Computation-informed optimization of Ni(PyC)₂ functionalization for noble gas separations

Nickolas Gantzler¹, Min-Bum Kim², Alexander Robinson², Maxwell W. Terban³, Sanjit Ghose⁴, Robert E. Dinnebier³, Arthur Henry York⁵, Davide Tiana⁶, Cory M. Simon⁷, and Praveen K. Thallapally⁸

¹Department of Physics. Oregon State University. Corvallis, OR.
²Pacific Northwest National Laboratory. Richland, WA.
³Max Planck Institute for Solid State Research. Stuttgart, Germany.
⁴National Synchrotron Light Source II. Brookhaven National Laboratory. Upton, NY.
⁵School of Electrical Engineering and Computer Science. Oregon State University. Corvallis, OR.
⁶School of Chemistry. University College Cork. Ireland.
⁷School of Chemical, Biological, and Environmental Engineering. Oregon State University. Corvallis, OR.
⁸cory.simon@oregonstate.edu, praveen.thallapally@pnnl.gov

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Abstract

Metal-organic frameworks (MOFs) are promising nanoporous materials for the adsorptive capture and separation of noble gases at room temperature. Among the numerous MOFs synthesized and tested for noble gas separations, Ni(PyC)₂ (PyC = pyridine-4-carboxylate) exhibits one of the highest xenon/krypton selectivities at room temperature. Like lead-optimization in drug discovery, here we aim to tune the chemistry of Ni(PyC)₂, by appending a functional group to its PyC ligands, to maximize its Xe/Kr selectivity. To guide experiments in the laboratory, we virtually screen Ni(PyC-X)₂ (X=functional group) structures for noble gas separations by (i) constructing a library of Ni(PyC-X)₂ crystal structure models then (ii) using molecular simulations to predict noble gas (Xe, Kr, Ar) adsorption and selectivity at room temperature in each structure. The virtual screening predicts several Ni(PyC-X)₂ structures to exhibit a higher Xe/Kr, Xe/Ar, and Kr/Ar selectivity than the parent Ni(PyC)₂ MOF, with Ni(PyC-m-NH₂)₂ among them. In the laboratory, we synthesize Ni(PyC-m-NH₂)₂, determine its crystal structure by X-ray powder diffraction, and measure its Xe, Kr, and Ar adsorption isotherms (298 K). In agreement with our molecular simulations, the Xe/Kr, Xe/Ar, and Kr/Ar selectivities of Ni(PyC-m-NH₂)₂ exceed those of the parent Ni(PyC)₂. Particularly, Ni(PyC-m-NH₂)₂ exhibits a [derived from experimental, equilibrium adsorption isotherms] Xe/Kr selectivity of 20 at dilute conditions and 298 K, compared to 17 for Ni(PyC)₂. According to in situ X-ray diffraction, corroborated by molecular models, Ni(PyC-m-NH₂)₂ presents well-defined binding pockets tailored for Xe and organized along its one-dimensional channels. In addition to discovering the new, performant Ni(PyC-m-NH₂)₂ MOF for noble gas separations, our study illustrates the computation-informed optimization of the chemistry of a "lead" MOF to target adsorption of a specific gas.
1 Introduction

The inert, noble gases xenon (Xe), krypton (Kr), and argon (Ar) have several industrial applications, such as: filler gas for lamps (Xe, Kr, Ar), insulation in multiple-pane windows (Xe, Kr, Ar), anaesthetic and imaging agent in medicine (Xe), propellant for ion thrusters on spacecraft (Xe), gain medium for lasers (Xe, Kr, Ar), and medium to detect and measure ionizing radiation (Ar, Xe). Ar is used in bulk quantities, as a protective gas, during the production of metals and semiconductors. [1,2]

Xe, Kr, and Ar naturally occur in the atmosphere of the earth at 0.0000086 mol %, 0.000114 mol %, and 0.9300 mol %, respectively (troposphere, dry conditions) [1]. Radioactive isotopes of Xe and Kr are produced by the nuclear fission of both uranium and of plutonium—whether controlled, to generate power, or uncontrolled, to generate an explosion [3,4].

The tasks of separating Xe/Kr and Ar/O\textsubscript{2}/N\textsubscript{2} mixtures are encountered during the industrial production of pure Xe, Kr, and Ar by isolating them from air. Cryogenic distillation plants that (primarily) produce pure O\textsubscript{2} and N\textsubscript{2} from air also produce impure or mixed byproduct streams highly enriched with noble gases – a Xe/Kr stream and an Ar stream contaminated with O\textsubscript{2} and N\textsubscript{2}. These streams are then subject to further cryogenic separations to obtain pure Xe, Kr, and Ar for their many uses. [1]

The task of capturing dilute Xe and/or Kr from air is encountered in (i) the reprocessing and recycling of spent nuclear fuel (SNF) [4,5] and (ii) the detection of nuclear explosions from (banned) nuclear weapons tests [3,7]. Expanding on (i), reprocessing and recycling the large US inventory of SNF [8] would recover unused fissile material for new fuel assemblies and reduce the volume of radioactive waste to sequester [9,10]. However, radioactive isotopes of xenon (Xe) and krypton (Kr) (fission products) evolve from the SNF during reprocessing (~400 ppm $^{127}$Xe, ~40 ppm $^{85}$Kr in the off-gases), which must be captured and (particularly, $^{85}$Kr) sequestered as opposed to released into the atmosphere [6].

In lieu of capital- and energy-intensive cryogenic distillation, metal-organic frameworks (MOFs) could be used to efficiently separate and capture noble gases [4,11,13]. MOFs are nanoporous materials with large internal surface areas to which gas selectively adsorbs [14]. The selectively adsorbed Xe and/or Kr in the MOF can be desorbed and recovered, regenerating the MOF for another adsorption cycle, by reducing the pressure and/or raising the temperature. An adsorption-based process for
noble gas separations at room temperature, in place of cryogenic distillation, could reduce costs and, in the case of SNF reprocessing off-gases, alleviate explosion hazards from the radiolytic formation of ozone that concentrates in the distillation column.

The pore size, shape, and internal surface chemistry of MOFs can be readily tuned to maximize their selectivity for a noble gas. MOFs are comprised of an extended network of metal ions or clusters (nodes) coordinated by organic ligands (linkers). A vast number of MOF structures are achievable via de novo synthesis, by combining different inorganic nodes and organic linkers within many different topologies, and via post-synthetic modification.

Virtual screenings can quickly and cost-effectively winnow a pool of candidate MOFs for noble gas separations to a prioritized shortlist for experimental pursuit. In a virtual screening, we (i) construct a library of candidate crystal structure models of hypothetical MOFs then (ii) conduct molecular simulations of gas adsorption in each to predict their noble gas adsorption properties. Among several virtual screenings of MOFs for noble gas separations, one directly motivated experimental measurements of Xe/Kr adsorption in SBMOF-1, which boasts one of the highest measured Xe/Kr selectivities (16 at 298 K in the dilute limit).

Among the many MOFs experimentally synthesized and tested for noble gas separation and capture, Ni(PyC)_2 (PyC = pyridine-4-carboxylate) is a formidable contender for Xe/Kr separations, exhibiting a higher Xe/Kr selectivity (17 at 298 K in the dilute limit) than SBMOF-1. Fig. 1 shows the crystal structure of Ni(PyC)_2, comprised of two-fold interpenetrated diamondoid networks of Ni ions coordinated to PyC ligands. The diameter of the largest included sphere in Ni(PyC)_2 is 5.2 Å (calculated by Zeo++), falling within the optimal window for Xe/Kr separations.

Figure 1: The parent MOF, Ni(PyC)_2. (a, b) The crystal structure of Ni(PyC)_2 is composed of two-fold interpenetrated diamondoid networks of Ni ions coordinated by PyC (pyridine-4-carboxylate) ligands. The atomistic crystal structure is shown in (a) [gray: C, blue: N, red: O, green: Ni, white: H]. Each Ni ion is coordinated by two bidentate carboxylate groups and two pyridine units. The structure forms one-dimensional channels for gas adsorption. The two-fold disconnected, interpenetrated networks (red and blue) forming the crystal are highlighted in (b) [green nodes: Ni atoms, blue/red edges: ditopic, PyC linkers]. (c) From the naked eye, Ni(PyC)_2 (as-synthesized) appears as a powder with a dark aqua color.
Akin to lead-optimization in drug discovery, here we aim to leverage the tunability of MOFs to optimize the chemistry of the "lead", parent Ni(PyC)$_2$ MOF for Xe/Kr selectivity. In particular, we wish to determine which functional group X is optimal to append to the PyC linker to give the new Ni(PyC-X)$_2$ MOF the highest Xe/Kr selectivity. To guide experimental pursuits, we conduct a virtual screening of Ni(PyC-X)$_2$ structures for noble gas separations. First, we show that molecular models and simulations accurately reproduce the experimentally measured Xe, Kr, and Ar adsorption isotherms in the parent Ni(PyC)$_2$ MOF. Then, we construct a library of 21 Ni(PyC-X)$_2$ crystal structure models and use molecular simulations to predict their Xe, Kr, and Ar Henry coefficients and selectivities at room temperature. The virtual screening predicts that several Ni(PyC-X)$_2$ MOFs will exhibit a higher Xe/Kr selectivity and Xe Henry coefficient than the parent Ni(PyC)$_2$ MOF. Among them, we targeted Ni(PyC-m$_2$-NH$_2$)$_2$ for synthesis in the lab owing to the commercial availability of the PyC-m$_2$-NH$_2$ ligand. We synthesized Ni(PyC-m$_2$-NH$_2$)$_2$ (solvothermal, de novo), determined its crystal structure by X-ray powder diffraction (XRPD), and measured its Xe, Kr, and Ar adsorption isotherms. In agreement with our molecular simulations, the experimentally measured (dilute) Xe/Kr selectivity and Xe Henry coefficient (20.98 mmol/(g-bar)) of Ni(PyC-m$_2$-NH$_2$)$_2$ are greater than those of the parent Ni(PyC)$_2$ MOF (17.54 mmol/(g-bar)). More, based on changes in the XRPD pattern of the samples upon exposure to air, Ni(PyC-m$_2$-NH$_2$)$_2$ shows greater stability to air exposure than the parent Ni(PyC)$_2$ MOF. In situ X-ray diffraction studies elucidate the well-defined Xe adsorption pockets in Ni(PyC-m$_2$-NH$_2$)$_2$, corroborated by molecular modeling. In addition to discovering Ni(PyC-m$_2$-NH$_2$)$_2$ for enhanced noble gas separations, our study illustrates the computation-informed optimization of the chemistry of a "lead", parent MOF to enhance its selectivity for an adsorbate.

2 Results

First, we show that the molecular models and simulations reproduce the experimentally measured, pure-component Xe, Kr, and Ar equilibrium adsorption isotherms (298 K) in Ni(PyC)$_2$. Second, we construct a library of Ni(PyC-X)$_2$ crystal structure models by, in silico, appending various functional groups X to the PyC ligand of the parent Ni(PyC)$_2$ and optimizing the geometry. Next, in each Ni(PyC-X)$_2$ structure, we conduct molecular simulations of noble gas adsorption at dilute conditions and 298 K to predict their Xe, Kr, and Ar Henry coefficients and, from those, their Xe/Kr, Xe/Ar, and Kr/Ar selectivities. Among several Ni(PyC-X)$_2$ structures predicted to exhibit a higher Xe/Kr selectivity than the parent Ni(PyC)$_2$ MOF, we then target Ni(PyC-m$_2$-NH$_2$)$_2$ for experimental synthesis, characterization via XRPD, and noble gas adsorption measurements. Finally, we conduct in situ X-ray diffraction studies to elucidate the prominent Xe adsorption sites in Ni(PyC-m$_2$-NH$_2$)$_2$, corroborated by molecular models and simulations.

2.1 Comparing simulated and experimental Xe, Kr, and Ar adsorption in Ni(PyC)$_2$

We first assess how accurately our molecular models and simulations predict noble gas (Xe, Kr, and Ar) adsorption in the parent Ni(PyC)$_2$ MOF. For the molecular model that describes the potential energy of gas-MOF and gas-gas interactions, we use the Universal Force Field (UFF) [57]. UFF is commonly used to predict adsorption in MOFs [21] and can rank MOFs according to their adsorption with
Figure 2: Pure-component xenon, krypton, and argon adsorption isotherms (298 K) in the parent Ni(PyC)$_2$ MOF. Our simulated (via grand-canonical Monte Carlo) adsorption isotherms closely match the experimentally-measured adsorption $^{[41]}$. Xenon uptake saturates at two Xe atoms per unit cell, indicating commensurate adsorption. A library of Ni(PyC-X)$_2$ (X=functional group) crystal structures

We next construct a library of crystal structure models of functionalized Ni(PyC)$_2$ derivatives by appending a functional group X on each PyC ligand of the parent Ni(PyC)$_2$ crystal structure $^{[41]}$, mimicking covalent post-synthetic modification $^{[16]}$. The functionalized PyC linkers in our library, PyC-X, chosen in consideration of synthetic accessibility, are shown in Fig. 3. Let PyC-m-X and PyC-o-X be the PyC ligand functionalized with an X functional group at the meta and ortho position, respectively. We aim to construct Ni(PyC-m-X)$_2$ and Ni(PyC-o-X)$_2$ crystal structure models for each X group in Fig. 3. Be-
Figure 3: A list of PyC-X ligands used to construct our library of Ni(PyC-X)$_2$ MOFs. (left) PyC-m-X and PyC-o-X: PyC ligands functionalized with an X functional group in the meta and ortho position, respectively. (right) The functional groups with which we decorate the PyC ligand. N.b. X=H gives the PyC ligand of the parent Ni(PyC)$_2$ MOF.

cause we construct each Ni(PyC-X)$_2$ structure starting with the parent Ni(PyC)$_2$ structure, each MOF in our library shares the same topology, unit cell, and coordination environment as the parent MOF in Fig. 1.

We develop an automated procedure to construct each Ni(PyC-X)$_2$ crystal structure model, culminating in our PoreMatMod.jl software [60]. See Sec. 4.1 for details. First, we use the bonding graph of the parent Ni(PyC)$_2$ crystal to find, group, and label the substitution sites on the PyC ligands of the parent MOF. Once we specify a substitution site (ortho or meta), we align geometry-optimized molecular fragments, containing the functional group X, onto the PyC ligand of the parent MOF. After alignment, we remove the H at the substitution site and install the X group in its place—in a reasonable geometry with respect to the PyC ligand. Finally, we use density functional theory (DFT) calculations to optimize the geometry of the new Ni(PyC-X)$_2$ MOF under a fixed unit cell constraint. This refines the geometry and allows, e.g., the PyC-X linkers to rotate from their positions in the parent MOF, and the X groups to reorient, into more energetically favorable positions. See Sec. 4.1.2 for details. After discarding structures where DFT-based geometry optimizations did not converge, likely due to the functional groups being too bulky to fit in the pore, our final Ni(PyC-X)$_2$ library contains 21 total (12 meta, 9 ortho) crystal structure models of functionalized Ni(PyC)$_2$ derivatives.
2.3 Virtual screening of the Ni(PyC-X)$_2$ library for noble gas separations

We now use molecular simulations to predict the Xe, Kr, and Ar Henry coefficients at 298 K in each structure in our Ni(PyC-X)$_2$ library—using the same molecular model that produced simulated adsorption isotherms matching experimental measurements in the parent MOF in Fig. 2. See Sec. 4.2.4 for details. The Xe/Kr selectivity (at dilute conditions) follows from the ratio of the Xe to Kr Henry coefficients. Fig. 4 shows the results of our computational screening by displaying the performance of each Ni(PyC-X)$_2$ MOF in our library. For Xe/Kr separations, we wish for a MOF to exhibit both a high Xe/Kr selectivity and a high Xe uptake (a high Henry coefficient, at dilute conditions). Thus, the most desirable MOFs reside in the top-right quadrant of Fig. 4. Several Ni(PyC-X)$_2$ MOFs (X $\in$ {m-o-NH$_2$, m-o-CH$_3$, o,m-OH, m-F, m-Cl}) are predicted to perform better than the parent Ni(PyC)$_2$ (X=H) MOF for Xe/Kr separations. While other Ni(PyC-X)$_2$ MOFs perform on par with the parent MOF, conversely, functionalization of the PyC ligand with several groups (X $\in$ {m-O-CH$_3$, m,o-N=C=O, o-C≡CH}) severely detriments the performance of the parent MOF by introducing steric interactions with adsorbed xenon.

Sec. S2 presents performance plots for Xe/Ar and Kr/Ar separations.

Particularly, Ni(PyC-m-NH$_2$)$_2$ is predicted to have a higher Xe/Kr selectivity and Xe Henry coefficient than the parent Ni(PyC)$_2$. With considerations of synthetic accessibility, we target Ni(PyC-m-NH$_2$)$_2$ for synthesis. First, however, we will leverage the molecular models to visualize and compare the Xe adsorption pockets in Ni(PyC-m-NH$_2$)$_2$ and Ni(PyC)$_2$—in an attempt to explain the [predicted] enhanced selectivity of Ni(PyC-m-NH$_2$)$_2$.

2.4 Visualizing the xenon adsorption pockets in Ni(PyC-m-NH$_2$)$_2$ and Ni(PyC)$_2$

We now exploit the molecular model (see Sec. 4.2.1) to elucidate and compare the prominent Xe adsorption pockets in Ni(PyC)$_2$ and the predicted Ni(PyC-m-NH$_2$)$_2$ structure by inspecting (i) level surfaces of the potential energy field of a xenon adsorbate in their pores and (ii) the spatial probability densities of xenon in their pores during a molecular simulation.

Fig. 5a displays level surfaces of the potential energy field of a xenon adsorbate in the pores of both Ni(PyC)$_2$ and Ni(PyC-m-NH$_2$)$_2$. See Sec. 4.2.2 for methods. Each MOF presents well-defined, distinct adsorption pockets for Xe (cyan: -30 kJ/mol, dark blue -35 kJ/mol) organized along its one-dimensional channels (orange level surface at -2.41 kJ/mol). This corroborates commensurate Xe adsorption [59] suggested by the saturation of the Xe adsorption isotherms at 2 atoms per unit cell (see Figs. 2 and 6b). Comparing the Xe adsorption pockets in Ni(PyC-m-NH$_2$)$_2$ and the parent Ni(PyC)$_2$ MOF, the appendage of the NH$_2$ functional group on the PyC ligand alters the pore environment for Xe by changing (i) the size and shape of the adsorption pocket (cyan) and (ii) the minimum energy of the field (-31 kJ/mol in the parent MOF vs. -35 kJ/mol in Ni(PyC-m-NH$_2$)$_2$). I.e, the addition of NH$_2$ creates a more energetically favorable Xe adsorption pocket, accounting for the higher predicted Xe Henry coefficient in Ni(PyC-m-NH$_2$)$_2$ than in Ni(PyC)$_2$.

Fig. 5b shows the spatial probability density of Xe adsorbates in Ni(PyC-m-NH$_2$)$_2$ during our GCMC simulations at 298 K and three successive pressures (0.01 bar, 0.1 bar, and 1 bar). See Sec. 4.2.3 for details. As the pressure of Xe increases, each adsorption pocket becomes more likely to be occupied.
Figure 4: Simulated Xe/Kr separation performance of each Ni(PyC-X)\textsubscript{2} MOF in our library. Each marker represents a Ni(PyC-X)\textsubscript{2} MOF (labels and colors indicate X group; shape indicates aromatic substitution position). The location of each marker representing Ni(PyC-X)\textsubscript{2} indicates its simulated Xe Henry coefficient and dilute Xe/Kr selectivity. The parent MOF, Ni(PyC)\textsubscript{2}, is represented by the black diamond. Ni(PyC-X)\textsubscript{2} MOFs falling in the upper-right corner (highlighted green) are predicted to exhibit both a higher Xe/Kr selectivity and higher Xe Henry coefficient than the parent MOF.

The Xe adsorbates, indeed, reside in the well-defined, distinct adsorption pockets depicted by our level surfaces of the potential energy field in Fig. 5\textsubscript{a}, confirming commensurate adsorption.

2.5 Experimental synthesis, characterization, and gas adsorption measurements in Ni(PyC-m-NH\textsubscript{2})\textsubscript{2}

Among the several Ni(PyC-X)\textsubscript{2} MOFs predicted to exhibit a higher Xe/Kr selectivity and Xe Henry coefficient than the parent Ni(PyC)\textsubscript{2} MOF (those in the shaded green region in Fig. 4), we target Ni(PyC-m-NH\textsubscript{2})\textsubscript{2} for experimental synthesis, characterization, and gas adsorption measurements owing to
Figure 5: Visualizing the prominent Xe adsorption pockets in Ni(PyC-m-NH$_2$)$_2$ (predicted structure). (a) Level surfaces (orange: 2.41 kJ/mol, cyan: -30 kJ/mol, and dark blue: -35 kJ/mol) of the potential energy field of a Xe adsorbate in the pores of the parent Ni(PyC)$_2$ and its functionalized derivative Ni(PyC-m-NH$_2$)$_2$. (b) The spatial probability density of Xe in the pores of the Ni(PyC-m-NH$_2$)$_2$ MOF during a molecular simulation at 298 K and three different pressures.

the commercial availability of the PyC-m-NH$_2$ ligand

We also attempted solvothermal synthesis of Ni(PyC-CH$_3$)$_2$ using the same procedure as for Ni(PyC-m-NH$_2$)$_2$, but we failed to recover a MOF crystal from the solution.
2.5.1 Synthesis and characterization.

We synthesized samples of Ni(PyC)$_2$ and Ni(PyC-$m$-NH$_2$)$_2$ by de novo, solvothermal synthesis and subsequently activated it (to evacuate solvent from its pores) by raising the temperature and pulling a vacuum. See Sec. 4.3.1 for the detailed synthesis and activation procedures. Fig. 6C shows a sample of the as-synthesized Ni(PyC-$m$-NH$_2$)$_2$ powder, an evergreen color that differs from the dark aqua color of the parent Ni(PyC)$_2$ in Fig. 1C (colors determined by app from Ref. [61]).

We conducted an elemental analysis (composition) of the as-synthesized, activated, and air-exposed samples of both Ni(PyC)$_2$ and Ni(PyC-$m$-NH$_2$)$_2$. See Sec. 4.3.2 for methods and Tab. S2 for results. After activation, both samples undergo a slight decrease in C and H content, attributed to the removal of the solvent (DMF and methanol) from the pores of the MOF by the activation process. Compared to the parent Ni(PyC)$_2$, Ni(PyC-$m$-NH$_2$)$_2$ has a higher N content due to the appended NH$_2$ group on the ligand.

Based on nitrogen adsorption/desorption isotherms at 77 K (see Sec. 4.3.2 for methods and Fig. S11 for the isotherm), the BET surface area of Ni(PyC)$_2$ and Ni(PyC-$m$-NH$_2$)$_2$ is 616 m$^2$/g and 765 m$^2$/g, respectively. The larger surface area of Ni(PyC-$m$-NH$_2$)$_2$ than of Ni(PyC)$_2$ is consistent with the geometric surface area calculated by Zeo++ (Ni(PyC)$_2$: 904 m$^2$/g, Ni(PyC-$m$-NH$_2$)$_2$: 930 m$^2$/g).

2.5.2 Structure determination by X-ray powder diffraction.

We determined the structure of Ni(PyC-$m$-NH$_2$)$_2$ from its X-ray powder diffraction (XRPD) pattern measured with Cu-Kα$_1$ radiation at room temperature after re-activation at 423 K for 5 h. See Sec. 4.3.2 for detailed methods. Similar to Ni(PyC)$_2$ [62], Ni(PyC-$m$-NH$_2$)$_2$ shows a two-fold interpenetrated diamondoid network in a unit cell with space group symmetry $P$nn2 (no. 34). As further evidence of a two-fold interpenetrated network, simulated Xe adsorption in a two-fold interpenetrated Ni(PyC-$m$-NH$_2$)$_2$ structure model matches the experimentally measured adsorption significantly better than in a single network Ni(PyC-$m$-NH$_2$)$_2$ structure model; see Sec. S4.1. Fig. 6A shows the experimentally determined Ni(PyC-$m$-NH$_2$)$_2$ crystal structure. A cis configuration of the carboxylates coordinating Ni is preferred, as in Ni(PyC)$_2$. We also tested the trans configuration with a space group symmetry of $P2_1/n$ (no. 14), but it resulted in significantly poorer agreement with the XRPD pattern.

Judging by the ratio of the lattice parameters $a:c$, the unit cell of Ni(PyC-$m$-NH$_2$)$_2$ is less anisotropic than the parent Ni(PyC)$_2$ (11.879 Å:10.618 Å versus 12.497 Å:10.379 Å for Ni(PyC)$_2$). This appears to be a result of new hydrogen bonding interactions between the amino groups and the carboxylate groups of the neighboring network, which are observed in the Ni(PyC-$m$-NH$_2$)$_2$ structure with N-O distances of ~3 Å. The lattice parameter $b$ governs the distance between neighboring diamondoid networks along [010], which is greater in Ni(PyC-$m$-NH$_2$)$_2$ (7.092 Å) than in Ni(PyC)$_2$ (6.356 Å), apparently to accommodate the new functional group. Overall, the distortion of the network gives Ni(PyC-$m$-NH$_2$)$_2$ a larger unit cell volume than the parent Ni(PyC)$_2$ (894.5 Å$^3$ versus 824.4 Å$^3$ for Ni(PyC)$_2$). See Sec. S10 for further details.

In situ XRPD measurements showed that humidification of Ni(PyC)$_2$ results in transformation to the known non-porous hydrate phase (a new crystal structure phase that incorporates water into the
framework) Ni(PyC)$_2$(H$_2$O)$_4$ [63] (see Sec. S11). We observed a similar transformation for Ni(PyC-\textit{m}-NH$_2$)$_2$ at high humidification. After one day storage at 100% RH and room temperature, Ni(PyC-\textit{m}-NH$_2$)$_2$ converted to the pure hydrated phase. We determined the new structure as Ni(PyC-\textit{m}-NH$_2$)$_2$(H$_2$O)$_4$, isomorphous with Ni(PyC)$_2$(H$_2$O)$_4$, but with an expanded unit cell to accommodate the amino groups (381.46 Å$^3$ vs. 341.76 Å$^3$). In this case, the water ligands and the amino groups coordinating Ni both appear to form a hydrogen bonding network with neighboring carboxylates.

### 2.5.3 Noble gas adsorption measurements

Fig. 6b shows the experimentally measured, single-component Xe, Kr, and Ar equilibrium adsorption isotherms (298 K) in Ni(PyC-\textit{m}-NH$_2$)$_2$ up to 1 bar. See Sec. 4.3.3 for protocols. Like the parent MOF, the Xe adsorption saturates (slightly above) 2 Xe atoms per unit cell, suggesting commensurate adsorption. Fig. 6b also shows simulated Xe, Kr, and Ar adsorption isotherms (298 K) in the experimentally-resolved Ni(PyC-\textit{m}-NH$_2$)$_2$ structure, which agree very well with the experimental measurements. Fig. S10 compares the simulated adsorption in the experimentally-resolved and predicted Ni(PyC-\textit{m}-NH$_2$)$_2$ structure in our library. While the simulated adsorption in the two different Ni(PyC-\textit{m}-NH$_2$)$_2$ structures is distinguishable, our computational screening (results in Fig. 4) correctly predicted that the Ni(PyC-\textit{m}-NH$_2$)$_2$ MOF would exhibit a higher Xe/Kr selectivity and Xe Henry coefficient than the parent Ni(PyC)$_2$ MOF.

We identified the Xe, Kr, and Ar Henry coefficients in Ni(PyC)$_2$ and Ni(PyC-\textit{m}-NH$_2$)$_2$ at 298 K from the experimentally measured adsorption isotherms in Fig. 2 and Fig. 6b respectively, by fitting Henry’s law to the low-pressure measurements. Fig. S7 shows the resulting fits of Henry’s law to the data. See Sec. S3 for detailed methods. Tab. 1 displays the Henry coefficients and selectivities at dilute conditions, which follow from the ratio of the Henry coefficients. Indeed, Ni(PyC-\textit{m}-NH$_2$)$_2$ exhibits a higher Xe Henry coefficient and Xe/Kr selectivity than the parent Ni(PyC)$_2$. For comparison, we also include in Tab. 1 the benchmark material SBMOF-1, which Ni(PyC-\textit{m}-NH$_2$)$_2$ also out-performs for Xe/Kr separations. Ni(PyC-\textit{m}-NH$_2$)$_2$ also has a greater Ar Henry coefficient than the parent MOF.

Table 1: Henry coefficients $H_g$ of gas $g \in \{\text{Xe}, \text{Kr}, \text{Ar}\}$ at 298 K in SBMOF-1, Ni(PyC)$_2$, and Ni(PyC-\textit{m}-NH$_2$)$_2$, identified from the experimentally-measured, pure-component, equilibrium adsorption isotherms and $g'/g$ selectivities calculated from $H_{g'}/H_g$.

| MOF                 | $H_{\text{Xe}}$ (mmol/g-bar) | $H_{\text{Kr}}$ (mmol/g-bar) | $H_{\text{Ar}}$ (mmol/g-bar) | $S_{\text{Xe}/Kr}$ | $S_{\text{Xe}/Ar}$ | $S_{\text{Kr}/Ar}$ | source of data |
|---------------------|-------------------------------|-------------------------------|-------------------------------|---------------------|---------------------|---------------------|----------------|
| SBMOF-1             | 38.42                         | 2.37                          | -                             | 16.2                | -                   | -                   | [28]           |
| Ni(PyC)$_2$         | 53.78                         | 3.14                          | 0.45                          | 17.1                | 120.6               | 7.1                 | Fig. 2         |
| Ni(PyC-\textit{m}-NH$_2$)$_2$ | 98.25                 | 4.85                          | 0.55                          | 20.2                | 179.4               | 8.9                 | Fig. 6b        |

As a possible explanation for the greater affinity of Ni(PyC-\textit{m}-NH$_2$)$_2$ for Xe than of Ni(PyC)$_2$, the permanent dipole of the amino group appended to the PyC ligand likely enhances the van der Waals interactions between Xe adsorbate and the Ni(PyC-\textit{m}-NH$_2$)$_2$ MOF [64], though, the shape of the Xe adsorption pocket is also altered by (i) the modification of the crystal lattice (discussed above), (ii) protrusion of the functional group in the pore, and (iii) slight rotation of the PyC-NH$_2$ ligand.
Figure 6: The Ni(PyC-m-NH₂)₂ MOF and its noble gas adsorption isotherms. (a) The crystal structure, determined from XRPD, presents one-dimensional channels and shares the same two-fold interpenetrated diamondoid network and Ni coordination environment as the parent Ni(PyC)₂ MOF. (gray: C, blue: N, red: O, green: Ni, white: H) (b) Experimentally measured and simulated pure-component xenon, krypton, and argon adsorption isotherms (298 K) in (for the case of the simulations, experimentally-resolved) Ni(PyC-m-NH₂)₂. (c) From the naked eye, Ni(PyC-m-NH₂)₂ (as-synthesized) appears as an evergreen-colored powder.

Fig. S8 shows the Xe/Kr selectivity of Ni(PyC)₂ and Ni(PyC-m-NH₂)₂ under non-dilute conditions, when immersed in a 20/80 mol% Xe/Kr mixture at 298 K (relevant to industrial recovery of Xe and Kr) of varying pressure, calculated using ideal adsorbed solution theory [65,66]. Under non-dilute conditions, Ni(PyC-m-NH₂)₂ still exhibits a higher Xe/Kr selectivity than Ni(PyC)₂.

2.5.4 Stability evaluation under humid condition and water adsorption

Next, we assess and compare the water-stability of Ni(PyC-m-NH₂)₂ and the parent Ni(PyC)₂ MOF by examining the (i) changes in their XRPD patterns upon activation and exposure to air or humidification and (ii) water adsorption isotherms over two cycles.

Fig. S13 shows the measured XRPD patterns of as-synthesized, activated, and air-exposed (25-30% relative humidity) samples of Ni(PyC)₂ and Ni(PyC-m-NH₂)₂. The pattern of the synthesized Ni(PyC)₂ sample matches well with the simulated pattern of synthesized Ni(PyC)₂ published with space group symmetry Pn [66]. Changes in peak positions and relative intensities suggest solvent removal on activation and structural decomposition when exposed to air for two weeks. The pattern for Ni(PyC-m-NH₂)₂ also shows changes due to solvent removal after activation, but is relatively unchanged after exposure to air for two weeks.

To gain further insights, we performed in situ XRPD measurements during the activation and humidification processes of the as-synthesized powders of Ni(PyC)₂ and Ni(PyC-m-NH₂)₂ at beamline 28-ID-2 (XPD) at the National Synchrotron Light Source II (see S8). The as-synthesized powders both were mixtures of solvent-filled MOF and hydrate phase, though Ni(PyC-m-NH₂)₂ contained signifi-
cantly less hydrate phase. Under the conditions of this experiment, the activation procedure successfully transformed all hydrate phase and removed all solvent from Ni(PyC)₂, resulting in activated Ni(PyC)₂ (published with space group symmetry Pnna \[62\]). Further humidification resulted in rapid and complete transformation to the hydrate phase, equilibrating after roughly 30 min. For Ni(PyC-m-NH₂)₂, activation successfully transformed the hydrate, but did not remove all solvent from the as-synthesized sample. The humidification process then resulted in a partial transformation to a 30:70 mixture of pore-filled anhydrate to hydrate phase. Ni(PyC-m-NH₂)₂ was more resistant to hydration, converting to the hydrate phase more slowly and not reaching full conversion after 124 min. We could not completely rule out the possibility that remaining solvent in Ni(PyC-m-NH₂)₂ may have hindered the subsequent hydration processes.

N.b., for some samples used for lab- and synchrotron-measured patterns of the parent Ni(PyC)₂ (but not Ni(PyC-m-NH₂)₂), we observed extra low angle reflections with d-spacings of ~11.5, 10.8, and 7.9 Å. These could not be identified using the software Match v.3.9.0 \[67\] to search the International Centre for Diffraction Data (ICDD) powder diffraction database \[68,69\] nor through a search of reasonable structures of precursors and building units in the Inorganic Crystal Structure Database (ICSD) \[70,71\] and Cambridge Crystallographic Data Centre (CCDC) database \[72–76\]. Since the peaks do not appear to change significantly during the processing steps, and were not observed in all batches from separate syntheses, we suspect that they may come from an unknown impurity phase, which does not partake significantly in the moisture or gas uptake.

Fig. S14 shows the water adsorption and desorption isotherms at 298 K, taken over two cycles with re-activation (100 °C, 6 hr under N₂ purge) between them, in Ni(PyC)₂ and Ni(PyC-m-NH₂)₂. See Sec. 4.3.3 for methods. Both water isotherms show strong hysteresis and indicate that the water is not fully desorbed at very low relative humidity (RH). In the adsorption branch of the first cycle, Ni(PyC-m-NH₂)₂ adsorbs more water than Ni(PyC)₂ at low RH, perhaps due to its hydrophilic NH₂ group. However, pore filling, reflected by the steps in the isotherms, occurs at ~60% RH in Ni(PyC-m-NH₂)₂ as opposed to ~30% RH in Ni(PyC)₂. The lack of pore filling at low RH in Ni(PyC-m-NH₂)₂ could possibly contribute to its greater stability to air exposure at low RH than Ni(PyC)₂. For both MOFs, the water ad/desorption isotherms lack repeatability over cycles; the isotherm in the second cycle differs from in first cycle.

We provide two possible explanations for the greater stability to moisture of Ni(PyC-m-NH₂)₂ compared to Ni(PyC)₂. First, the PyC-m-NH₂ ligand has a higher basicity than the PyC ligand, in line with trends on water stability of MOFs \[77\]. Second, the amino functional groups of Ni(PyC-m-NH₂)₂ could sterically hinder water adsorption around the coordination site of the ligand and Ni metal, thereby "shielding the coordination site" \[77\] and improving moisture stability.

### 2.5.5 In situ X-ray diffraction study

Finally, we performed laboratory and synchrotron XRPD experiments in situ with Xe and Kr (see Sec. S12 to locate adsorbed gas in Ni(PyC)₂ and Ni(PyC-m-NH₂)₂ by Rietveld refinement (of the gas site position, occupancy, and displacement ellipsoids). Fig. 7 displays the Fourier electron density difference (with gas - without gas) maps. Adsorbed Xe and Kr both primarily reside within the distinct pockets located in the channels running along the b (y, in figures) axis, in agreement with the
simulations in Fig. 5, though with density in the connections between channels. Lobes of density, slightly more isotropic for Ni(PyC)$_2$, span out from the primary adsorption pocket toward the linkers forming the walls of the pore. For Ni(PyC-$m$-$NH_2$)$_2$, the lobes suggest some interaction with the two amino groups rotated away from the pocket, which corroborates the more energetically favorable adsorption environment observed in the molecular model in Fig. 5a.

3 Conclusions and Discussion

Much like lead-optimization in drug discovery, we aimed to judiciously tune the chemistry of a "lead" MOF, Ni(PyC)$_2$ in Fig. 1, for Xe/Kr separations to enhance its Xe/Kr selectivity and Xe uptake at room temperature. We conducted a virtual screening of Ni(PyC)$_2$ analogues to guide experimental pursuits in the laboratory. First, we confirmed that molecular models and simulations reproduce the experimentally measured Xe, Kr, and Ar adsorption isotherms in Ni(PyC)$_2$ (see Fig. 2). Second, we constructed a library of 21 Ni(PyC-X)$_2$ crystal structure models by appending a functional group X (for each X in Fig. 3) on the PyC ligand of the parent Ni(PyC)$_2$ MOF; then, we optimized the geometry using DFT calculations. Finally, we used molecular simulations to predict the Xe, Kr, and Ar Henry coefficients and dilute selectivities in each Ni(PyC-X)$_2$ MOF in the library. Our screening predicted that several functional groups X would enhance the Xe/Kr selectivity and Xe Henry coefficient of the parent MOF (see Fig. 4). Among them, we targeted Ni(PyC-$m$-$NH_2$)$_2$ in the laboratory owing to the commercial availability of the PyC-$m$-$NH_2$ ligand. We synthesized Ni(PyC-$m$-$NH_2$)$_2$ (solvothermally, de novo) and determined its crystal structure via XRPD. Ni(PyC-$m$-$NH_2$)$_2$ indeed shares the same two-fold interpenetrated diamondoid network as the parent Ni(PyC)$_2$ MOF (see Fig. 6a). We measured the Xe, Kr, and Ar adsorption isotherms (298 K) in Ni(PyC-$m$-$NH_2$)$_2$; in agreement with the virtual screening, Ni(PyC-$m$-$NH_2$)$_2$ exhibits both a higher dilute Xe/Kr selectivity and Xe Henry coefficient (20, 98 mmol/(g-bar)) than the parent Ni(PyC)$_2$ MOF (see Tab. 1). Additionally, Ni(PyC-$m$-$NH_2$)$_2$ shows greater stability than Ni(PyC)$_2$ upon exposure to air. In situ XRPD experiments with Xe indicate that Ni(PyC-$m$-$NH_2$)$_2$ creates well-defined adsorption pockets for Xe, corroborated by our molecular models and simulations.

We now discuss limitations of our study. First, in the construction of our Ni(PyC-X)$_2$ library, we assumed de novo synthesis of a new Ni(PyC-X)$_2$ MOF would result in a two-fold interpenetrated diamondoid network with a cis Ni coordination environment, as in the parent Ni(PyC)$_2$ MOF. This assumption turned out to be valid for Ni(PyC-$m$-$NH_2$)$_2$. We also assumed the unit cell of the Ni(PyC-X)$_2$ MOF would be identical to the Ni(PyC)$_2$ MOF. For Ni(PyC-$m$-$NH_2$)$_2$, Tab. 2 shows that the unit cell was altered by the addition of the NH$_2$ group. To see the difference in predicted adsorption, Fig. 5(a) shows the simulated adsorption in Ni(PyC-$m$-$NH_2$)$_2$ using the (i) experimentally determined structure and (ii) predicted structure. Still, our virtual screening correctly predicted that functionalizing the parent Ni(PyC)$_2$ structure with an amino group would enhance its Xe/Kr selectivity. Second, our molecular models and simulations of noble gas adsorption in the MOFs assumed that each MOF was rigid, neglecting e.g. the rotation of the PyC-X ligands and fluctuations in the pore size, which could affect adsorption [44, 78]. Still, the simulations predicted noble gas adsorption in Ni(PyC)$_2$ and Ni(PyC-$m$-$NH_2$)$_2$ quite well (see Figs. 2 and 6b) without modification of the off-the-shelf force field (UFF). Also, our virtual screening of the Ni(PyC-X)$_2$ library for noble gas separations (i) pertained to dilute con-
Figure 7: In situ X-ray diffraction study. Visualization of the Fourier difference maps of (a) Xe in Ni(PyC)\textsubscript{2} at $P = 1.0$ bar and (b) Xe and (c) Kr in the pores of Ni(PyC-$m$-NH\textsubscript{2})\textsubscript{2} at 298 K as the [pure] Xe/Kr pressure increases from $P = 0.1$ bar to 1.7 bar.

ditions and (ii) ignored other gases (e.g., CO\textsubscript{2}) that could be present and compete for adsorption sites. Third, our gas adsorption measurements were single-component, in contrast to the mixed-gas
setting if the Ni(PyC-m-NH2)_2 MOF were to be deployed for noble gas separations. Fourth, Ni(PyC-m-NH2)_2 lacks robust water stability, but e.g., for the application of capturing Xe from SNF reprocessing off-gases, the gas stream is relatively dry.

Future work remains to address these limitations of our study. First, we wish to test the separation performance of Ni(PyC-m-NH2)_2 with a column breakthrough experiment. In this more practically relevant test, we pass air contaminated with a known, dilute concentration of Xe and Kr through a column packed with the MOF and measure the composition of the gas at the exit of the column [4]. More, we wish to assess the impact of humidity (competitive adsorption) on the separation performance. For applications in SNF reprocessing, we wish to study the stability of Ni(PyC-m-NH2)_2 under radiation [5,79]. Second, in our molecular simulations, we wish to include competing gases such as CO₂ present in the capture of Xe from air and model the flexibility of the MOF structure [78,80]. To increase the throughput of the virtual screening, we could train a supervised machine learning model [8,82] or devise an evolutionary search strategy [83,84] to predict or guide how to functionalize a MOF structure to enhance its selectivity for a gas. Third, we wish to screen, for Xe/Kr separations, Ni(PyC)_2 analogues constructed with different metal centers; changing the metal of a "lead" MOF is another way to tune its adsorption properties [85]. Fourth, we wish to incorporate predictions of water-stability of the MOFs [77,86] in our virtual screening (e.g., as in Ref. [87]).

In addition to discovering a new MOF Ni(PyC-m-NH2)_2 for Xe/Kr separations—which could be useful for the industrial recovery of Xe and Kr from air separation units, capturing Xe and Kr from off-gases of spent nuclear fuel reprocessing, or detecting illicit nuclear weapons tests—our study illustrates the computation-informed optimization of the chemistry of a "lead" MOF for an adsorption task. In the future, models and algorithms will be able to automatically orchestrate autonomous, robotic platforms to tune the chemistry of MOFs for their various adsorption-based applications [88,91].

4 Methods

We describe our (1) approach to constructing the library of Ni(PyC-X)_2 crystal structure models, (2) methods for classical molecular modeling and simulation of noble gas adsorption in the structures, and (3) experimental protocols for the synthesis, activation, and gas adsorption measurements.

4.1 Constructing a library of Ni(PyC-X)_2 crystal structure models

4.1.1 Appending a functional group X on the PyC ligand of the parent Ni(PyC)_2 MOF

We develop an automated procedure to append a functional group X at a specific substitution site on each PyC ligand of the parent Ni(PyC)_2 structure to arrive at a crude Ni(PyC-X)_2 crystal structure model.

Preparing the parent Ni(PyC)_2 crystal structure. We begin with the crystal structure of the experimentally-determined (from XRPD), as-synthesized parent Ni(PyC)_2 MOF from Ref. [56]. The crystallographic information (.cif) file of Ni(PyC)_2 contains (1) the lattice parameters and angles of the unit cell and (2) a list of the atoms and their fractional coordinates. We remove the DMF solvent
molecule to mimic experimental activation of the structure. We replicate the unit cell twice in the $a$-direction to give a super-cell with eight PyC ligands. Finally, using DFT calculations (see Sec. 4.1.2), we optimize the atomic positions while keeping the cell parameters fixed. This gives the prepared Ni(PyC)$_2$ crystal structure whose PyC ligands we will append with functional groups X.

**Preparing molecular fragments with each functional group X.** Next, for each functional group X in Fig. 3 we prepare molecular fragments containing X. By later aligning these fragments onto the substitution sites in the parent MOF, we can append functional groups onto the PyC ligand of the parent MOF with a reasonable geometry relative to the PyC ligand.

In Avogadro [92], we build isolated PyC-$m$-X and PyC-$o$-X ligands—PyC ligands in which an H atom at the *meta* and *ortho* position, respectively, is replaced by functional group X—and optimize their geometry using the Universal Force Field (UFF) [57]. We then store the coordinates of the C-(C-X)-C and N-(C-X)-C fragments belonging to the optimized PyC-$m$-X and PyC-$o$-X ligands, respectively.

**Finding and labeling the substitution sites on the parent Ni(PyC)$_2$ MOF.** We identify the two possible *meta* and two possible *ortho* substitution sites on each PyC ligand of the prepared parent Ni(PyC)$_2$ MOF.

We start by inferring the bonding graph (nodes: atoms, edges: bonds) of Ni(PyC)$_2$. For each pair of atoms in the crystal, we assign a bond if the periodic pairwise interatomic distance is less than the sum of the covalent radii [93] of the two atoms plus a tolerance. Periodic distance ensures bonds across the faces of the unit cell are included.

Next, we identify, group, and categorize the atoms belonging to the PyC ligands in the parent Ni(PyC)$_2$ crystal structure. We search the bonding graph of Ni(PyC)$_2$ for cycles of length six using LightGraphs.jl [94]. This gives the C and N atoms in the ring of each PyC ligand; the hydrogen atoms connected to these atoms are the H atoms of the PyC ligand. We apply a set of logical filters to label each C atom on the ring of each PyC ligand as *ortho*, *meta*, or *para*. We label the H atoms bonded to these C atoms as *ortho* or *meta*. This grouping and categorization of atoms gives, for the parent Ni(PyC)$_2$ crystal structure, a handle on the two possible *meta* and two possible *ortho* substitution sites on each PyC ring and (2) the C-(C-H)-C or N-(C-H)-C fragments on the PyC ligand in the parent MOF to which we next align the C-(C-X)-C or N-(C-X)-C fragments for the *in silico* H → X substitution.

**Choosing the substitution sites.** To construct a Ni(PyC-$o$-X)$_2$ (Ni(PyC-$m$-X)$_2$) crystal-structure model, there are two possible *ortho* (*meta*) substitution sites. For each of the eight PyC ligands in the prepared parent MOF, we choose one of these two *ortho* (*meta*) positions at random to mimic random rotational orientations of the PyC-$o$-X (PyC-$m$-X) ligand in the MOF. Our intention in replicating the reported crystal structure of the parent MOF twice in the $a$-direction was to enable exploration of different relative orientations of the functional groups.

**Applying the functional group X on a PyC ligand with a reasonable geometry.** Finally, given a functional group X, we align it onto the specified *ortho* or *meta* substitution site on each PyC ring
of the parent MOF and replace the H atom at the substitution site with the X group in a reasonable geometry.

Suppose we are given a targeted substitution site on the parent MOF. The C-C-C/N-C-C fragment on the PyC ring of the parent MOF—with the meta/ortho substitution site C in the middle—serves as an "anchor" or reference for the alignment (translation and rotation) of the prepared C-(C-X)-C/N-(C-X)-C fragment containing the functional group X. We first translate the entire C-(C-X)-C/N-(C-X)-C fragment so that the center of mass of the C-C-C/N-C-C fragment of it matches the center of mass of the anchor C-C-C/N-C-C fragment of the PyC ligand of the parent MOF. Then, we rotate the entire C-(C-X)-C/N-(C-X)-C fragment to align the C-C-C/N-C-C fragment of it with the anchor C-C-C/N-C-C fragment on the PyC ligand of the parent MOF. We use the orthogonal Procrustes algorithm \[95,96\] to determine the rotation matrix for the optimal alignment. Finally, we replace the H atom on the C-(C-X)-C/N-(C-X)-C fragment of the PyC ligand in the parent Ni(PyC)\(_2\) structure with the functional group X whose coordinates are determined by those of the aligned C-(C-X)-C/N-(C-X)-C fragment. Thereby, we convert a PyC ligand of the parent MOF to a PyC-m-X/PyC-o-X ligand, where the X group is in a reasonable geometry.

For every functional group X in Fig. 3, we begin with a "fresh" prepared Ni(PyC)\(_2\) structure and carry out this in silico H → X substitution procedure on each of its eight PyC ligands. This gives us a library of crude \{Ni(PyC-o-X)\(_2\), Ni(PyC-m-X)\(_2\)\} crystal structure models. By construction, each Ni(PyC-X)\(_2\) structure in the library inherits (i) the two-fold interpenetrated diamondoid network topology (see Fig. 10), (ii) the cis Ni coordination environment, and (iii) the unit cell parameters (well, 2×1×1 replicated) of the reported parent Ni(PyC)\(_2\) MOF structure.

**Remarks on mimicking an in silico substitution reaction on Ni(PyC)\(_2\) as opposed to de novo in silico synthesis of Ni(PyC-X)\(_2\).** In de novo MOF construction algorithms \[97–99\], linkers and metal centers are placed into a properly-scaled template pertaining to a topological network. In contrast, our method of MOF construction, in silico H → X substitution on the parent MOF, facilely preserves the orientations of the rings of the PyC ligands, Ni-N and Ni-O coordination bond lengths, and unit cell parameters of the parent Ni(PyC)\(_2\) structure. An in-house code FunctionalizeThis \[100\] operates in a similar manner. We generalized our MOF functionalizer tool as a find-and-replace tool for crystal structures and released it as open source software PoreMadMod.jl \[60\].

### 4.1.2 Structural relaxation via DFT calculations

We next use density functional theory (DFT) calculations to optimize the geometry, under a fixed unit cell constraint, of each crude Ni(PyC-X)\(_2\) structure constructed in Sec. 4.1.

To carry out the electronic structure calculations, we use the pw.x module from the free and open-source software package Quantum ESPRESSO v6.5 (QE) \[101–103\]. Modeling each MOF as periodic crystal, QE uses a plane-wave basis set representation of Kohn-Sham orbitals. We adopt standard computational settings commonly used for MOF structures \[104–107\]. In details, we perform spin-polarized calculations using the Perdew-Burke-Ernzerhof (PBEsol) \[108\] functional; norm-conserving pseudopotentials (PP) were used with a cut-off of 100.0 Ry. We acquire the pseudopotential files from the complementary, complete PP library, pslibrary v1.0.0 \[109\] in unified pseudopotential
format (UPF, v2.0.1). Along with these PPs, we use the semiempirical Grimme-D2 (D2) dispersion correction.

During structure relaxation, the unit cell parameters remain fixed while the atoms are allowed to move to minimize the energy of the structure. We elected to fix the unit cell lattice parameters during structural relaxation based on the comparison of (1) the lattice parameters and (2) the simulated Xe isotherm (298 K) in (a) the experimental Ni(PyC)$_2$ structure and (b) the DFT-optimized Ni(PyC)$_2$ structure without unit cell constraints. When we allow, in the DFT structure optimization of Ni(PyC)$_2$, (i) the lattice constants to vary (but fixed angles) or (ii) the lattice constants and unit cell angles to vary, the resulting lattice parameters are inconsistent with those of the experimental structure; moreover, the simulated Xe isotherms for these structures over-predict the experimentally measured adsorption at saturation. See Fig. S1 and Sec. S1.1.

A fraction of the functionalized structures failed to converge on the first round of structural relaxation. For those, to encourage convergence and produce a reasonable structure (i.e., no overlapping atoms, drifting atoms, or contorted aromatic rings) as a starting configuration for DFT relaxation, we apply one of the following protocols: (i) start with loose convergence criteria, then run multiple relaxations with progressively stricter convergence criteria in each consecutive iteration and (ii) perform an energy minimization using a classical force field, using LAMMPS (see Sec. S1.2) (with a fixed unit cell constraint), to obtain a more reasonable starting configuration for the DFT structure optimization. Nevertheless, a number of structures, typically containing large or easily ionized functional groups, failed to converge to reasonable structures and resulted in incorrectly dissociated bonds or distorted aromatic rings. Tab. S1 lists the functional groups which we initially investigated, but failed to converge under the DFT geometry optimization routines.

To demonstrate the need for computationally expensive, DFT-based geometry optimizations following our crude geometry-based construction of Ni(PyC-X)$_2$ models in Sec. 4.1, we examine e.g. Ni(PyC-m-CH$_3$)$_2$ before and after optimization in Sec. S1.4. Fig. S2 compares the pre- and post-optimized Ni(PyC-m-CH$_3$)$_2$ structures. The PyC-m-CH$_3$ linker rotation displaces the methyl group from its initial, pre-optimized, position inside the pore.

### 4.2 Classical molecular modeling and simulation

We use PorousMaterials.jl for molecular modeling and simulation of Xe, Kr, and Ar adsorption in the MOFs.

#### 4.2.1 Force field for guest-host and guest-guest (van der Waals) interactions

We describe the molecular model for the potential energy of a configuration of Xe, Kr, or Ar adsorbates in a MOF crystal structure, comprised of guest-host and guest-guest interactions. We approximate the crystal structure of each MOF as rigid during the molecular simulations of noble gas adsorption, negating the need for an intrahost force field.

We model nonbonded, atomistic guest-guest and guest-host interactions as pairwise additive and with 12-6 Leonard-Jones atom-pair potentials truncated at $r_{cutoff} = 14.0$ Å. We take Lennard-Jones
parameters (\(\epsilon\): well depth, \(\sigma\): distance such that potential is zero) for \(a-a\) interactions (\(a\) denotes a chemical element) from the Universal Force Field (UFF) \(^5\) and use Lorentz-Berthelot mixing rules to obtain the parameters for \(a-b\) interactions (\(b \neq a\) denotes a chemical element).

We apply periodic boundary conditions over the simulation box, consisting of the Ni(PyC-X)\(_2\) MOF unit cell replicated appropriately, to approximate an infinite crystal.

We use this force field for guest-guest and guest-host interactions to (i) visualize the level surfaces of the potential energy field of an adsorbate inside the MOF, (ii) conduct grand-canonical Monte Carlo simulations, and (iii) calculate Henry coefficients.

### 4.2.2 Level surfaces of the Xe-MOF potential energy field

Here, we describe how we visualize the level surfaces of the potential energy field \(E(x)\), where \(E\) is the potential energy of a xenon adsorbate at position \(x \in \mathbb{R}^3\) inside the pores of the Ni(PyC-X)\(_2\) MOF. First, we lay a regular 3D grid of points (in fractional coordinate space) over the unit cell of the MOF. Second, we compute the Xe-MOF potential energy of interaction \(E(x)\) at each grid point \(x\) using the molecular model described in Sec. 4.2.1. Then, we write the Xe-MOF potential energy grid to a .cube file and visualize the level surfaces \(\{x : E(x) = E_0\}\) for various energies \(E_0\) using the VisIt visualization tool \(^{114}\).

### 4.2.3 Grand-Canonical Monte Carlo (GCMC) simulations

We predict the equilibrium, pure-component Xe, Kr, and Ar adsorption isotherms using grand-canonical Monte Carlo (GCMC) simulations \(^{115,116}\). GCMC simulations are Markov Chain Monte Carlo (MC) simulations of the grand-canonical (GC) statistical mechanical ensemble. In the GC ensemble, a fixed volume of the (rigid) MOF is immersed in a bath of pure gas at a fixed chemical potential and temperature. Our simulation volume consists of the Ni(PyC-X)\(_2\) unit cell replicated sufficiently such that a sphere of radius \(r_{\text{cutoff}} = 14\) Å fits inside of it (e.g. \(3 \times 3 \times 3\) for functionalized MOFs). In the GCMC simulation, we propose, as transitions between microstates, particle insertions, deletions, translations, and re-insertions with probabilities: 0.35, 0.35, 0.25, and 0.05, respectively. We compute the change in the potential energy of the system upon each proposed microstate transition using the force field described in Sec. 4.2.1. The acceptance criteria for the microstate transitions are dictated by the Metropolis-Hastings acceptance rules. For each GCMC simulation, we use 50 000 burn cycles followed by 50 000 production cycles over which samples of the number of adsorbates, potential energy, and adsorbate positions are collected. A cycle is defined as \(\max(20, n)\) microstate transition proposals, where \(n\) is the number of adsorbates in the system at the beginning of the cycle.

We relate the chemical potential of the gas in the GC ensemble to its pressure using the ideal gas equation of state.

The pure-component adsorption isotherms in Figs. 2 and 6b follow from a set of independent GCMC simulations at different chemical potentials but fixed temperature.
Spatial probability density of the adsorbates. During a GCMC simulation, we estimate the spatial probability density of adsorbates inside the MOF as follows. First, at the beginning of the simulation, we partition the volume in the simulation box into a regular grid (in fractional coordinate space) of volume elements (voxels) and initialize adsorbate counts in each voxel as zero. We chose the number of voxels in each direction so that the side length is $< 0.20 \, \text{Å}$, giving a $14 \times 27 \times 22$ grid of voxels. For each voxel, we wish to estimate the probability that it is occupied by an adsorbate in the GC ensemble. During the simulation, at the end of each production cycle, we take a "snapshot" by, for each adsorbate in the system, incrementing by one the count associated with the voxel to which it belongs. At the end of the simulation, the adsorbate counts in each voxel serve as a histogram for the adsorbates over the simulation volume; normalizing by the total number of snapshots taken gives an estimation of the spatial probability density of the adsorbates in the MOF during the simulation of the GC ensemble. We write this grid to a .cube file and visualize the density for Fig. 5 using the VisIt visualization tool.

4.2.4 Henry coefficient calculations

Henry's law specifies the amount of a gas species adsorbed in a fixed volume of MOF [mol/m$^3$] as $Hp$, with $p$ the partial pressure of the gas species [bar] and $H$ the Henry coefficient [mol/(m$^3$-bar)]. Henry's law is a good approximation only at dilute conditions, i.e., when the density of gas in the MOF is very low. The Henry coefficient is given as:

$$H = \beta \langle e^{-\beta E(x)} \rangle_x,$$

(1)

with $\beta = 1/(k_B T)$, $k_B$ the Boltzmann constant, $E(x)$ the potential energy of the adsorbate at position $x \in \mathbb{R}^3$ inside the MOF (given by the force field described in Sec. 4.2.1), and $\langle \cdot \rangle_x$ an average over the volume comprising the unit cell of the MOF. We compute the average in eqn. (1) thereby obtaining the Henry coefficient $H$, by Monte Carlo integration (Widom particle insertions) with 500 insertions/Å$^3$.

4.3 Experimental synthesis, characterization, and gas adsorption measurements

4.3.1 Synthesis and activation

Ni(PyC)$_2$ synthesis. Ni(PyC)$_2$ was synthesized according to the procedure in Ref. [56]. Nickel acetate (0.249 g) and 4-pyridinecarboxylic acid (0.244 g) is dissolved in solution containing 6 mL of dimethylformamide (DMF) and 4 mL of acetonitrile. Stirring the mixture for 30 min at room temperature, we then add 75 μL of triethylamine. The solution is placed in a Teflon lined Parr stainless steel autoclave and heated at 150°C for 72 hrs followed by slow cooling to room temperature for 12 hrs. The resulting solid is recovered by filtration and washed with fresh DMF, fresh MeOH, and fresh acetone. The obtained Ni(PyC)$_2$ is dried at 333 K overnight.

Ni(PyC-m-NH$_2$)$_2$ synthesis. The synthesis procedure for Ni(PyC-m-NH$_2$)$_2$ is similar to that of Ni(PyC)$_2$. Nickel acetate (1.245 g) and 3-aminopyridine-4-carboxylic acid (1.375 g) is added to a solution
containing 30 mL of DMF and 20 mL of acetonitrile, followed by 30 min of sonication. After sonication, 0.375 mL of triethylamine is added to the solution. The solution is then placed in a Teflon lined Parr stainless steel autoclave and heated at 423 K for 72 hrs. It is subsequently cooled, slowly, to room temperature for 12 hrs. The resulting evergreen-colored solid is purified with fresh DMF, fresh MeOH, and fresh acetone. The obtained Ni(PyC-m-NH₂)₂ is dried at 333 K overnight.

**Sample activation.** Post-synthesis, in order for samples to undergo activation, they degas (purge with N₂) under vacuum at 433 K for a duration of 24 hrs.

### 4.3.2 Characterization.

**BET surface area.** We measured nitrogen adsorption/desorption isotherms at 77 K with an Autosorb-iQ system (Quantachrome Instruments, USA) to obtain the surface area of these materials via BET analysis.

**Elemental Characterization.** CHN elemental analysis is carried out on a VarioMACROcube (Elementar, Germany). The oxygen analysis is measured with an Oxycube (Elementar, Germany).

**Structure determination.** The sample powder was activated at 423 K for 5 hrs to remove pore content. The X-ray powder diffraction (XRPD) pattern was collected at room temperature on a STOE Stadi-P diffractometer with Cu-Kα₁ radiation (λ = 1.540596 Å), a Ge(111) Johann monochromator, and a DECTRIS Mythen 1K detector in Debye-Scherrer geometry over an angular range of 2 - 110.54° 2θ with a step size of 0.405° and 100 s count time per step. Activated powder was loaded into a 0.5 mm borosilicate glass capillary, flame-sealed to minimize further moisture uptake, and spun during the measurement to improve the crystallite orientation sampling statistics.

Structure solution and refinement of Ni(PyC-m-NH₂)₂ was carried out using the program TOPAS 6.0. Reflections in the powder pattern were indexed by an iterative use of singular value decomposition to determine the unit cell and possible space group symmetries. More precise lattice parameters and the instrumental profile were determined by constrained Pawley refinement, applying the fundamental parameters approach along with Gaussian and Lorentzian strain and crystalline size broadening. The background was modeled by employing Chebychev polynomials of 16th order along with an additional Pseudo-Voigt peak. A zero error correction was used, and the Lorentz-Polarization factor was set to 27.3 for the Ge(111) monochromator. The crystal structure was solved by applying the global optimization method of simulated annealing in real space. The PyC-m-NH₂ molecules were defined as rigid bodies in point-for-site notation using the conformation of the Ni(PyC-m-NH₂)₂ crystal structure model in our library and allowed to translate and rotate freely. The obtained structure model was refined by the Rietveld method, with two isotropic atomic displacement parameters used for Ni and for the linker atoms respectively. A final refinement was performed with all parameters freed. Starting unit cell parameters for Ni(PyC-m-NH₂)₂(H₂O)₄ were determined by starting with the structure model for Ni(PyC)₂(H₂O)₄, fixing the entire complex as a rigid body, and then running simulated annealing on the lattice parameters using reasonable bounds. The rest of the structure solution process was as described above.
The refined parameter values for the resulting crystal structure models are given in Table S3. In Table 2, the unit cell parameters and volume for Ni(PyC-m-NH$_2$)$_2$ are compared to those given for Ni(PyC)$_2$ (CSD code UFATEA01) [62] and those for Ni(PyC-m-NH$_2$)$_2$(H$_2$O)$_4$ compared to Ni(PyC)$_2$(H$_2$O)$_4$ (CSD code XAWOOF) [63]. The structure models are available in the .cif files included with the SI, and deposited to the Cambridge Structure Database (CSD) with deposition numbers CCDC 2114661 and CCDC 2114690 respectively.

Table 2: Comparison of the unit cells obtained for Ni(PyC-m-NH$_2$)$_2$ and Ni(PyC-m-NH$_2$)$_2$(H$_2$O)$_4$ with those published for Ni(PyC)$_2$ and Ni(PyC)$_2$(H$_2$O)$_4$.

| Parameter      | Ni(PyC-m-NH$_2$)$_2$ | Ni(PyC)$_2$ [62] | Ni(PyC-m-NH$_2$)$_2$(H$_2$O)$_4$ | Ni(PyC)$_2$(H$_2$O)$_4$ [63] |
|----------------|---------------------|-----------------|---------------------------------|-------------------------------|
| Space group    | $P$n2               | $P$n2           | $P$1                            | $P$1                          |
| $a$ / Å        | 11.8787(4)          | 12.497(1)       | 9.4547(7)                       | 6.2862(3)                     |
| $b$ / Å        | 7.0920(2)           | 6.3559(7)       | 6.8950(7)                       | 6.8598(2)                     |
| $c$ / Å        | 10.6184(3)          | 10.378(1)       | 6.7321(6)                       | 9.2394(4)                     |
| $\alpha$ / Å   | 90.0                | 90.0            | 102.378(6)                      | 96.51(3)                      |
| $\beta$ / Å    | 90.0                | 90.0            | 107.930(6)                      | 104.929(2)                    |
| $\gamma$ / Å   | 90.0                | 90.0            | 105.239(5)                      | 113.692(3)                    |
| $V$ / Å$^3$    | 894.54(5)           | 824.3(2)        | 381.46(6)                       | 341.77(2)                     |

**In situ XRPD** Additional XRPD measurements were performed using a STOE Stadi-P diffractometer with Mo-Kα$_1$ radiation ($\lambda = 0.7091$ Å) (similar instrumental setup as for Cu-Kα$_1$ described above; measurements over 0–50° 2θ with a step size of 0.405° and 10 s count time per step). Gas loading experiments were performed as in a previous study, [124] using a modified version of an in situ capillary cell, [125] which allows for 180° rocking of the capillary. In order to be able to switch between vacuum pumping and gas loading, a T-connector to a turbo pump and a Xe or Kr gas bottle equipped with a needle valve was attached. The valves were adjusted manually to change the gas pressure in the cell. Scans were collected in 30 min increments at each pressure and later summed when no further changes to the pattern were observed.

Synchrotron XRPD measurements were carried out using the high energy X-ray Powder Diffraction beamline 28-ID-2 (XPD), National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory. The diffraction data were collected using a large-area 2D PerkinElmer detector (2048×2048 pixels, 200×200 µm$^2$ each) with a sample-to-detector distances of approximately 1.4 m. The wavelengths $\lambda$ of the X-rays used were 0.1893 Å (humidity sorption experiment) and 0.1917 Å. Powdered Ni(PyC)$_2$ or Ni(PyC-m-NH$_2$)$_2$ was loaded into a 1 mm ID polyimide capillary gas flow cell. Both ends of the capillary were loaded with quartz wool to keep the sample in place, while allowing gas to flow through. The capillary was attached to the flow cell with Swagelok fittings and graphite ferrules. The input of the cell was connected to a gas inlet system that carried humidified air or Xe to the cell. The temperature of the sample was controlled using an Oxford Cryostream. Ni or LaB$_6$ was measured at room temperature as a standard for calibration. Scans were collected in 300 s intervals during the activation and moisture or Xe sorption steps.
4.3.3 Gas adsorption measurements

Noble gases. Three single-component adsorption isotherms (278 K, 288 K, and 298 K) for Xe, Kr, and Ar are measured up to 1 bar using an Autosorb-iQ. See Fig. S12. Constant temperature is maintained using a water circulation system. Each adsorption experiment performed on (activated or as-synthesized) Ni(PyC)$_2$ and Ni(PyC-$m$-NH$_2$)$_2$ uses approximately 100 mg of sample.

Water vapor. We measured water sorption in Ni(PyC)$_2$ and Ni(PyC-$m$-NH$_2$)$_2$ using a VTI-SA+ instrument (TA instruments, USA) at room temperature. For the first cycle, the activated samples are degassed (purged with N$_2$) at 373 K for 2 hrs. Before the second water adsorption cycle could begin, the sample required a degassing period of 6 hrs at 373 K.

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Author contributions

N.G., A.H.Y., D.T., and C.M.S. contributed the computational portion of the work. M.K., A.R., and P.K.T. contributed the experimental portion of the work, along with M.W.T., S.G., and R.E.D. who specifically contributed the crystal structure analysis.

Data availability

The data, input scripts, computer codes to reproduce the computational portion of this work, in addition to the Ni(PyC-X)$_2$ library of .cif files, are available at https://github.com/SimonEnsemble/NiPyC_analogues.

Competing interests

The authors do not have competing interests to declare.
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