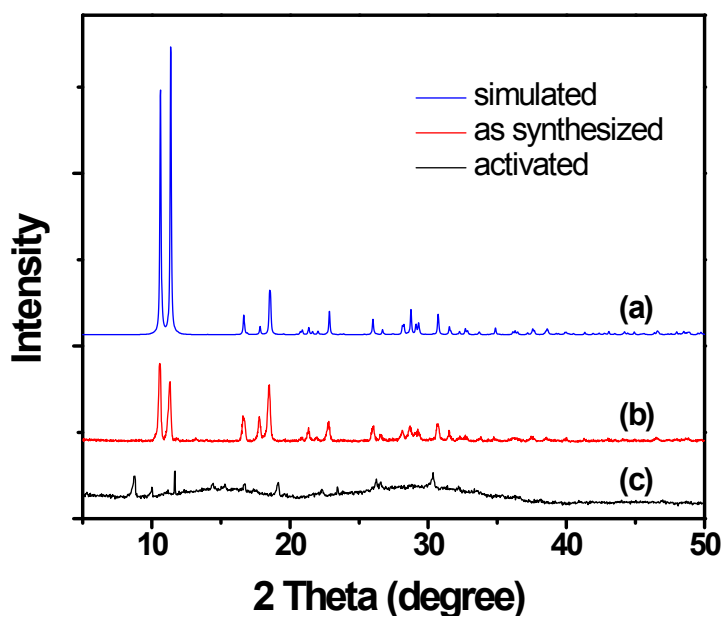
Figure S2. PXRD patterns of as-synthesized **[Zn(mtz)$_2$]** (b) and activated **[Zn(mtz)$_2$]** (c) along with the simulated pattern from its single crystal X-ray structure (a).
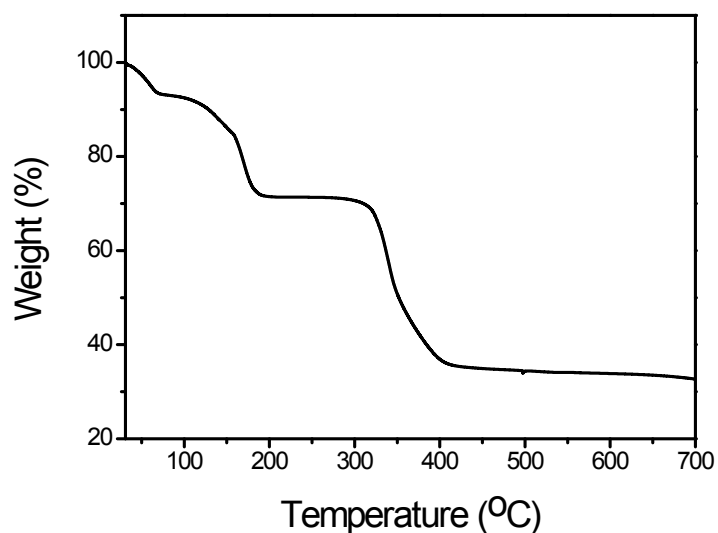
Figure S3. TGA curves of as-synthesized **[Zn(mtz)₂]**
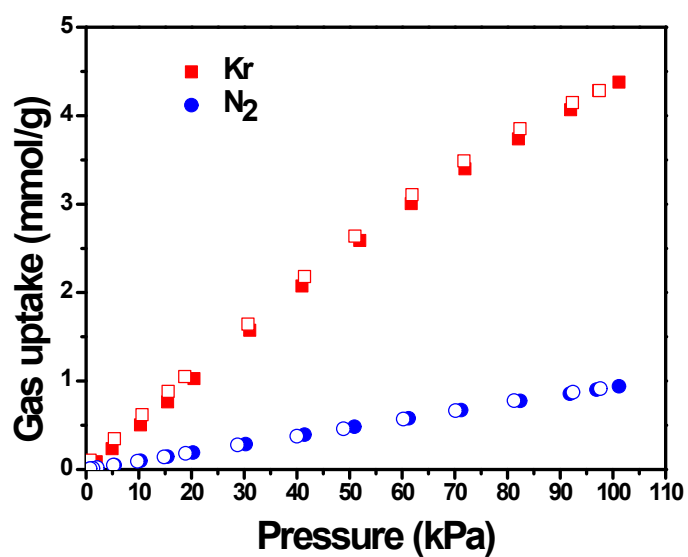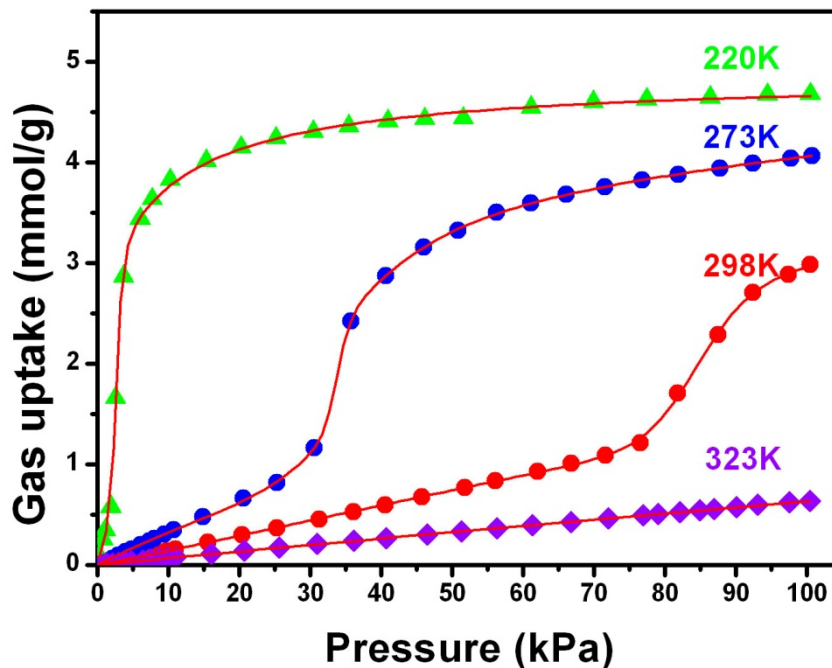

Figure S4. Adsorption (solid) and desorption (open) isotherms of Kr (red squares) and N₂ (blue circles) on [Zn(mtz)₂] at 220K.

1. Calculation procedures of isoteric adsorption enthalpy

The isosteric enthalpy (Qst) were calculated by the Clausius-Clapeyron equation :

$$\frac{Q_{st}}{R} = \frac{d(lnP)}{d(1/T)} \qquad (1)$$

Figure S5. Adsorption isotherms of xenon on **[Zn(mtz)₂]**. Filled symbols, adsorption; solid lines, equations fitting. The S shape adsorption isotherms (273K and 298K) were fitted using a modified dual-site Sips equation (2) (Langmuir-Freundlich equation). The 220K adsorption isotherm was fitted using dual-site Sips equation Langmuir-Freundlich equation. The 323K adsorption isotherm was fitted using Langmuir equation.

The modified dual-site Sips equation (Langmuir-Freundlich equation):

$$q = a\frac{bp}{1+bp} + q_{m,A}\frac{(b_AP)^{1/n_A}}{1+(b_AP)^{1/n_A}} + q_{m,B}\frac{(b_BP)^{1/n_B}}{1+(b_BP)^{1/n_B}} \tag{2}$$

where q is the amount adsorbed of the pure component in mole per unit mass (mmol/g), P is the pressure of the bulk gas at equilibrium (kPa), $q_{m,A}$, $q_{m,B}$, and a (mmol/g) are the maximum loading capacities at adsorption sites A, B and C of the adsorbent, b_A, b_B, and b (kPa⁻¹) are the affinity parameters for sites A, B, and C, n_A and n_B are solid heterogeneity parameters for sites A and B.

Table S2. The fitted equation parameters for the xenon isotherms in Figure S. ([a]modified dual-site sips equation, [b]dual-site sips equation, [c]Langmuir equation)

T(K)	a(mmol/g)	b(ka⁻¹)	$Q_{m,A}$(mmol/g)	b_A(ka⁻¹)	n_A	$Q_{m,A}$(mmol/g)	$b_B$ka⁻¹)	n_B	R^2
298[a]	0.12387	0.05528	1.57104	0.01178	0.04492	5.10537	0.00435	0.79197	0.999
273[a]	3.37099	0.01052	1.04996	0.02959	0.02778	1.28605	0.02693	0.16785	0.999
220[b]			2.37101	0.12262	1.0353	2.49443	0.00156	0.15423	0.999
323[c]	11.5925	5.77937E-4							0.999
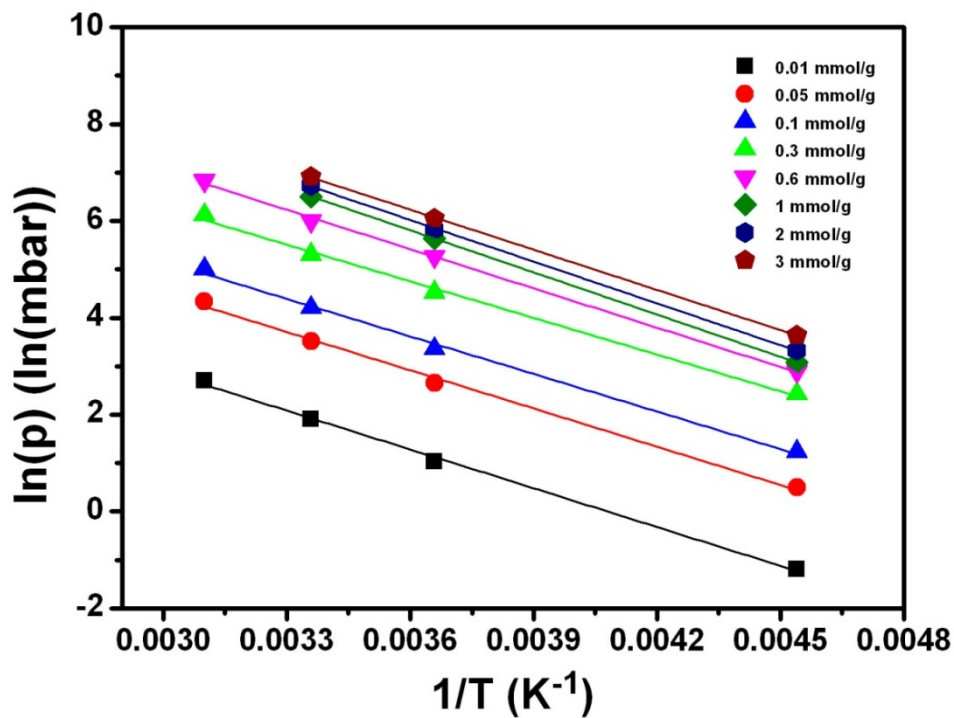
Figure. S6. Van't Hoff isochore graphs for Xe adsorption on **[Zn(mtz)₂]** for temperatures 220K, 273K, 298K and 323K, as a function of the amount adsorbed (n) ranging from 0.01-3.0 mmol/g.
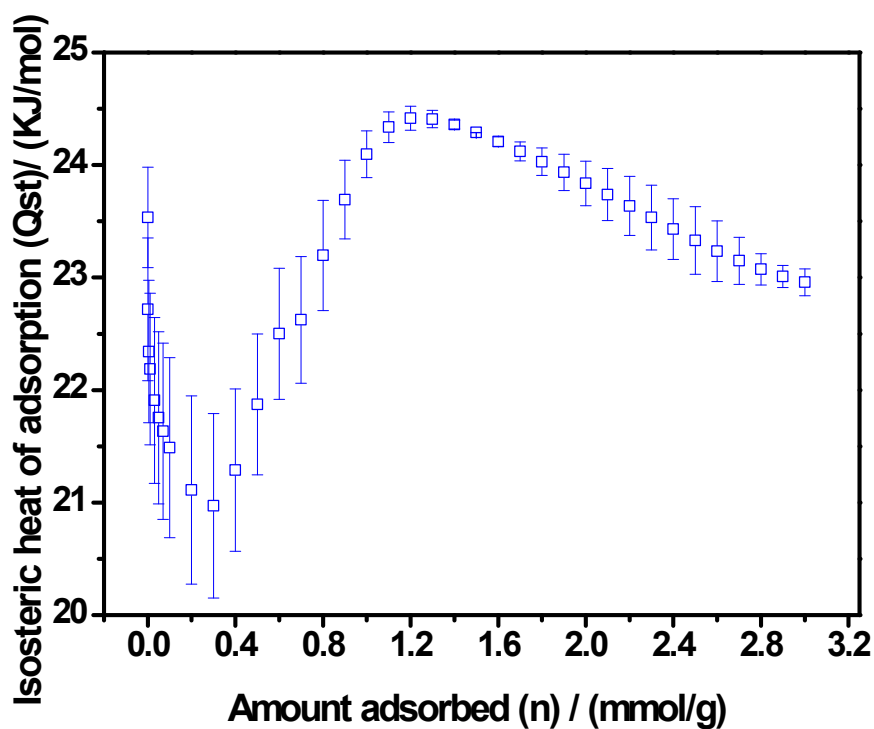
Figure S7. Isosteric heat (Qst/ kJmol⁻¹) of adsorption for Xe as a function of amount adsorbed (mmol/g) for the temperature range 220~323K.
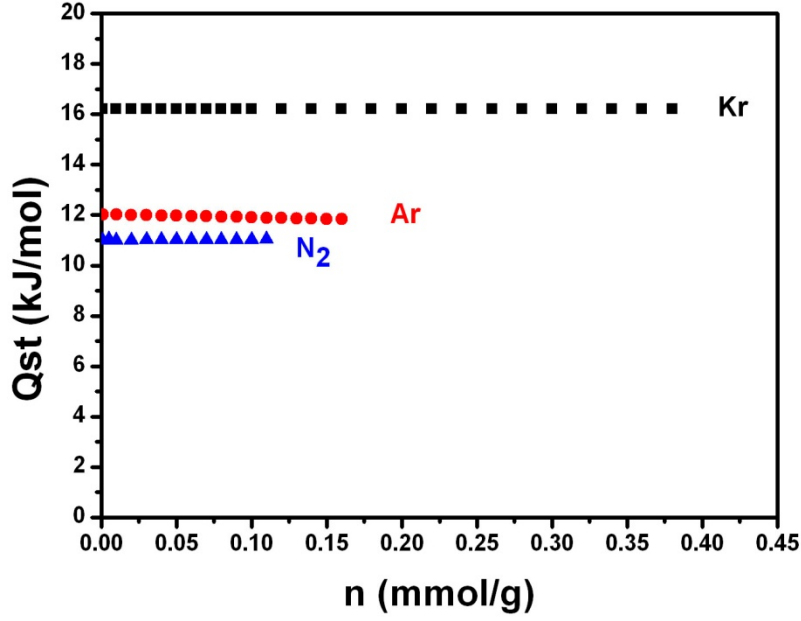
Figure S8. The variation of isosteric heat (Q_{st}) with amount adsorbed for Kr (black squares), Ar (red circles) and CH_4 (blue triangles).

2. The calculation of ΔF_{host}, ΔH_{host} and ΔS_{host} .

The adsorption isotherms were fitted using the data from $p = 0$ to $p = P_{trans}$. to derive a hypothetical isotherm for the rigid np form. Accordingly, the desorption isotherms were fitted using the data from $p = P_{trans}$ to $p = 1$ bar to derive a hypothetical isotherm for the lp form. where P_{trans} is the pressure at which the phase transition occurs. With these data the free energy difference ΔF_{host} of the **np** and **lp** forms can be calculated using the equation below based on the osmotic potential Ω_{os}.

$$\Delta\Omega_{os}(T,P) = \Delta F_{host}(T) + P\Delta V - RT\left[N_{max}^{(2)}ln\left(1 + \frac{K_2 P}{N_{max}^{(2)}}\right) - N_{max}^{(1)}ln\left(1 + \frac{K_1 P}{N_{max}^{(1)}}\right)\right] \quad (3)$$

At the transition pressure P_{trans} the difference of the osmotic potential of the **np** form and the **lp** form is equal to zero. And the product of P_{trans} and ΔV is negligible. Therefore, ΔF_{host} calculated using the equation below:

$$\Delta F_{host}(T) = RT\left[N_{max}^{(2)}ln\left(1 + \frac{K_2 P}{N_{max}^{(2)}}\right) - N_{max}^{(1)}ln\left(1 + \frac{K_1 P}{N_{max}^{(1)}}\right)\right] \quad (4)$$

Where K_i is the Henry constant for adsorption, which measures the adsorption affinity, and the N_{max}^i is the amount of the adsorbed gas at the plateau of the isotherm. If the $N^{(1)}_{max}$ is big enough, the $N^{(1)}_{max}$ usually cannot be extracted from the isotherm. That means the fitted isotherm data is among the very low pressure part of the whole Langmuir-type adsorption isotherm. Therefore, the $N_{max}^{(1)}ln\left(1 + \frac{K_1 P}{N_{max}^{(1)}}\right)$ can be approximated to be $K_1 P$. And the equation X can be written as follows:

$$\Delta F_{host}(T) = RT\left[N_{max}^{(2)}ln\left(1 + \frac{K_2 P}{N_{max}^{(2)}}\right) - K_1 P\right] \qquad (5)$$

The transition enthalpy value ($\Delta H_{host} = H_{lp}-H_{np}$) and entropy value ($\Delta S_{host} = S_{lp}-S_{np}$) are calculated using the equation below:

$$\Delta F_{host}(T) = \Delta H_{host}(T) - T\Delta S_{host} \qquad (6)$$

Table S3. Values of parameters for the Langmuir fits of the experimental isotherms.

T	Host structure	K (KPa^{-1})	N$_{max}$(mol/kg)
220K	lp	2.06816	4.74608
	np	0.42322	1.74989
273K	lp	0.21298	5.06868
	np	0.0321	*
298K	Lp	0.0573	6.38542
	np	0.01491	*
323K	np	0.0067	11.59349

*linear fit (i.e. Nmax cannot be extracted from the fit of the isotherms)

Langmuir equation :
$$N(P) = \frac{KP}{1 + \frac{KP}{N_{max}}} \qquad (7)$$
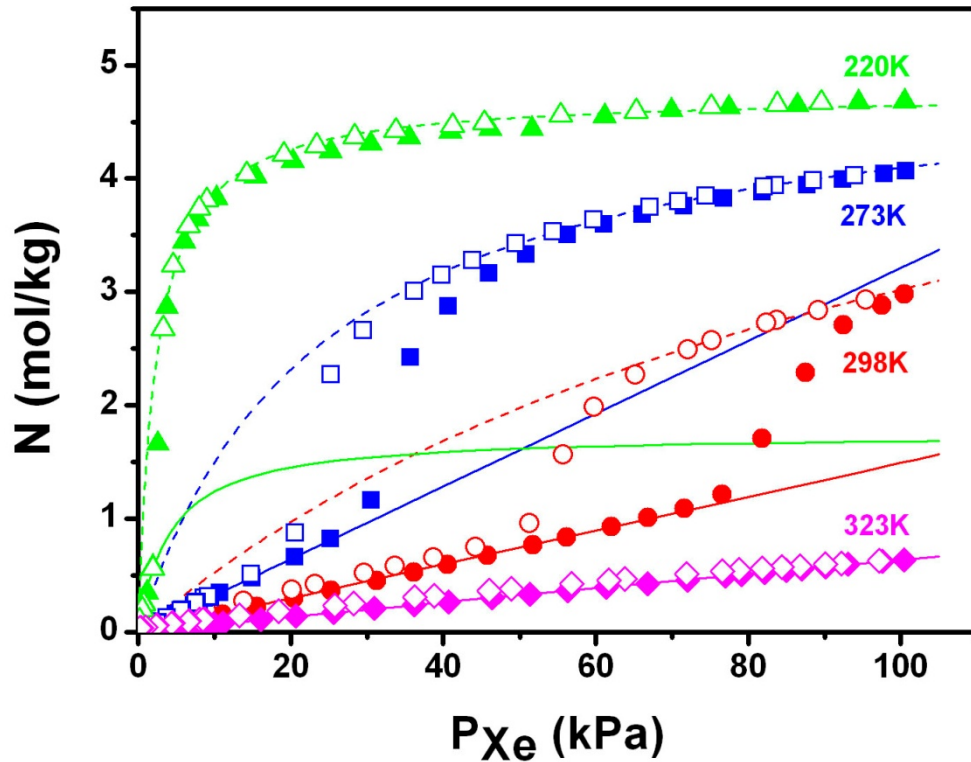
Figure S9. Experimental xenon adsorption isotherms fitted by Langmuir equation:

solid and dashed lines correspond to fits in the pressure ranges of the **np** and **lp** structural domains respectively.

Table S4. The estimated free-energy change of **[Zn(mtz)₂]** associated with the phase transition induced by Xe at 298 and 273 K.

| T/K	L Fit Parameters				P_{trans}(Pa)	ΔF_{host} (kJ/mol)
	lp		np			
	N^2_{max} (mol/kg)	K_2(kPa)	N^1_{max} (mol/kg)	K_1(kPa)		
298	6.39	0.0573	*	0.0149	76.5	5.45
273	5.07	0.213	*	0.0321	30.6	7.28

3. Calculation of selectivity using S(DIH) equation:

The S(DIH) equation based on the difference of isosteric heats (DIH) has been demonstrated to be precise in prediction of the selectivity of two components gases mixture at low pressure (1~1 bar). It requires only adsorption equation isotherms and adsorption heats of pure components. The pressure dependent selectivity can be calculated using the equation below:

$$S_{ads}(i/j) = \sqrt{S_{ideal} \cdot S_0} \qquad (8)$$

Where $S_{ideal} = \dfrac{N_i(p)}{N_j(p)}$, and $lnS_0 = 0.716\dfrac{\Delta q^0_{st}}{RT}$. N_i(p) and N_j(p) are the uptakes of the pure components at the pure components at the corresponding partial pressures. S_0 is only related with the Δq^0_{st}, whereas Δq^0_{st} is the difference of the interaction strengths between materials and the two gases.

4. The ideal Xe capture capacity in hypothetical PSA cycle:
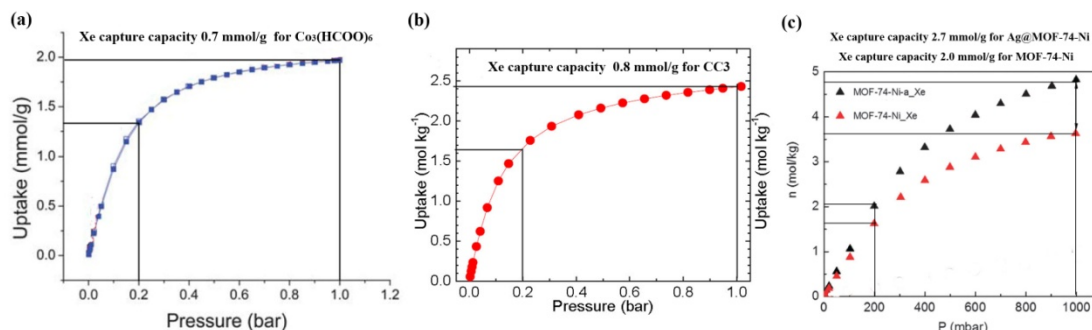
Figure S10. Determination of ideal working capacities of Co$_3$(HCOO)$_6$ (a), CC3 (b), MOF-74Ni and Ag@MOF-74Ni (c) in a hypothetical pressure swing adsorption (PSA) cycle.

5. Breakthrough experiments

~2.4g [Zn(mtz)$_2$] crystals were packed into a stainless steel column (the steel column was 18cm in length with 4 mm of inner（6.4 mm outer）diameter with silica wool filling the void space. The sorbent was vacuumed at room temperature for 8 hours firstly and activated in the column with a helium flow at 50 ℃ for 3 hours before the temperature of the column was decreased to 23 ℃. The flow of He was then turned off while a gas mixture (Xe /Kr: 50:50, V/V) was sent into the column. The flow of He and sample gas mixture was measured by a Mass Flow controller to be ~ 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.

The adsorption capacity was estimated from the breakthrough curves using the following equation:

$$n_{adsi} = FC_i t_i \qquad (9)$$

Where n_{adsi} is the adsorption capacity of the gas i, F is the total molar flow, C_i is the concentration of the gas I entering the column and the ti is the time corresponding to the gas i, which is estimated from the breakthrough profile.

The selectivity was then calculated according to the equation:

$$S_{A/B} = \frac{X_A/X_A}{Y_B/Y_B} \qquad (10)$$

Where X_A and X_B are the mole fractions of the gases A and B in the adsorbed phase and Y_A and Y_B are the mole fractions of the gases A and B in the bulk phase.

Table S5. Xe uptakes and separation in selected porous materials.

Material	Xe uptake (mmol/g)	Xe/Kr selectivity	Xe/Ar selectivity	Xe/N$_2$ selectivity	Q$_{st}$(kJ/mol)	Ref.
MOF-5	1.98	-	-	-	15	[1]
MIL-53-Al	3.0	-	-	-	-	[2]
Cu(HFIPBB)	0.8	~2[c]	-	-	~15	[3]
MFU-4l	1.8	4.7	-	-	20	[4]
HKUST-1	3.3	8.4	24.92	20.73	26.9	[4]&[9]
MOF-505	2.2	~8[d]	-	-	-	[5]
Co$_3$(HCOO)$_6$	2	~12[a]/6[b]	-	-	29	[6]
MOF-74Ni	4.2	5/7.3[f]	-	-	9.5	[7]
Ag@MOF-74Ni	4.6	6.8	-	-	11	[8]
Activated Carbon	4.2	4	-	-	-	[7]
[Zn(mtz)$_2$]	3	9.2[e]/15.5[c]	32.5[e]	44.0[e]	23.53	This work
MOF-74-Mg	~5.58	5.92	19.71	5.3	-	[9]
MOF-74-Co	~6.1	10.37	44.95	18.18	-	[9]
MOF-74-Zn	~3.88	5.76	21.5	14.7	-	[9]
NOTT-100	~6.1	6.89	22.68	20.93	-	[9]
NOTT-101	~4.7	5.34	14.36	17.32	-	[9]
NOTT-102	~2.2	3.90	12.67	11.70	-	[9]
NOTT-103	~4.1	5.49	17.96	18.06	-	[9]
PCN-14	~7.2	6.46	22.39	24.67	-	[9]
CC3	~2.3	20[f]	-	-	25.2	[10]

[a]From IAST calculation (Xe-Kr: 10:90); [b] From breakthrough experiment (Xe-Kr: 10:90); [c]From breakthrough experiment (Xe-Kr: 50:50); [d] From breakthrough experiment (Xe-Kr: 20:80); [e]From S(DIH) calculation (Xe-Kr: 50:50); [f] From breakthrough experiment (gas mixtures containing 400ppm Xe and 40ppm Kr in air). The Xe uptakes and Selectivities of MOF-74-Mg, MOF-74-Co, MOF-74-Zn, NOTT-100, NOTT-101, NOTT-102, NOTT-103 and PCN-14 were mearsured at 292K. The Xe uptakes and Selectivities of Cu(HFIPBB) and HKUST-1 were measured at 310K. The Xe uptakes and Selectivities of other porous materials were measured at 298K.

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