Supporting Information for: Thermodynamic exploration of xenon/krypton separation based on a high-throughput screening

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Exchange equilibrium



Figure S1: Representation of the fictitious exchange equilibrium between xenon and krypton considered in our study.

Other correlations

It is possible to define an entropy of adsorption of a guest g for a given standard state (P°=1 atm):

$$\Delta_{\rm ads}S_0^{\rm g} = R\ln(P^{\rm o}M^{\rm f}K^{\rm g}) + \frac{1}{T}\Delta_{\rm ads}H_0^{\rm g}$$
(S1)

where *R* is the ideal gas constant, *T* is the temperature equals to 298 K, P° is the pressure at atmospheric pressure and $M_{\rm f}$ is the framework's molar mass in g mol⁻¹, $K^{\rm g}$ the Henry's constant of g and $\Delta_{\rm ads}H_0^{\rm g}$ the adsorption enthalpy of g.



Figure S2: Entropy pair-plots in both linear and log scale.



Figure S3: Correlation between henry coefficient and enthalpy for both xenon and krypton

Difference of selectivity: the 90:10 composition case



Figure S4: Overview at linear and log scale, comparison between s_0 and $s_1(90:10)$



Figure S5: Overview at linear and log scale, comparison between $s_1(20:80)$ and $s_1(90:10)$



Entropy and enthalpy between low an high selectivity

Figure S6: Split view of the figures 4 and 5 of the article. The iso-selectivity lines for the limit considered are represented with blue and orange lines.



Figure S7: The energetic equivalent of exchange equilibrium entropy $T\Delta_{exc}S_1$ and enthalpy $\Delta_{exc}H_1$ at ambient pressure labeled using the selectivity s_1 at ambient pressure.



Distribution of the exchange enthalpy and entropy

Figure S8: Distribution of the enthalpy and entropy of exchange at low pressure on the 630 most selective structures



Figure S9: Distribution of the enthalpy and entropy of exchange at ambient pressure on the 630 most selective structures

Raw data for the archetypal structures presented in the main

article

Table S1: Raw thermodynamic quantities associated for a few representative examples of MOFs. Henry's constant K^{Xe} , K^{Kr} are in mmol g^{-1} Pa⁻¹, loadings q_1^{Xe} and q_1^{Kr} are in mmol g^{-1} , enthalpies $\Delta_{ads}H_0^{Xe}$, $\Delta_{ads}H_0^{Xe}$, $\Delta_{ads}H_1^{Xe}$ and $\Delta_{ads}H_1^{Xe}$ are in kJ mol⁻¹, and diameters D_i and D_f in Å

CSD Refcode	<i>s</i> ₀	K ^{Xe}	K ^{Kr}	$\Delta_{\rm ads} H_0^{\rm Xe}$	$\Delta_{ m ads} H_0^{ m Kr}$	s_1	$q_1^{ m Xe}$	$q_1^{ m Kr}$	$\Delta_{\rm ads} H_1^{\rm Xe}$	$\Delta_{\rm ads} H_1^{\rm Xe}$	D_{i}	D_{f}
VOKJIQ	157	7.9210^{-1}	5.0410^{-3}	-53.9	-38.2	243	2.57	0.04	-61.1	-44.5	4.8	2.9
KAXQIL	104	3.0110^{-2}	2.9010^{-4}	-44.6	-30.5	133	1.41	0.04	-41.5	-26.8	5.1	3.8
JUFBIX	106	1.5910^{-2}	1.5010^{-4}	-45.6	-31.4	115	0.80	0.03	-45.7	-31.3	5.0	2.7
FALQOA	162	2.2310^{-2}	1.3810^{-4}	-47.3	-32.0	171	0.68	0.02	-48.6	-33.1	5.1	3.1
GOMREG	114	9.1610^{-2}	8.0310^{-4}	-44.7	-31.1	74	2.59	0.14	-47.5	-33.8	5.4	3.6
JAVTAC	117	1.2410^{-1}	1.0610^{-3}	-47.7	-33.5	67	1.50	0.09	-48.5	-34.9	5.1	3.9
GOMRAC	124	1.1710^{-1}	9.4510^{-4}	-45.6	-31.8	47	2.51	0.21	-47.3	-34.8	5.3	3.4
MISQIQ	139	6.8710^{-1}	4.9410^{-3}	-51.9	-37.4	37	2.30	0.25	-45.6	-32.8	4.2	4.1
BAEDTA01	154	1.3910^{-2}	9.0410^{-5}	-47.7	-31.7	38	1.05	11	-34.0	-23.1	5.3	4.3
VIWMOF	81	$7.87 10^{-3}$	9.7010^{-5}	-46.3	-30.1	13	2.99	0.90	-26.0	-17.8	9.8	5.2
LUDLAZ	166	9.0410^{-2}	5.4610^{-4}	-45.4	-30.9	16	1.59	0.39	-38.3	-28.3	6.6	4.2
WOJJOV	146	4.1910^{-2}	2.8610^{-4}	-46.4	-30.7	14	2.82	0.81	-33.0	-24.4	7.8	6.4
VAPBIZ	147	3.5410^{-2}	2.4110^{-4}	-46.4	-30.5	13	2.50	0.78	-34.1	-25.3	6.3	3.6

Lennard-Jones (LJ) potentials The van der Waals interaction can be approximately modeled by the following potential V_{LJ} :

$$V_{\rm LJ} = 4\varepsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right)$$
(S2)

where ε is the depth of the well (minimal energy), σ is the distance from which the interaction becomes stabilizing and *r* is the distance between the two interacting atoms.

Lorentz-Berthelot rules From LJ parameters of interactions between the same type of atoms we can determine interactions between different types of atoms:

$$\begin{aligned} \boldsymbol{\varepsilon}_{ij} &= \sqrt{\boldsymbol{\varepsilon}_{ii} \times \boldsymbol{\varepsilon}_{jj}} \\ \boldsymbol{\sigma}_{ij} &= \frac{\boldsymbol{\sigma}_{ii} + \boldsymbol{\sigma}_{jj}}{2} \end{aligned} \tag{S3}$$

where i and j are indexes corresponding to two different types of atoms (e.g., i=Xe and j=Kr)

Langmuir 1-site At given temperature, some mono-site materials' isotherm can be described by the following equation:

$$q(P) = N_{\max} \frac{KP}{1 + KP}$$
(S4)

where q is the loading of a given mono-component gas, K is the adsorption equilibrium constant and P is the pressure.

Langmuir 2-site At given temperature, some two-site materials' isotherm can be described by the following equation:

$$q(P) = N_{\max}\left((1 - \alpha_2)\frac{K_1P}{1 + K_1P} + \alpha_2\frac{K_2P}{1 + K_2P}\right)$$
(S5)

where *q* is the loading of a given mono-component gas, K_1 and K_2 are the adsorption equilibrium constants in the respective sites, α_2 is the proportion of secondary sites, and *P* is the pressure.



Figure S10: The LJ potentials for xenon and krypton interactions. The xenon-xenon interaction is more stabilizing than the krypton-krypton interaction for inter-atomic distance higher than 4.2 Å.



Figure S11: VOKJIQ: On the left side, an illustration of a clean version (all solvent removed) of the open-framework aluminophosphate $[HAl_3P_3O_{13}]\cdot C_3NH_{10}$ loaded with xenon and krypton obtained by GCMC calculations. Color code: Al in silver, P in orange, O in red, H in white ; Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 1-site Langmuir model for both xenon and krypton at 298 K is represented on the right side.



Figure S12: KAXQIL: On the left side, an illustration of a clean version (all solvent removed) of the calcium coordination framework $[Ca(SDB)] \cdot H_2O$, where SDB = 4,4'-sulfonyldibenzoate loaded with xenon and krypton obtained by GCMC calculations. Color code: Ca in dark cyan, C in gray, O in red, H in white, S in yellow ; Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 1-site Langmuir model for both xenon and krypton at 298 K is represented on the right side.



Figure S13: JUFBIX: Representation of a clean version (all solvent removed) of the cobalt(II) coordination framework $[Co_2(L)(ppda)_2]_2 \cdot H_2O$, where the ligand L is 2,8-di(1*H*-imidazol-1-yl)dibenzofuran and the carboxylic acid ligand H₂ppda is 4,4'-(perfluoropropane-2,2-diyl)dibenzoic acid loaded with xenon and krypton obtained by GCMC calculations. Color code: Co in dark cyan, C in gray, O in red, H in white, N in blue, F in green ; Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 1-site Langmuir model for both xenon and krypton at 298 K is represented on the right side.



Figure S14: FALQOA: Representation of a clean version (all solvent removed) of the Nd-Cu heterometallic coordination polymer $[Nd_2Cu_3(ANMA)_6]\cdot 3(H_2O)$, where the ligand ANMA is the deprotonated form of H₂ANMA = L-alanine-*N*-monoacetic acid loaded with xenon and krypton obtained by GCMC calculations. Color code: Cu in dark green, Nd in dark cyan, C in gray, O in red, H in white, N in blue ; Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 1-site Langmuir model for both xenon and krypton at 298 K is represented on the right side.



Figure S15: GOMREG: Representation of a clean version (all solvent removed) of this aluminophosphate AlPO₄-*n* that has a zeotype LAU topology with one-dimensional 10-ring channels loaded with xenon and krypton obtained by GCMC calculations. Color code: Al in silver, P in orange, O in red ; Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 1-site Langmuir model for both xenon and krypton at 298 K is represented on the right side.



Figure S16: JAVTAC: Representation of a clean version (all solvent removed) of this openframework fluoroaluminophosphate SIZ-3 $[Al_5P_5O_{20}F_2] \cdot 2(C_6H_{11}N_2)$ that has an AlPO-11 framework structure loaded with xenon and krypton obtained by GCMC calculations. Color code: Al in silver, P in orange, O in red, F in green ; Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 1-site Langmuir model for both xenon and krypton at 298 K is represented on the right side.



Figure S17: GOMRAC: Representation of a clean version (all solvent removed) of this aluminophosphate AlPO₄-*n* that has a zeotype LAU topology with one-dimensional 10-ring channels loaded with xenon and krypton obtained by GCMC calculations. Color code: Al in silver, P in orange, O in red ; Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 1-site Langmuir model for both xenon and krypton at 298 K is represented on the right side. It seems that this aluminophosphate is just a smaller version of GOMREG.



Figure S18: MISQIQ: Representation of a chiral open-framework fluoroaluminophosphate $[Al_6P_3O_{12}F_6(OH)_6]\cdot C_4N_3H_{16}$ denoted AlPO-JU89 on the left side. Color code: Al in silver, P in orange, O in red, H in white and F in green for the framework ; and Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 2-site Langmuir model for both xenon and krypton at 298 K on the right side.



Figure S19: BAEDTA01: Representation of a baryum-based MOF $[Ba_2(EDTA)] \cdot 2.5(H_2O)$, where EDTA is the deprotonated form of H_2EDTA = ethylenediaminetetraacetic acid, on the left side. Color code: Ba in dark green, C in gray, O in red, H in white, N in blue for the framework ; and Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 2-site Langmuir model for both xenon and krypton at 298 K, on the right side.



Figure S20: VIWMOF: Representation of a chiral cadmium-based MOF conglomerate $[Cd(tipa)(\mu_3 - OH)]$ ·NO₃·EtOH·DMF where tipa is tris(4-(1*H*-imidazol-1-yl)phenyl)amine and DMF is dimethyl-formamide, on the left side. Color code: Cd in dark pink, C in gray, H in white, N in blue for the framework ; and Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 2-site Langmuir model for both xenon and krypton at 298 K, on the right side.



Figure S21: LUDLAZ: Representation of a copper-based MOF known as STAM-1 $[Cu_3O_{21}C_{30}H_{24}]$ ·5(H₂O), on the left side. Color code: Cu in dark cyan, C in gray, O in red, H in white for the framework ; and Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 2-site Langmuir model for both xenon and krypton at 298 K, on the right side.



Figure S22: WOJJOV: Representation of an aluminium-based MOF $[Al(OH)(1,4-NDC)]\cdot 2(H_2O)$ where NDC means naphthalenedicarboxylate, on the left side. Color code: Cu in dark cyan, C in gray, O in red, H in white for the framework ; and Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 2-site Langmuir model for both xenon and krypton at 298 K, on the right side.



Figure S23: VAPBIZ: Representation of a europium-based homochiral MOF $[EuL(NO_3)_3(H_2O)] \cdot 13(H_2O)$ where L is an achiral hexacarboxylic ligand, on the left side. Color code: Cu in dark cyan, C in gray, O in red, H in white for the framework ; and Xe in transparent pink and Kr in cyan for the adsorbates. The mono-component isotherms fitted with a 2-site Langmuir model for both xenon and krypton at 298 K, on the right side.