Supporting Information for:

Thermodynamic exploration of xenon/krypton separation based on a high-throughput screening

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Exchange equilibrium

$$Xe_{(g)} + Kr_{(ads)} = Xe_{(ads)} + Kr_{(g)}$$

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):

\[
\Delta_{\text{ads}} S_g^0 = R \ln(P^* M^* K^g) + \frac{1}{T} \Delta_{\text{ads}} H_g^0
\]  

(S1)

where \( R \) is the ideal gas constant, \( T \) is the temperature equals to 298 K, \( P^* \) is the pressure at atmospheric pressure and \( M_i \) is the framework’s molar mass in g mol\(^{-1}\), \( K^g \) the Henry’s constant of \( g \) and \( \Delta_{\text{ads}} H_g^0 \) 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 $T\Delta_{\text{exc}}S_1$ and enthalpy $\Delta_{\text{exc}}H_1$ 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 $\Delta_{ads}H_0^{Xe}$, $\Delta_{ads}H_0^{Kr}$, $\Delta_{ads}H_1^{Xe}$ and $\Delta_{ads}H_1^{Kr}$ are in kJ mol$^{-1}$, and diameters $D_i$ and $D_f$ in Å.

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

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

(S2)

where $\varepsilon$ is the depth of the well (minimal energy), $\sigma$ 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:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}}$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$$

(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:

\[ q(P) = N_{\text{max}} \frac{K P}{1 + K P} \]  

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:

\[ q(P) = N_{\text{max}} \left( (1 - \alpha_2) \frac{K_1 P}{1 + K_1 P} + \alpha_2 \frac{K_2 P}{1 + K_2 P} \right) \]  

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, \( \alpha_2 \) 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 [HAL₃P₃O₁₃]·C₃NH₁₀ 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)]·H₂O, 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)$_2$]$_2$·H$_2$O, where the ligand L is 2,8-di(1$H$-imidazol-1-yl)dibenzofuran and the carboxylic acid ligand H$_2$ppda 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$_2$Cu$_3$(ANMA)$_6$]·3(H$_2$O), where the ligand ANMA is the deprotonated form of H$_2$ANMA = 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 AlPO$_4$-$n$ 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 open-framework fluoroaluminophosphate SIZ-3 [Al$_5$P$_5$O$_{20}$F$_2$]$_2$(C$_6$H$_{11}$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 AlPO$_4$-$n$ 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$_6$P$_3$O$_{12}$F$_6$(OH)$_6$]$_{-}$C$_4$N$_3$H$_{16}$ 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 \([\text{Ba}_2(\text{EDTA})\cdot2.5(\text{H}_2\text{O})]\), where EDTA is the deprotonated form of \(\text{H}_2\text{EDTA} = \text{ethylenediaminetetraacetic acid}\), 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 \([\text{Cd}(\text{tipa})(\mu_3-\text{O})\cdot\text{NO}_3\cdot\text{EtOH} \cdot \text{DMF}\) where tipa is tris(4-(1H-imidazol-1-yl)phenyl)amine and DMF is dimethylformamide, 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 \( [\text{Cu}_3\text{O}_{21}\text{C}_{30}\text{H}_{24}].5(\text{H}_2\text{O}) \), 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 \( [\text{Al}((\text{OH})(1,4-\text{NDC}))\cdot2(\text{H}_2\text{O}) \) 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(NO₃)₃(H₂O)]·13(H₂O) 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.