Molecular Insight into Fluorocarbon Adsorption in Pore Expanded Metal–Organic Framework Analogs


ABSTRACT: The rapid growth in the global energy demand for space cooling requires the development of more efficient environmental chillers for which adsorption-based cooling systems can be utilized. Here, in this contribution, we explore sorbents for chiller use via a pore-engineering concept to construct analogs of the 1-dimensional pore metal–organic framework MOF-74 by using elongated organic linkers and stereochemistry control. The prepared pore-engineered MOFs show remarkable equilibrium adsorption of the selected fluorocarbon refrigerant that is translated to a modeled adsorption-based refrigeration cycle. To probe molecular level interactions at the origin of these unique adsorption properties for this series of Ni-MOFs, we combined in situ synchrotron X-ray powder diffraction, neutron powder diffraction, X-ray absorption spectroscopy, calorimetry, Fourier transform infrared techniques, and molecular simulations. Our results reveal the coordination of fluoride (of CH2F in R134a) to the nickel(II) open metal centers at low pressures for each Ni-MOF analog and provide insight into the pore filling mechanism for the full range of the adsorption isotherms. The newly designed Ni-TPM demonstrates exceptional R134a adsorption uptake compared to its parent microporous Ni-MOF-74 due to larger engineered pore size/volume. The application of this adsorption performance toward adsorption-based cooling system yields a working capacity increase for Ni-TPM of about 400% from that of Ni-MOF-74, which combined with kinetics directly correlates to both a higher coefficient of performance and a higher average cooling capacity generated in a modeled chiller.

INTRODUCTION

The International Energy Agency (IEA) estimated that c.a. 20% of the total electricity used in buildings around the world today is consumed by climate control units. This value is expected to triple by 2050 due to the rapid growth of global energy demand for space cooling. Such significant energy consumption is mostly industrially supplied via electricity. Adsorption cooling, a thermally driven alternative to the traditional compression-based refrigeration cycle, has the potential for significantly reducing this electricity demand. Sorption-based cooling relies on the cyclic transfer of refrigerant gas from a high energy state to a low energy state by adsorption and desorption to provide the pseudocompensation effect that a traditional mechanical compressor would, where the driving force for energy transfer relies on heat rather than electricity. However, this process has currently shown limited applicability given its lower potential cooling performance due to a lack of highly effective sorbent/refrigerant pairs. For example, existing thermally driven sorption chillers typically use halogen salts (LiBr) or porous materials like silica gels, activated carbons, and zeolites as the sorbents. These sorbents suffer from either risk of toxicity (LiBr), lack of tunability and functionalization, or poor sorption capacity. The advancement and optimization of these pairs can lead to the enhancement of heat and mass recovery thereby improving the overall performance of such systems. The performance of a sorption chiller is largely influenced by the refrigerant adsorption capacity of the porous material which directly translates into a more compact and efficient cooling system. Compared to traditional adsorbents, metal–organic frameworks (MOFs) typically possess much higher porosity and tunability which provide great benefits for refrigerant-based adsorption. Recent achievements have started to highlight the unique adsorption behavior and enhanced loading capacities of MOFs for potential use in adsorption chiller systems. Strategies to enhance the gas...
adsorption capacity in MOFs include (i) introduction of unsaturated metal sites,\textsuperscript{23−24} (ii) postmodification of the inorganic node or organic linker with appropriate functional groups,\textsuperscript{25,26} or (iii) increase of the MOF porosity via pore-engineering.\textsuperscript{27,28} This pore-engineering concept garnered recent attention in the MOF community by pioneering contributions from the Yaghi group,\textsuperscript{8,29} the Long group,\textsuperscript{30−32} and others.\textsuperscript{33,34} These works have shown the possibility of controlling and tuning the expansion of pore apertures from micropore sizes to mesopores. More recently, Zheng et al. showed that Ni-MOF-74 could also be engineered in a similar manner to provide larger pore analogs with enhanced adsorption uptakes for target molecules including water and fluorocarbon.\textsuperscript{35}

To this end, we further extend this pore expansion methodology to design analogs of Ni-MOF-74, not only by using dihydroxyterephthalic acid ligands with 1 to 2 and 3 phenylene rings but also by adjusting the relative locations of the hydroxyl- and carboxylate moieties within these ligand analogs. In fact, this has led us to design a novel framework containing 4,4″-dihydroxy-2′,5′-dimethyl-[1,1′:4′,1″-terphenyl]-3,3″-dicarboxylate-“meta” in combination with a nickel node cluster to form an enlarged pore analog of MOF-74 (triphenyl-“meta”, Ni-TPM). Accordingly, using these approaches, three more Ni-MOF-74 analogues were developed for comparison including Ni-BPP (3,3″-dioxido-4,4′-biphenyldicarboxylate, or simply bi-phenyl-“para”), Ni-BPM (biphenyl-“meta”), and Ni-TPP (tri-phenyl-“para”). Herein, we explore how these pore-engineered MOFs interact with a model fluorocarbon refrigerant, R134a (HFC-134a or 1,1,1,2-tetrafluoroethane) on a molecular level providing insights that are important for the design and applicability of such materials in industrial adsorption chiller systems.

Among appealing refrigerants that have already shown applicability with traditional mechanical compression-based chillers, hydrofluoroalkanes possess favorable properties...
including chemical stability and associated thermodynamic parameters such as boiling point, saturation pressures, enthalpy of evaporation, etc.  

Upon the basis of its low cost and current widespread industrial use among hydrofluorocarbon (HFCs) refrigerants, R134a was selected as the model fluorocarbon refrigerant. R134a is known to have a very low ozone depletion potential (ODP), but it has a high global warming potential (GWP). We acknowledge that such typical HFCs refrigerants are scheduled to be phased out/down as per the Kigali Amendment to the Montreal Protocol (UNEP, 2016), which requires the reduction of HFCs usage by 80–85% by the late 2040s. Although low-GWP hydrofluoroolefins (HFOs) are among the promising candidates proposed as replacements, their current high costs make them practically nonapplicable at this point of time. Here, our intention is to gain an in-depth understanding of the structure-dependence of the host–guest chemistry to further guide the design of sorbents in combination with fluorocarbon refrigerants; thus, the relatively inexpensive and readily available R134a refrigerant was utilized. We also note that since the refrigerant in chiller units is purified without open access to competing sorbates like water or other light gases, equilibrium and kinetic measurements on sorbents using pure R134a would be directly applicable in providing insight into potential performance. Only recently, initial studies on fluorocarbon/MOF working pairs, a fundamental underpinning to the host–guest interactions observed from X-ray absorption spectroscopy (XAS). The reported COP, which we refer to as the BPP (biphenyl-

### Table 1. Summary of Physicochemical Properties, Coordination Environment, and Adsorption Cooling Performance for the Whole Series of Ni-MOFs

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>BET area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Ni–F distance (Å)</th>
<th>PD</th>
<th>COP,</th>
<th>Cooling Capacity (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-MOF-74</td>
<td>1150</td>
<td>1229.7</td>
<td>0.51</td>
<td>2.19</td>
<td>0.35 (0.22)</td>
<td>2.52</td>
</tr>
<tr>
<td>Ni-BPP</td>
<td>2040</td>
<td>1831.6</td>
<td>0.89</td>
<td>2.15</td>
<td>0.41 (0.24)</td>
<td>2.66</td>
</tr>
<tr>
<td>Ni-BPM</td>
<td>2340</td>
<td>1869.0</td>
<td>1.01</td>
<td>2.02</td>
<td>0.44 (0.24)</td>
<td>2.91</td>
</tr>
<tr>
<td>Ni-TPP</td>
<td>1980</td>
<td>2246.9</td>
<td>1.14</td>
<td>2.26</td>
<td>0.55 (0.20)</td>
<td>3.01</td>
</tr>
<tr>
<td>Ni-TPM</td>
<td>2420</td>
<td>2514.1</td>
<td>1.49</td>
<td>2.20</td>
<td>0.56 (0.22)</td>
<td>3.56</td>
</tr>
</tbody>
</table>

“Detailed physicochemical properties given in Tables S1 and S10. The error in these measurements between different sample batches is less than 8%. The coordination environment determined by X-ray absorption spectroscopy data and the molecular interaction distances based on refinements from powder diffraction experiments (details in Tables S2 and S3). The adsorption cooling performance was examined with a two-bed chiller model (see Figure 5c). The COP, and average cooling capacities were obtained with varying cycle times and a sorbent quantity of 20 kg (see Tables S11 and S12 for detailed parameters used in the numerical model). The number in parentheses corresponds to the Ni–F distance obtained from X-ray absorption spectroscopy (XAS).”

### EXPERIMENTAL SECTION

#### Synthesis and Experimental Methodology

On the basis of the two isomers of the (dioxidobiphenyl-dicarboxylate) ligand which we refer to as the BPP (biphenyl-

#### RESULTS AND DISCUSSION

**Structural Integrity and Poremetry Analysis.** The five framework structures showing the accessible Ni²⁺ nodes
and their connections with the oxygen atoms of the carboxylate-containing organic linkers are depicted in Figure 1b,c. The varying pore sizes that can be engineered with this approach range from a diameter of ca. 11 Å, as derived from the native Ni-MOF-74, up to ca. 27 Å with Ni-TPM (Table S1). The structural integrity of these synthesized MOFs was initially characterized using powder X-ray diffraction (PXRD) (Cu Kα, λ = 1.5406 Å) as shown in Figure 1f. The most intense diffraction peaks are indexed based on reflections from the ab-plane of the MOF-74 rhombohedral structure and shift to smaller diffraction angles (2θ°) for the larger, pore-engineered analogues. This shift of the Bragg peaks to lower angles is consistent with the increase in the a lattice parameter, indicative of increasing pore sizes. Further confirmation of the variation in pore sizes were quantified for each analogue using non localized DFT simulations from nitrogen isotherms measured at 77 K (Figure 1g). The observed trend of increasing pore sizes is as follows: Ni-MOF-74 (11 Å) < Ni-BPP (17 Å) < Ni-BPM (19 Å) < Ni-TPP (23 Å) < Ni-TPM (27 Å) as shown in Figure 1e. Brunauer−Emmett−Teller (BET) areas and pore volumes derived from nitrogen isotherms collected at 77 K are shown in Table 1. As expected, the pore volumes for Ni-TPP and Ni-TPM are larger than those of Ni-BPP and Ni-BPM, attributed to the increase in mesoporosity.45 Moreover, the meta-analogs show higher total pore volumes and pore sizes than the para-analogs. The measurement of BET areas, known to be inconsistent for microporous materials, show no particular trend given their strong dependence on the range of points selected. These values fall in the range of 1900 to 2400 m²/g, similar to the previously reported Zn (typically lower BET areas) and Mg (typically higher BET areas) analogs.30,32 The successful synthesis of these frameworks with increasing porosity indicates the capability of engineering targeted pore sizes for specific applications.

**Equilibrium Adsorption of R134a via Experiments and Simulations.** The R134a adsorption isotherms measured at 298 K for each of the five MOF materials are shown in Figure 2. Comparison of experimentally collected equilibrium adsorption (solid) and desorption (open) R134a isotherms for two different series of pore-engineered MOFs at 298 K: (a) para-series and (b) meta-series. Snapshots from GCMC simulations showing pore filling with fluorocarbon as a function of the pressure in (c) Ni-TPM and (d) Ni-MOF-74. (e) DFT optimized geometry of R134a interaction with Ni-sites for Ni-TPM.
Figure 2a,b. Type I isotherms are evident for Ni-MOF-74, Ni-BPP, and Ni-BPM with saturation uptakes between 0.5 and 0.7 g/g while Ni-TPP and Ni-TPM show a Type IV isotherm. Ni-TPM in particular shows immense uptake at higher pressures with a saturation capacity higher than 1.4 g/g (≈300% increase compared to Ni-MOF-74). These experimentally obtained R134a isotherm profiles show a similar trend for nitrogen adsorption as shown in Figure S47. Adsorption kinetic profiles also collected during isotherm measurements between each equilibration point show that for all MOF analogs, R134a uptake quickly reaches steady state concentration within 5 min of exposure (Figures S52−S54). To capture the mechanism of adsorption for the full isotherm range, R134a sorption on pore-engineered MOFs was calculated via GCMC simulations. Importantly, the simulated R134a adsorption isotherms were in good agreement with the corresponding experimental data for the whole series of Ni-MOFs (Figure S47). Moreover, the experimentally observed trend in nitrogen adsorption as well as the free pore volume for each MOF are consistent with those estimated from simulations (Figure S46 and Table S10).

Figure 3. (a) Normalized Ni−K edge XANES (inset shows the pre-edge feature) and (b) \(k^2\)-weighted Ni−K edge EXAFS (insets show the respective \(x(k)\) plots) spectra of Ni-TPM before activation (i.e., fresh), after activation (i.e., activated), and after R134a uptake (i.e., adsorbed). (c) Enthalpy of adsorption as a function of R134a uptake at low loadings in the meta-pore-engineered MOFs as measured by calorimetric techniques. (d) In situ FTIR spectra at 5 mbar, 298 K of R134a adsorbed in the meta-pore-engineered MOFs. IR spectrum of free R134a is shown as a reference.

Intermolecular Sorbate/Sorbent Interactions. While equilibrium isotherms and GCMC simulations characterize the gradual pore filling of fluorocarbon R134a, an accurate assessment of atomic level interactions between fluorocarbon molecules and the MOFs is equally important. As a preliminary step, the analysis of the DFT-optimized geometry reveals that the very initial stage of adsorption involves an interaction between the fluorine of R134a and the Ni-open metal sites (Figure 2e and Figure S50). Interestingly, this optimized geometry evidences a favorable fluorine interaction. R134a has two unique fluorine-containing branches, one with CF₃ and the other with CH₂F (i.e., CF₃−CH₂F). DFT optimization suggests that the CH₂F moiety of R134a rather than the CF₃ moiety interacts with the metal in the vicinity of the pore wall interacting with both the inorganic node and the organic linker of the MOF. This is followed by a pore filling at higher pressure. In contrast, while the initial stage of adsorption is similar for the smaller pore frameworks Ni-MOF-74, Ni-BPP, and Ni-BPM, the filling of their porosity occurs at much lower pressures as observed by the snapshot at \(P = 0.02\) bar in Figure 2d and Figure S48. Interestingly, both experimental and simulated data revealed that Ni-TPM achieves the highest R134a saturation uptake of ca. 1.4 g/g even outperforming Ni-TPP. This observation is consistent with Ni-TPM having the highest pore volume (Table S10).
node of the MOF. This prediction encouraged us to further probe this fluorine–nickel interaction using advanced characterization tools. Experimental techniques to interpret this sorption mechanism involve direct measurement to probe the sorbate/sorbent interactions. Therefore, X-ray absorption spectroscopy (XANES and EXAFS) was used to explore the structural changes to the Ni$^{2+}$ nodes in the MOFs upon fluorocarbon adsorption. Due to the similarity in the Ni$^{2+}$ nodes contained in each MOF independent of linkers, we noticed negligible differences in the Ni$^{2+}$ first shell coordination environment for all three meta-series MOFs (Figures S9–S11). With specific focus on Ni-TPM, which possesses the highest R134a uptake, the XANES spectra before activation, after activation, and after R134a uptake are shown in Figure 3a. For all three curves, the position of the peak at ∼8349 eV and a pre-edge feature at 8332–8333 eV, correspond to the 1s−4p and 1s−3d electronic transitions, respectively, evident for Ni$^{2+}$ after different treatments. The decrease in the peak intensity upon activation and slight increase following R134a loading is consistent with the removal of terminal H$_2$O and binding of the fluorocarbon to the Ni$^{2+}$ sites. It should also be noted that the intensity of the pre-edge peak increases after activation (inset, Figure 3a). This suggests an increased distortion of the Ni$^{2+}$ structure, i.e., from 6-coordinated pseudo-octahedral (NiO$_6$) to 5-coordinated square-pyramidal (NiO$_5$) structure due to the removal of one H$_2$O molecule (Figure S5). With the loading of R134a, a small decrease in the pre-edge feature is observed, although this intensity is still higher than that of the fresh sample. This might be due to a longer/weaker Ni−F bond than the Ni−O (H$_2$O) of the fresh sample representing a distorted 6-coordinated octahedral (NiO$_6$F) structure.

Figure 3b and Figure S33 show the EXAFS spectra for Ni-TPM under the same treatment condition as the XANES spectra in Figure 3a. A decrease of the amplitude of the peak at ∼1.5 Å (phase uncorrected) assigned to the Ni−O scattering after heating the sample in vacuum indicates a lower number of first shell coordination (Ni−O). Upon exposure to R134a, this feature slightly increases and it is accompanied by an additional peak at ∼1.95 Å, suggesting again that the R134a is adsorbed via a longer Ni−F bond than Ni−O. The R134a uptake also affects the Ni−Ni scattering signal at ∼2.6 Å, similar to the observation previously reported for Ni adsorption in Ni-MOF-74. Yet another peak alteration is observed at the scattering distance of the two branches this C−F stretching mode at 1034 cm$^{-1}$, which can be attributed to the C−F stretching frequency in the R134a molecule. In order to determine which of the two branches this C−F stretch originates from during R134a adsorption, other fluorocarbons, namely R116 (hexa-fluoroethane, CF$_3$−CF$_3$) and R161 (fluoroethane, CH$_3$−CH$_2$F), were also examined. The IR spectra of gas-phase and adsorbed R116 and R161 (in Ni-BPM) are given in Figures S20–S23. In a comparison of the spectra of all three probe gases, we observed the same absorption band at 1034 cm$^{-1}$ with R161 adsorption (Figure S23) as with R134a adsorption. Although a similar absorption band with a slight upward shift to ∼1050 cm$^{-1}$ is observed during R116 adsorption (Figure S21), which did not appear in the IR spectra of free R116, this can be attributed to the C−F stretching frequency of the CF$_3$ moiety. These results suggest, in agreement with the DFT optimized geometry (Figure 2e), that this C−F stretching mode at 1034 cm$^{-1}$ can be assigned to the CH$_2$F moiety that is perturbed by the interaction of fluorine with the open Ni$^{2+}$ node. Further comparison of the intensity of the band at ∼1034 cm$^{-1}$ among the meta-type engineered MOFs is shown in Figure S17–S19. It is observed that the overall IR band intensities are in the order of Ni-MOF-74 > Ni-BPM > Ni-TPM, consistent with the calorimetric results (Figure 3c). This signature can be associated with the F−Ni interactions as predicted by DFT calculations, similar to prior observation in the para-type engineered MOFs. In addition, we also note a slight red-shift of −CH$_3$ rocking band of free R134a at ∼975 to ∼966 cm$^{-1}$ of adsorbed gas, which further confirms that the CH$_2$F moiety of R134a is perturbed by the interaction of the fluorine with Ni$^{2+}$ node.

Preferred Molecular Orientation of Adsorbed R134a.

To further confirm the EXAFS and in situ IR results, crystallographic analysis was performed using in situ neutron and synchrotron X-ray powder diffraction to ultimately resolve crystal structures of our pore-engineered MOFs with and without R134a. These atomistic-level observations are summarized in Figure 4. The diffraction data were fitted with a model that represents not only the location of the R134a molecules in the unit cell but also the orientation and bond distances of the fluorocarbon with the metal node and the MOF framework. To the best of our knowledge, in combination with in situ IR analysis, this is the first direct experimental evidence that R134a coordinates toward the metal node of the MOF framework and even more importantly, there is a strong favorable interaction between...
the fluorine atoms of the fluorocarbon and the Ni\textsuperscript{2+}-containing backbone of these MOFs. Table S3 gives a summary of the notable R134a interaction distances, while Figures S12–S14 and Figures S34–S39 show the refinements to the diffraction data. The most notable interaction is the Ni–F distance, with an average distance of 2.16(9) Å. This is shorter than typical metal site adsorbed species. However, such a short distance is consistent with the high electronegativity of fluorine as well as the relatively short Ni–F distance measured using EXAFS and the resulting high enthalpy of adsorption. More surprising is the secondary hydrogen bonding distance of 2.34(15) Å between the H from R134a and O from the linker. However, this interaction makes chemical sense and highlights why the R134a linker preferentially adsorbs from the H\textsubscript{2}CF side, rather than the CF\textsubscript{3} side, where a highly electronegative F would unfavorably interact with an electronegative O. This validation helps to further fortify the elucidated molecular mechanism of adsorption at the initial stage of adsorption and supports the conclusion regarding R134a orientation in these MOFs. Lastly, a tertiary interaction between H from the linker and F from the CF\textsubscript{3} side of the R134a molecule can be seen, with a weaker interaction distance of 3.0(3) Å. Once again, this is chemically favorable, as F from the R134a molecule avoids the electronegative \pi-orbitals from the phenyl ring and instead interacts with the slightly electropositive H. Thus, the so-obtained geometry reflecting the orientation of R134a in the pore and resulting interactions is consistent with the geometry of DFT-optimized structure mentioned earlier (Figure 2e).

In addition, for the larger pore Ni-TPM and Ni-TPP MOFs, the R134a molecule rotates slightly into the pore due to the presence of the bulky methyl group on the central phenyl ring, consistent with the R134a enthalpy of adsorption decreasing as pore size increases. The larger pore MOFs would be expected to adsorb a larger amount of fluorocarbon; however, given the lack of sensitivity to low-Z elements in the X-ray data, their positions were not resolved in the current experiments. More details on the structural characterization are provided in SI.

**Performance and Stability toward Adsorption Cooling.** Given the equilibrium behavior of R134a on these MOFs, it is necessary to interpret differences between each material in the context of the targeted application. To do this, the applicability of these materials for adsorption cooling systems is compared in terms of their potential for high fluorocarbon throughput in the refrigeration cycle. In short, the optimization of the sorbate/sorbent pair will result in a high working capacity combined with fast loading kinetics that yield higher fluorocarbon throughput resulting in more cooling output. Therefore, the working capacity has been evaluated for each MOF-R134a system as shown in Figure 5a. This capacity is defined as the theoretical limit of adsorption and desorption for a given pair of thermodynamic state points. Since the optimization of operating conditions is not the focus of this work, predetermined state point conditions from a prior study have been chosen for the working capacity calculation.\textsuperscript{50} This relation is derived from equilibrium uptakes between the adsorption and desorption temperature/pressure state points. From this chart and the calculations shown in Figure S51, it is observed that the working capacity of Ni-TPM is more than 60 wt %, a value significantly higher than that of Ni-TPP (160% increase) as well as that of Ni-MOF-74 (400% increase). Moreover, the robustness of this promising high-performance material must be tested for applicability. To simulate this, the stability was probed by cycling a constant partial pressure of R134a in an enclosed thermogravimetric balance between fixed adsorption and desorption temperatures. From this experiment, as shown in Figure 5b, it is evident that Ni-TPM maintains a high-level of performance even after more than 50 cycles with no decay in adsorption amount.

Ultimately, regardless of working capacity benefits, the potential applicability of these pore-engineered MOFs for adsorption cooling relies on their performance in a chiller system. The performance of any sorbate/sorbent pair is based on working capacity, thermophysical properties, and the associated mass transfer rate. To understand these effects, we developed and validated a lumped numerical model for a refrigeration cycle (Figure 5c) with a two-bed adsorption/desorption configuration as per previously reported methods (details given in SI section 5.3).\textsuperscript{50}\textsuperscript{51} The parameters specific to the MOF systems utilized here are tabulated in Tables S11 and S12. It should be noted that a reported lumped numerical model that combines the thermophysical properties such as packing density along with the heat and mass transfer rates into lumped parameters was utilized in the development of this model. The performance of the refrigeration cycle is typically represented by the coefficient of performance (COP\textsubscript{c}), a ratio of the cooling effect to the heat input, as well as the average cooling capacity (CC) assuming a fixed amount of adsorbent utilized. In this model, we utilized the same operating conditions as those previously reported to demonstrate the superior performance of Ni-TPM over other analogs. Figure 5d and Figure S55 show the comparison of COP\textsubscript{c} and CC between the parent Ni-MOF-74 and the pore-engineered Ni-TPM as a function of cycle time. Although the performance at very low cycle times is comparable between the two MOFs, it is clearly evident that with increasing cycle times, the performance of the chiller using Ni-TPM is significantly better...
The maximum COPc values for wider pore Ni-TPM were 110% larger, and the maximum cooling capacity value was $\sim 30\%$ larger than that of Ni-MOF-74. Per unit mass of sorbent, an optimal cycle time on the order of 3−5 min exists that generates both maximum cooling power and maximum corresponding COPc. At a cycle time of 5 min, the average cooling capacity increased with an expansion in pore size from Ni-MOF-74 to Ni-TPM. Our pore-engineered MOF Ni-TPM shows a cooling capacity of more than 3.5 kW (Table 1). This value is $\sim 40\%$ larger than the parent Ni-MOF-74 at the same condition, further emphasizing the importance of engineering larger pores.

On the basis of conventional intuition, we pursued this pore-engineering concept to increase the pore geometry of the MOF framework under the primary assumption that larger pore volume and BET area would lead to better adsorption cooling performance. To this end, the application and subsequent analysis of Ni-TPM, a pore-engineered MOF that has favorable kinetics and strong sorption sites, was probed in a modeled adsorption chiller to reveal promising cooling potential compared to its parent analog. This analysis conducted in conjunction with the fundamental characterizations of the sorbent/sorbate interactions provides confidence in our approach for the design of higher performing sorbents for adsorption cooling applications. Further research in optimizing this model and corresponding parameters such as adsorption/desorption pressures and temperatures as well as heat/mass transfer coefficients for these and other MOF materials is ongoing.

### CONCLUSIONS

Pore-engineered MOF analogs containing ligands of expanding lengths and alternate carboxylate/hydroxyl linker locations were explored in this contribution for the adsorption of the R134a fluorocarbon refrigerant. The influence of pore geometries on bulk phase adsorption properties, potential adsorption cooling performance, and proposed molecular interactions of R134a with each Ni-MOF framework was thoroughly interpreted. From our findings, it is observed that the combination of high pore volume and accessibility to a high density of open metal centers contributes to nearly a 300% increase in saturation uptake for Ni-TPM compared with Ni-MOF-74 as determined via equilibrium isotherm measurements. By increasing these saturation limits, we allow more fluorocarbon to be taken up by the sorbent per cycle of adsorption and desorption based on specified chiller process conditions. This increased throughput translates to a 400% increase in the theoretical working capacity to cycle between adsorption/desorption state points. Ultimately, correlation of its bulk sorption performance under realistic chiller conditions results in modeled cooling capacities for Ni-TPM that are at least 40% larger than that of the parent MOF. These advancements in cooling potential and energy transfer represent implications at an engineered scale that have been designed from the molecular level.
Such atomic level manipulations to framework precursors that allow for significant differences in bulk sorption performance inspired probe sorbate–sorbent interactions to gain insight into how adsorption fundamentals can be further tuned for future improvements. Accordingly, we observed experimentally the favorable interactions between the fluorine of the CH₂F moiety of R134a and the Ni²⁺ backbone of the MOFs as per gas-loaded sXRD and X-ray absorption spectra, which are consistent with conclusions drawn from DFT calculations and GCMC simulations. These insights regarding the host–guest chemistry can be advantageous in elucidating effective sorbent/sorbate pairs for potential use with even lower GWP hydrofluorocarbons. More importantly, the ability to tailor porous frameworks, as shown in this joint experimental/theoretical study, allows us to reveal a favorable mechanism of refrigerant adsorption that is a building block for the design of future sorbent materials for such applications.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b11963.

Additional experimental details, structure models, nitrogen sorption data, Powder XRD, synchrotron XRD, TGA, XANES, EXAFS, kinetics measurement, calorimetric tests, in situ FTIR, COP calculation, and molecular simulation details (PDF)

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