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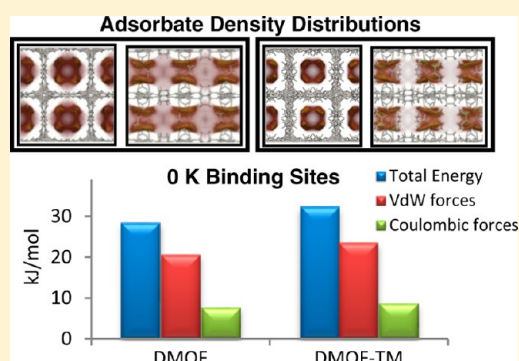
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Molecular-level Insight into Unusual Low Pressure CO<sub>2</sub> Affinity in Pillared Metal–Organic FrameworksNicholas C. Burtch,<sup>†</sup> Himanshu Jasuja,<sup>†</sup> David Dubbeldam,<sup>‡</sup> and Krista S. Walton<sup>\*,†</sup><sup>†</sup>School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive NW, Atlanta, Georgia 30332, United States<sup>‡</sup>Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166 Amsterdam, The Netherlands

## S Supporting Information

**ABSTRACT:** Fundamental insight into how low pressure adsorption properties are affected by chemical functionalization is critical to the development of next-generation porous materials for postcombustion CO<sub>2</sub> capture. In this work, we present a systematic approach to understanding low pressure CO<sub>2</sub> affinity in isostructural metal–organic frameworks (MOFs) using molecular simulations and apply it to obtain quantitative, molecular-level insight into interesting experimental low pressure adsorption trends in a series of pillared MOFs. Our experimental results show that increasing the number of nonpolar functional groups on the benzene dicarboxylate (BDC) linker in the pillared DMOF-1 [Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO)] structure is an effective way to tune the CO<sub>2</sub> Henry's coefficient in this isostructural series. These findings are contrary to the common scenario where polar functional groups induce the greatest increase in low pressure affinity through polarization of the CO<sub>2</sub> molecule. Instead, MOFs in this isostructural series containing nitro, hydroxyl, fluorine, chlorine, and bromine functional groups result in little increase to the low pressure CO<sub>2</sub> affinity. Strong agreement between simulated and experimental Henry's coefficient values is obtained from simulations on representative structures, and a powerful yet simple approach involving the analysis of the simulated heats of adsorption, adsorbate density distributions, and minimum energy 0 K binding sites is presented to elucidate the intermolecular interactions governing these interesting trends. Through a combined experimental and simulation approach, we demonstrate how subtle, structure-specific differences in CO<sub>2</sub> affinity induced by functionalization can be understood at the molecular-level through classical simulations. This work also illustrates how structure–property relationships resulting from chemical functionalization can be very specific to the topology and electrostatic environment in the structure of interest. Given the excellent agreement between experiments and simulation, predicted CO<sub>2</sub> selectivities over N<sub>2</sub>, CH<sub>4</sub>, and CO are also investigated to demonstrate that methyl groups also provide the greatest increase in CO<sub>2</sub> selectivity relative to the other functional groups. These results indicate that methyl ligand functionalization may be a promising approach for creating both water stable and CO<sub>2</sub> selective variations of other MOFs for various industrial applications.



## ■ INTRODUCTION

Metal–organic frameworks (MOFs) are a promising class of materials that have revolutionized the fields of materials science and adsorbent development since their discovery about a decade ago. Characterized by their inorganic metal–ion clusters and organic ligand linkers, the combination of extraordinarily high surface areas and tunable chemical properties make MOFs prime candidates for a broad range of commercial applications.<sup>1,2</sup> From a theoretical standpoint, the large number of potential building blocks makes the possibility for synthesis of new MOFs almost limitless. For example, over 137 000 structures were recently identified in a large-scale, systematic screening of MOFs that are considered reasonable synthetic targets with complexities similar to existing structures in the literature.<sup>3</sup> Functionalization of the organic linker is an attractive approach to fine-tuning the properties of these materials as it allows the isostructural nature to be retained

while adjusting adsorption properties through the appropriate choice of chemical functional groups.<sup>4,5</sup>

One promising application of MOFs is postcombustion CO<sub>2</sub> capture from flue gas.<sup>6–10</sup> The commercial application of MOFs in this field can reasonably be seen in the near future if the critical issues of hydrothermal stability and synthesis scale-up are addressed. Typical postcombustion flue gas conditions contain relatively low CO<sub>2</sub> partial pressures in the range of 0.13–0.15 bar,<sup>11</sup> making adsorption capabilities in the low pressure regime especially critical. Fundamental insight into how low pressure CO<sub>2</sub> affinity is affected by chemical functionalization in different structures is therefore of great value for the development of next generation MOFs for postcombustion CO<sub>2</sub> capture.

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The prototypic DMOF-1 ( $\text{Zn}_2(\text{BDC})_2(\text{DABCO})$ ) (BDC = 1,4-benzenedicarboxylate, DABCO = diazabicyclo-octane) is a well-studied pillared structure that has been the subject of a number of past experimental and computational adsorption studies.<sup>12–21</sup> This mixed-ligand MOF contains zinc clusters that are connected in the 2-D plane by BDC with the pillared linker DABCO connecting the third dimension. Recently, a flexible force field model for the parent structure was developed using *ab initio* calculations,<sup>22</sup> and an experimental characterization of the effects that various flexible functional groups have on breathing behavior in the presence of different adsorbates was explored.<sup>23</sup> Interesting studies reporting increased  $\text{CO}_2$  uptake in different pillared MOF systems due to substitution of their pillar ligand<sup>24</sup> or ligand forming the 2-D square grid<sup>25</sup> have also recently been reported. While some gas adsorption studies for functionalized versions of the DMOF-1 structure have been reported,<sup>16,26</sup> to date, a systematic investigation into the impact of functional groups on low pressure  $\text{CO}_2$  affinity has not been conducted.

Enhanced low pressure  $\text{CO}_2$  adsorption caused by polar functional groups is well understood in the literature.<sup>8,9</sup> For example, amino, nitro, and methoxy functional groups in UiO-66 were shown to enhance significantly the  $\text{CO}_2$  adsorption interactions at low pressure.<sup>27</sup> In another example, direct observation and subsequent modeling of  $\text{CO}_2$  binding sites in the amine-functionalized  $\text{Zn}_2(\text{Atz})_2(\text{ox})$  (Atz = 2-amino-1,2,4-triazole, ox = oxalate) provided valuable insight into the intermolecular interactions responsible for the strong binding interactions present in this structure.<sup>28</sup> In a separate study, density functional theory calculations on isolated ligands predicted that polar functional groups such as  $-\text{OH}$ ,  $-\text{NO}_2$ , and  $-\text{NH}_2$  would have enhanced adsorbate–adsorbent interactions due to lone pair and hydrogen bonding interactions that serve to polarize the  $\text{CO}_2$  molecule.<sup>29</sup> In the ZIF series, the polar groups  $-\text{CN}$  and  $-\text{CHO}$  were found to produce more favorable interactions with  $\text{CO}_2$  than  $-\text{CH}_3$  functional groups due to similar effects.<sup>30</sup>

In this work, we will show that the DMOF-1 series follows a different trend. The addition of methyl and other nonpolar functional groups provide the greatest increase in low pressure  $\text{CO}_2$  affinity whereas polar groups such as nitro, hydroxyl, chlorine, fluorine, and bromine produce little to no improvement. The majority of MOFs in the literature are unstable under humid conditions and are thus unsuitable for use as adsorbent materials in carbon capture technologies. We showed in recent work that methyl functionalization can also be used to turn the unstable parent DMOF-1 structure into a more chemically robust isostructural variation that maintains its BET surface area and crystallinity after adsorbing water during cyclic adsorption cycles, an attribute not observed in its isostructural variations containing polar functional groups.<sup>18</sup> Little attention has been given to the selective gas adsorption properties of methyl functional groups relative to their polar counterparts but, given their potential for improving the chemical stability of structures, there is great motivation to further understand the selective gas adsorption properties of such materials to explore their viability for gas separation applications under industrially relevant flue gas conditions. Such analysis would open the gates for the development of novel methyl functionalized materials that are superior to their parent structure in terms of both chemical stability and  $\text{CO}_2$  capture properties.

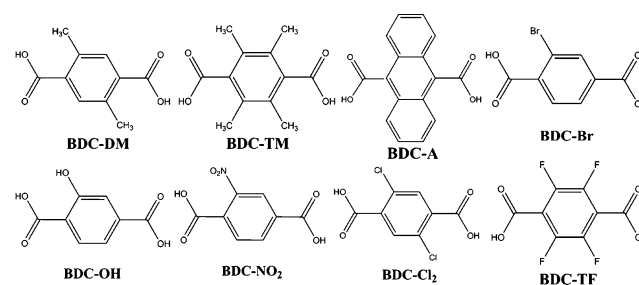
Here, we report the experimental  $\text{CO}_2$  Henry's coefficients obtained from functionalization of the BDC ligand on ten

variations of the DMOF series with different polar and nonpolar functional groups and apply a systematic approach to quantitatively understand the differences in  $\text{CO}_2$  affinity induced by these functional groups at the molecular level. Excellent agreement between the experimental and simulated Henry's coefficients obtained from this work validate the accuracy of our models and, through detailed analysis of simulated heats of adsorption, adsorbate density distributions, and minimum energy 0 K binding sites for  $\text{CO}_2$ , we uncover the interplay of intermolecular interactions which are responsible for the interesting trends in this series of pillared MOFs.

## ■ EXPERIMENTAL METHODS

All MOFs synthesized were of the isostructural family  $\text{Zn}_2(\text{BDC-X})_2(\text{DABCO})$ , or DMOF-X, where X signifies the functional group that was placed on the BDC ligand. Chart 1 shows the structure of all

**Chart 1. Functionalized Nonpolar and Polar Benzenedicarboxylic (BDC-X) Ligands Used in the Synthesis of Isostructural DMOF-X Structures in This Study**



the functionalized BDC-X ligands used in this study. Note that in some structures the numerical suffix 1/2 is given after the structure name (e.g., DMOF-TM<sub>1/2</sub>) to denote that only one-half of the BDC ligands in the structure contains the indicated functional group whereas the remaining half contains the unfunctionalized BDC ligand. For example, DMOF-TM is of the chemical formula  $\text{Zn}_2(\text{BDC-TM})_2(\text{DABCO})$  whereas DMOF-TM<sub>1/2</sub> is of the chemical formula  $\text{Zn}_2(\text{BDC})(\text{BDC-TM})(\text{DABCO})$ . Syntheses were performed according to reported procedures,<sup>16,18,26,31–33</sup> and all chemicals were commercially available and used as received.

Powder X-ray diffraction (PXRD) patterns were collected using  $\text{CuK}\alpha$  radiation at room temperature on an X'Pert PANalytical diffractometer to ascertain the purity of the as-synthesized structures. Surface areas were determined via  $\text{N}_2$  adsorption at 77 K using a Quadrasorb system (Quantachrome Instruments), and BET theory was applied using data points that are consistent with the applicable range for microporous materials.<sup>34</sup> All  $\text{CO}_2$  adsorption isotherms were obtained using an Intelligent Gravimetric Analyzer (IGA-1 series, Hiden Analytical Ltd.). The complete set of PXRD patterns,  $\text{N}_2$  adsorption isotherms, and  $\text{CO}_2$  adsorption isotherms can be found in the Supporting Information (Figure S1–S8).

## ■ COMPUTATIONAL METHODS

The inclusion of framework partial charges is critical to the accurate modeling of  $\text{CO}_2$  adsorption in the low pressure regime.<sup>35</sup> In order to ensure the electrostatic interactions arising from the quadrupole moment of  $\text{CO}_2$  were accurately captured, periodic quantum mechanics calculations were performed to derive framework partial charges for the framework models using the VASP package. Quantum mechanics calculations utilized projector-augmented wave method pseudopotentials<sup>36</sup> with the Perdew–Burke–Ernzerhof generalized-gradient approximation,<sup>37</sup> single k-point sampling, and 400 eV plane wave cut-offs. Ionic relaxations were first run on each of the unit cells until all forces were smaller than 30 meV/Å to obtain optimized

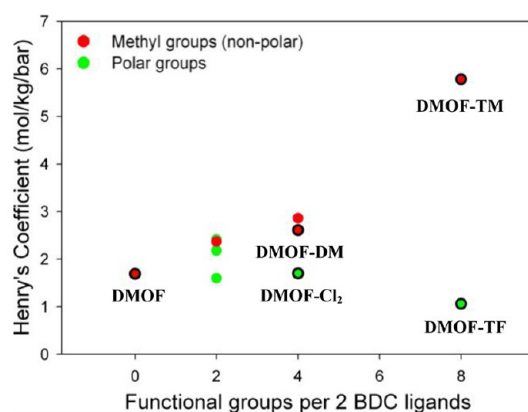
internal geometries. Classical point charges were then assigned to framework atoms using REPEAT,<sup>38</sup> a charge assignment method that was found to most accurately reproduce the periodic density functional theory electrostatic potential energy surface in MOF structures.<sup>39</sup> Lennard-Jones parameters for framework atoms were assigned based on the DREIDING force field<sup>40</sup> and carbon dioxide was modeled using the TraPPE forcefield,<sup>41</sup> a three-site CO<sub>2</sub> model with Lennard-Jones parameters and partial charges assigned to best reproduce experimental CO<sub>2</sub> vapor–liquid equilibrium data. Lorentz–Berthelot mixing rules were used to determine adsorbate–adsorbent and adsorbate–adsorbate Lennard-Jones interactions.

The parent DMOF-1 is weakly flexible and is only reported to display breathing effects in the presence of adsorbates such as benzene and isopropyl alcohol.<sup>14,15</sup> No such structural transformations have been reported during the adsorption of CO<sub>2</sub>, and the frameworks were therefore assumed rigid for the classical simulations presented in the main body of this article. To validate this assumption, isotension-isothermal ensemble (N $\sigma$ T) simulations were also run using flexible framework models for the parent structure (developed by Grosch and Paesani)<sup>22</sup> and newly developed flexible models for functionalized variations (developed in this work). The flexible framework simulations are in excellent qualitative agreement with rigid framework results, confirming that the experimental trends can be accurately captured independent of the particular molecular model parameters being used. Furthermore, we confirm that the structural parameters and CO<sub>2</sub> adsorption properties of the DMOF variations are quite insensitive to any flexible framework behavior. These structures also show positive thermal expansion in the channel-direction and negative thermal expansion in the orthogonal direction. All flexible framework parameters (Table S5–S9) and calculation results (Figure S26–S30, Table S10–12) are in the Supporting Information.

## RESULTS AND DISCUSSION

**Experimental Henry's Coefficients.** For this study, data points at pressures near 20 mbar were collected for all structures and experimental Henry's coefficients could therefore be directly calculated using the increase in loading from the activated sample to the first point on the experimental isotherm. An alternative approach is to fit the experimental data to an appropriate isotherm model and extract the Henry's coefficient from the best fit parameters. This was also carried out using the Toth model to yield a good overall fit with the experimental data (Figure S9–S19, Supporting Information). However, as also noted in a different study,<sup>42</sup> residual error between isotherm data and model predictions at the low pressure limit make the direct use of low pressure data more accurate for comparison purposes.

Figure 1 shows the experimental Henry's coefficients obtained for the functionalized DMOF structures at 298 K. There is a direct correlation between the number of nonpolar methyl groups and the experimental Henry's coefficient that becomes more pronounced as the total number of functional groups on the BDC ligand increases. Interestingly, the anthracene-based DMOF-A structure exhibits the greatest Henry's coefficient of all the variations in this study (Table 1). It is difficult to assign a number of "functional groups per 2 BDC ligands" corresponding to the two additional conjugated rings in the DMOF-A structure and it thus does not lend itself to the comparison given in Figure 1. While it is tempting to attribute the higher CO<sub>2</sub> affinity in DMOF-A to the greater confinement caused by its anthracene ligand, it is hard to decouple these effects from interactions due to the greater  $\pi$  electrons and increased quadrupole moment of this ligand (the axial component of the quadrupole tensor in benzene is roughly  $30 \times 10^{-40}$  C m<sup>2</sup> whereas anthracene's is twice as large).<sup>43</sup> In the case of polar functional groups (-NO<sub>2</sub>, -OH, -Br, -Cl, -F),



**Figure 1.** Experimental CO<sub>2</sub> Henry's coefficients in the DMOF series at 298 K. Circled data points were chosen as representative structures for further analysis via molecular simulation.

**Table 1.** Experimental CO<sub>2</sub> Henry's Coefficients for DMOF Structures at 298 K<sup>a</sup>

DMOF-X	groups per 2 BDC	polar group?	Henry's coefficient (mol/kg/bar)
DMOF-TF	8	Yes	1.1
DMOF-Br	2	Yes	1.6
DMOF	0	No	1.7
DMOF-Cl <sub>2</sub>	4	Yes	1.7
DMOF-NO <sub>2</sub>	2	Yes	2.2
DMOF-DM <sub>1/2</sub>	2	No	2.4
DMOF-OH	2	Yes	2.4
DMOF-DM	4	No	2.6
DMOF-TM <sub>1/2</sub>	4	No	2.9
DMOF-TM	8	No	5.8
DMOF-A		No	7.1

<sup>a</sup>Bold-faced DMOF variations were chosen as representative structures for analysis via molecular simulation.

the same pronounced increase in Henry's coefficient as a function of functional groups that is present in the nonpolar counterparts does not exist. Such trends are contrary to the common scenario reported in the literature and, from a molecular standpoint, the structure–property relationships responsible for such behavior are not well understood. Therefore, in order to gain fundamental insight into these trends, five representative structures were chosen for further investigation via molecular simulation. For this study, the five circled structures in Figure 1 (DMOF, DMOF-DM, DMOF-TM, DMOF-Cl<sub>2</sub> and DMOF-TF) were chosen based on their diversity in terms of degree (full vs partial) and type (polar vs nonpolar) of ligand functionalization. The relatively low experimental Henry's coefficients of the polar DMOF-TF and DMOF-Cl<sub>2</sub> structures are particularly interesting to explore as a recent screening of over 130 000 hypothetical MOFs identified fluorine and chlorine as the two functional groups most strongly correlated with increased selectivity for CO<sub>2</sub> over N<sub>2</sub> and CH<sub>4</sub> at 298 K in a range of gas mixture compositions.<sup>44</sup> In fact, nearly 50% of all structures exhibiting the highest CO<sub>2</sub> selectivity in this study contained fluorine atoms. As discussed in the Supporting Information (Table S4), good agreement between theoretical and experimental surface areas and void fractions were found for each of the representative structures presented in this work.



**Simulated Henry's Coefficients and Heats of Adsorption.** In order to validate the quantitative accuracy of the models developed for the five representative structures, a number of infinite dilution adsorption properties were calculated and compared to experiment. Theoretical Henry's coefficients at infinite dilution and 298 K were calculated from the Widom's ghost particle insertion method.<sup>45,46</sup> In this approach, the Henry's coefficient is related to the average Rosenbluth factor  $\langle W \rangle$  by the relationship:

$$K_H = \frac{1}{RT\rho_f} \frac{\langle W \rangle}{\langle W_{IG} \rangle} \quad (1)$$

where  $R$  is the universal gas constant,  $T$  is temperature,  $\rho_f$  is the density of the framework, and  $\langle W_{IG} \rangle$  is the average Rosenbluth factor of an isolated molecule.  $\langle W \rangle$  and  $\langle W_{IG} \rangle$  were obtained from Widom insertions in the empty host framework and the ideal gas phase, respectively. The isosteric heats of adsorption  $Q$  at infinite dilution and 298 K were obtained by single-molecule NVT Monte Carlo simulations using the relationship:

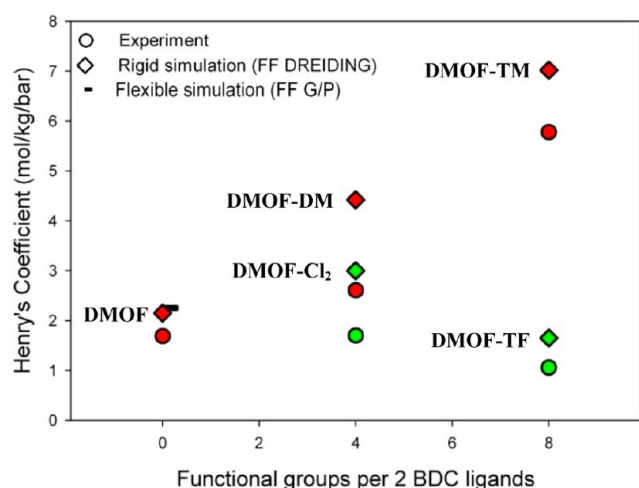
$$Q = -\Delta H = \Delta U - RT \quad (2)$$

where  $\Delta H$  is the enthalpy of adsorption at infinite dilution and  $\Delta U$  is obtained from the relationship:

$$\Delta U = \langle U_{HG} \rangle - \langle U_H \rangle - \langle U_G \rangle \quad (3)$$

where  $\langle U_{HG} \rangle$ ,  $\langle U_H \rangle$ , and  $\langle U_G \rangle$  are the average potential energies of the host–guest system, isolated host framework, and isolated guest molecule, respectively. Translation, rotation, and reinsertion moves were included in the phase space sampling of this calculation.

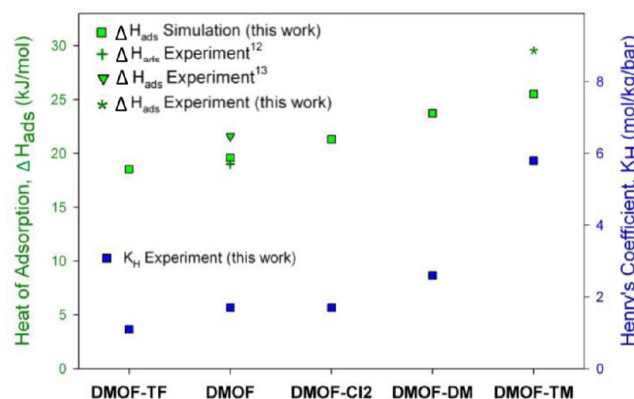
As shown in Figure 2, there is good quantitative agreement between experimental and simulated Henry's coefficients in the different representative structures. While the molecular models overestimate experimental values in each of the cases, there is excellent agreement in the qualitative trends in low pressure CO<sub>2</sub> affinity due to ligand functionalization. In particular, the simulations correctly predict the distinct increases in CO<sub>2</sub>



**Figure 2.** Comparison of simulated and experimental Henry's coefficients at 298 K in the five representative structures. Green symbols indicate structures containing polar functional groups whereas red symbols indicate structures with nonpolar functional groups. FF G/P indicates the value calculated using the flexible model developed by Grosch and Paesani<sup>22</sup> whereas FF DREIDING are results from the rigid framework models used throughout the remainder of this work.

affinity relative to the parent DMOF structure for the nonpolar methyl functionalized variations (DMOF-DM, DMOF-TM) yet only minor (DMOF-Cl<sub>2</sub>) or no (DMOF-TF) improvement for structures containing polar groups. The Henry's coefficient value of 2.24 mol/kg/bar calculated using the flexible DMOF model of Grosch and Paesani<sup>22</sup> is also in close agreement with the 2.15 mol/kg/bar result obtained using our rigid DREIDING force field models. Pore size is an important structural factor that can inversely correlate with low pressure adsorbate affinity due to increased van der Waals interactions with pore walls. Pore size distributions and void fractions were therefore calculated for each of the representative structures, giving the general trend in void fraction values of DMOF > DMOF-TF > DMOF-Cl<sub>2</sub> > DMOF-DM > DMOF-TM. While this has a general correlation with the experimental Henry's coefficients, this simple analysis fails to explain the decreased CO<sub>2</sub> affinity in the more confined DMOF-TF structure relative to the parent DMOF as well as other important quantitative trends in the data (Figure S22, Supporting Information). Instead, it is the detailed molecular analysis based on electrostatics and van der Waals interactions introduced by functional groups at their lowest energy binding sites, presented in the following section, that is needed to understand these trends.

Analysis of simulated heats of adsorption in the representative structures provides initial insight into the experimental Henry coefficient trends and further validates the quantitative accuracy of the molecular models. As shown in Figure 3, there



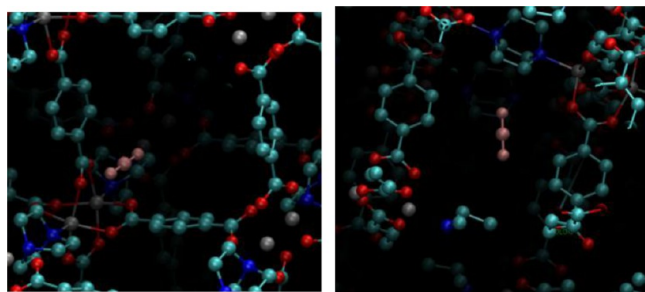
**Figure 3.** Simulated and experimental heats of adsorption (left axis, green) and experimental Henry's coefficients (right axis, blue) for CO<sub>2</sub> at infinite dilution in the representative structures.

is a direct correlation between the 298 K simulated heats of adsorption (left axis, green) at infinite dilution and the experimental Henry's coefficients (right axis, blue) at 298 K. The simulated heat of adsorption value for DMOF of 19.6 kJ/mol obtained in this work is in excellent agreement with the previously reported experimental values of 19.4 kJ/mol (Clausius–Clapeyron relation)<sup>12</sup> and 21.6 kJ/mol (differential thermal analysis at 298 K).<sup>13</sup> This value is higher than the 16.4 kJ/mol obtained from previous simulations of DMOF by our group due to the inclusion framework partial charges that were excluded in our previous work.<sup>17</sup> Experimental CO<sub>2</sub> isotherms at 278 K, 298 and 313 K were also collected for the DMOF-TM structure (Figure S20, Supporting Information) to calculate its heat of adsorption using the Clausius–Clapeyron equation. In agreement with simulation results, the experimental infinite dilution heat of adsorption for this structure is

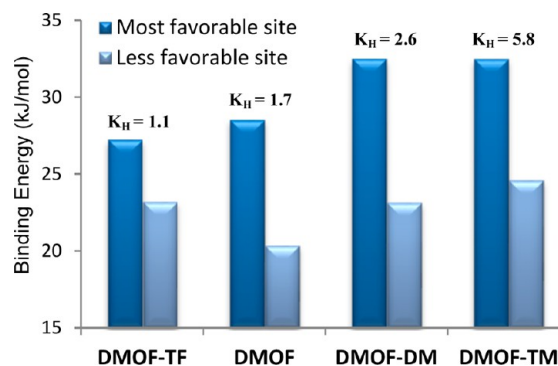
greater than that of the parent DMOF structure. The reason for the disproportionally large increase in experimental Henry's coefficient between DMOF-DM and DMOF-TM relative to their difference in heats of adsorption values is discussed in the following section and can be attributed to the more symmetric binding environment found in the DMOF-TM structure.

**CO<sub>2</sub> Binding Sites and Density Distributions.** Valuable molecular insight into the observed Henry's coefficient trends can be obtained from an analysis of the 0 K binding sites and 298 K atomic densities for CO<sub>2</sub> at infinite dilution within the structure. The Henry's coefficient is related to the spatially averaged weighted free energy of the adsorbate within the MOF framework at infinite dilution. At the limit as temperature goes to zero and infinite dilution, the most favorable 0 K binding sites would be the only adsorption sites for CO<sub>2</sub> (neglecting zero-point energies). While these are not the only possible adsorption sites under finite temperatures, molecules will still tend toward these lowest energy minimums. The energetic information obtained from these 0 K binding sites can therefore be combined with the adsorbate density information obtained at nonzero temperatures to extract valuable, quantitative insight into the intermolecular interactions which govern these adsorption trends.

In each representative structure, CO<sub>2</sub> energy minimizations were performed at 0 K using an application of Baker's method optimized for use in periodic systems.<sup>47</sup> This minimization technique finds the lowest energy 0 K binding sites by initially placing single adsorbates at random positions within the framework and then relaxing their atomic coordinates until the potential energy with respect to their center of mass and rotational elements have a first derivative equal to zero and all positive eigenvalues in the Hessian matrix. The last constraint, enforced by pushing the eigenvalues of the Hessian matrix to all positive values during the minimization, distinguishes this approach from Newton-Raphson algorithms and is critical to ensuring a true energetic minimum is found. The result of these CO<sub>2</sub> minimizations produced the same two strongest binding sites, shown in Figure 4, in the DMOF, DMOF-DM, DMOF-TM, and DMOF-TF structures. The most favorable binding site corresponds to a CO<sub>2</sub> molecule located close to the metal cluster whereas the less favorable binding site has CO<sub>2</sub> positioned between the benzene rings with oxygen atoms pointing toward the DABCO ligand. A comparison of the energetics of these 0 K binding sites, shown in Figure 5,



**Figure 4.** Two strong binding sites were found for CO<sub>2</sub> (pink) in each of the representative structures. The most favorable binding site (left, c-direction) has CO<sub>2</sub> located near the metal cluster whereas the less favorable binding site (right, a-direction) has CO<sub>2</sub> positioned between the benzene rings. Color code for framework atoms are red (oxygen), cyan (carbon), blue (nitrogen), gray (zinc). Functional groups are omitted for clarity.



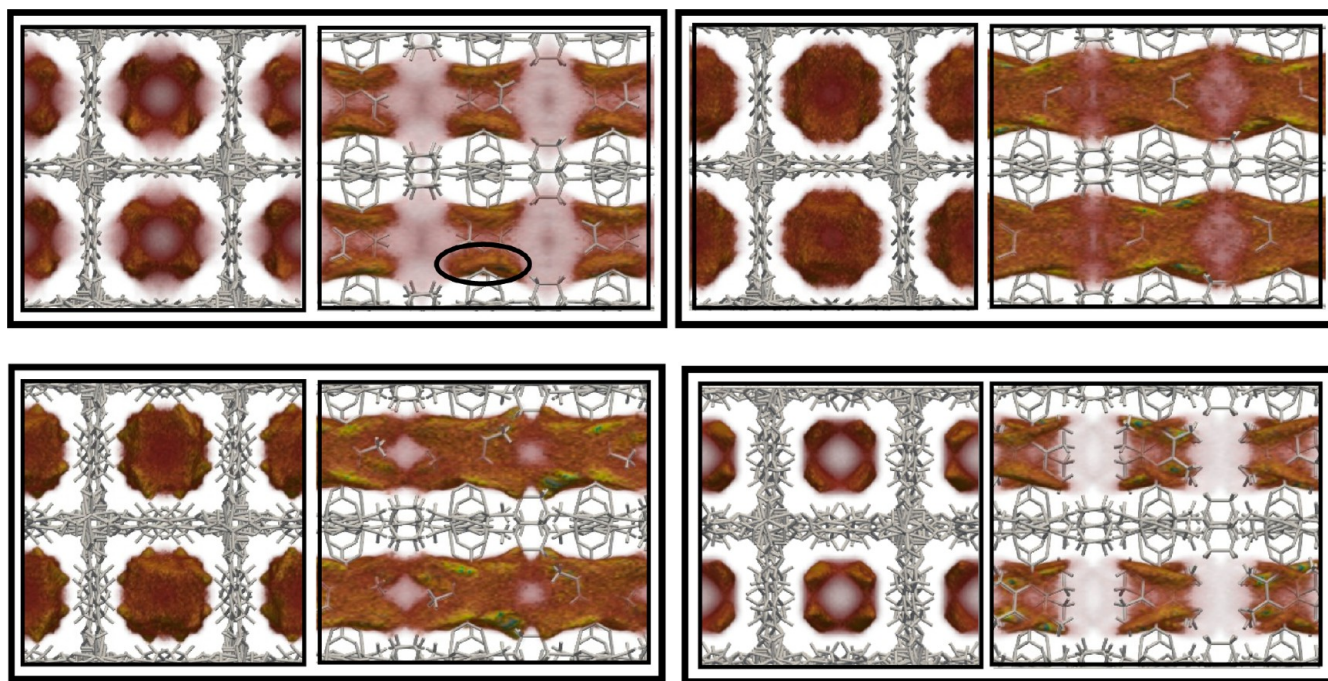
**Figure 5.** Zero Kelvin binding energies at the two strong binding sites for single CO<sub>2</sub> molecules in each of the structures. The experimental Henry's coefficients ( $K_H$ ) at 298 K in units of mol/kg/bar are also shown for reference.

provides powerful and illustrative insight into the reason for the interesting low pressure CO<sub>2</sub> affinity trends in these structures. A similar analysis can be used to understand the CO<sub>2</sub> affinity in DMOF-Cl<sub>2</sub>, which also possesses the same two lowest energy binding sites locations as those shown in Figure 4. However, the asymmetric incorporation of polar chlorine atoms on the BDC ligand in this structure creates a more complex electrostatic environment in the pore space that produces a greater diversity of energetics at these same 0 K binding sites, making this structure less illustrative for comparison purposes (Figure S24, Supporting Information).

Classical simulations do not explicitly account for many-body effects that have recently been suggested to have a potentially important impact on the adsorption behavior of CO<sub>2</sub>.<sup>48,49</sup> Quantum mechanical minimizations of single CO<sub>2</sub> molecules at their strongest binding sites in the parent DMOF structure were therefore also run to confirm that the physics of the more detailed quantum mechanical potential energy surface is correctly captured in our classical molecular models. There is strong agreement between the position and orientation of CO<sub>2</sub> at its strongest binding site in both the classical Baker's minimization and the quantum mechanical optimizations performed using VASP (Table S13–S14, Supporting Information). The CO<sub>2</sub> coordinates from the classical minimization represent an intermediate between the coordinates obtained from quantum mechanical minimizations performed with and without the van der Waals interactions correction method of Grimme,<sup>50</sup> confirming the accuracy of the classical simulation results relative to more detailed ab initio calculations.

While there is a general correlation between the classical 0 K binding site energetics and experimental Henry's coefficients, this description lacks a deeper quantitative insight into the observed trends. For example, an initial survey of the most favorable (28.4 kJ/mol vs 27.3 kJ/mol) and less favorable (20.3 kJ/mol vs 23.2 kJ/mol) 0 K binding sites in the DMOF and DMOF-TF structures indicate that the DMOF-TF structure may have the more favorable CO<sub>2</sub> interactions. However, because the Henry's coefficient is directly related to the *spatially averaged* weighted free energy in the framework, one must also consider the relative probability that the adsorbate will be present at these particular binding sites under nonzero temperatures. Figure 6 shows the center of mass density distributions for CO<sub>2</sub> at infinite dilution and 298 K within each of the representative structures. Analysis of the x-y and x-z planes given in Figure 6 indicate that, while the energetics of

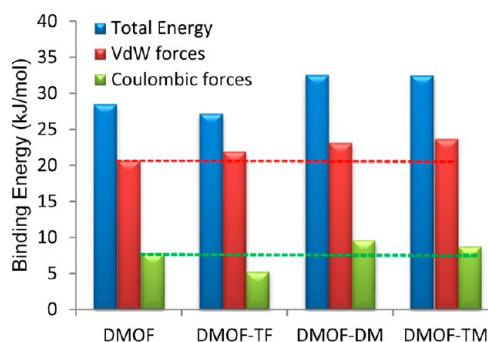




**Figure 6.** CO<sub>2</sub> density distributions at infinite dilution and 298 K. The  $x$ - $y$  and  $x$ - $z$  planes of DMOF (top left), DMOF-TF (top right), DMOF-DM (bottom left), and DMOF-TM (bottom right) are shown. The black oval on the  $y$ - $z$  plane of the parent DMOF structure highlights the concentrated adsorbate density around its strongest 0 K binding site.

the most favorable binding site for DMOF is only slightly favored over the most favorable site in DMOF-TF, the probability that a CO<sub>2</sub> molecule is actually present at this lowest energy site is much higher for DMOF versus DMOF-TF under nonzero temperatures. As a result, one would expect the Henry's coefficient, indicative of the spatially averaged weighted free energy in the structure, to be noticeably higher for DMOF versus DMOF-TF. This same argument can be applied to understand the difference in Henry's coefficient observed in the DMOF-DM versus DMOF-TM structures as well; in this case, while the energies of the most favorable binding sites in the two structures are also quite similar, the drastic increase in Henry's coefficient from the DMOF-DM to DMOF-TM structure at 298 K is directly related to the more symmetric binding environment in the DMOF-TM structure that serves to reduce the overall disorder in the adsorbate density distribution around its most favorable 0 K binding site.

Since the area closest to the metal cluster is both the most probable and energetically favorable binding site for CO<sub>2</sub> in each of the structures, an energetic analysis of this particular binding site can also provide important molecular insight into the structure–property relationships that are responsible for the CO<sub>2</sub> affinity trends in these structures. Figure 7 shows the contributions at the most favorable binding site due to van der Waals and Coulombic interactions in each structure. In each case, there is a modest increase in the van der Waals contributions to the binding energy that is roughly proportional to the strength of the Lennard-Jones parameters of the functional group. However, as also shown in Figure 7, the main factor distinguishing the adsorption affinities of the different functionalized MOFs are their contributions to the CO<sub>2</sub> binding energy due to Coulombic forces. Relative to the parent DMOF structure, there are more favorable Coulombic interactions for the DMOF-DM and DMOF-TM structures but less favorable interactions for the DMOF-TF structure. While



**Figure 7.** Contribution from van der Waals and Coulombic forces to the stronger 0 K CO<sub>2</sub> binding site. Dotted green and red lines are a reference to contributions in the parent DMOF structure.

the majority of the framework charges are unaffected by the chemical functionalization, one notable exception to this is the large discrepancy in charge between the electron withdrawing fluorine atoms ( $-0.13e$ ) and the hydrogens on electron donating methyl groups ( $+0.12e$ ). Because the most favorable binding site for CO<sub>2</sub> has its negatively charged oxygen atoms in close proximity to the functional groups on the BDC ligand (as shown in Figure 4), this difference in framework atomic charge also has a noticeable impact on the low pressure adsorption affinity in these structures. While the fluorine in DMOF-TF has stronger van der Waals interactions with CO<sub>2</sub> than the hydrogen in the parent DMOF structure, there are also less favorable Coulombic interactions present due to the repulsion forces which exist between its negatively charged fluorine ( $-0.13e$ ) and oxygen ( $-0.35e$ ) in the CO<sub>2</sub> molecule which serve to outweigh those benefits. However, in both the DMOF-DM and DMOF-TM structures, the electron donating methyl groups serve to increase van der Waals interactions without

compromising the Coulombic interactions with CO<sub>2</sub> near its adsorption site.

**CO<sub>2</sub> Selectivity Trends.** Typical postcombustion flue gas streams are predominantly CO<sub>2</sub>/N<sub>2</sub> mixtures with small amounts of CO, H<sub>2</sub>O, O<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub>, whereas natural gas reserves are composed predominantly of CH<sub>4</sub> with CO<sub>2</sub> and N<sub>2</sub> as contaminants. Given the strong agreement between experiment and simulation results, low pressure selectivity trends for CO<sub>2</sub> over N<sub>2</sub>, CO and CH<sub>4</sub> were also investigated in each of the representative structures. First, the quantitative accuracy of these molecular models at predicting the low pressure adsorption behavior for these adsorbates was confirmed through comparison of simulated and experimental infinite dilution heats of adsorption values for DMOF (Table 2). Given the excellent agreement, the selectivity for CO<sub>2</sub> over

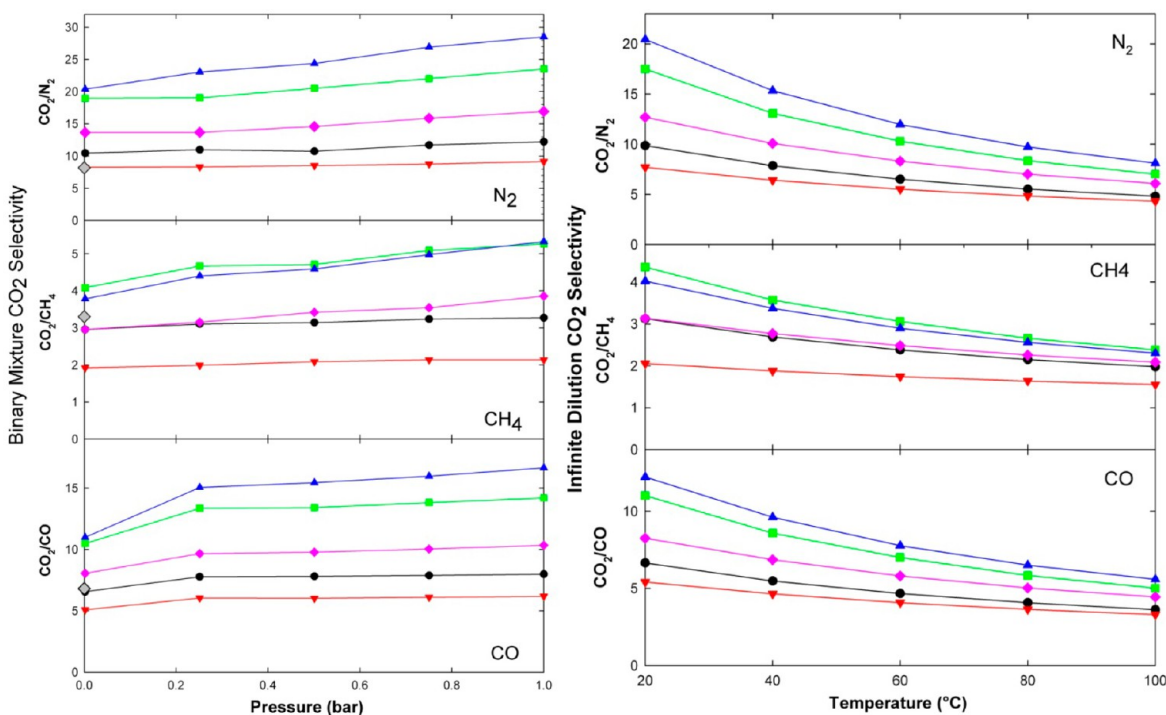
**Table 2. Experimental and Simulated Infinite Dilution Heats of Adsorption (kJ/mol) for DMOF**

	experiment <sup>12</sup>	simulation (298 K)
CO	10.0	12.1
CH <sub>4</sub>	13.9	13.7
N <sub>2</sub>	14.9	11.0
CO <sub>2</sub>	19.4	19.6

these adsorbates as a function of pressure at 298K in binary, equimolar mixtures and as a function of temperature at infinite dilution was also calculated (Figure 8). In each structure, the selectivity for CO<sub>2</sub> over the other adsorbates follows the general trend N<sub>2</sub> > CO > CH<sub>4</sub>. The agreement between binary GCMC simulations and selectivities obtained from ideal adsorbed solution theory (IAST) in the experimental work of Mishra et al.<sup>12</sup> for the parent DMOF is excellent. IAST can fail when the

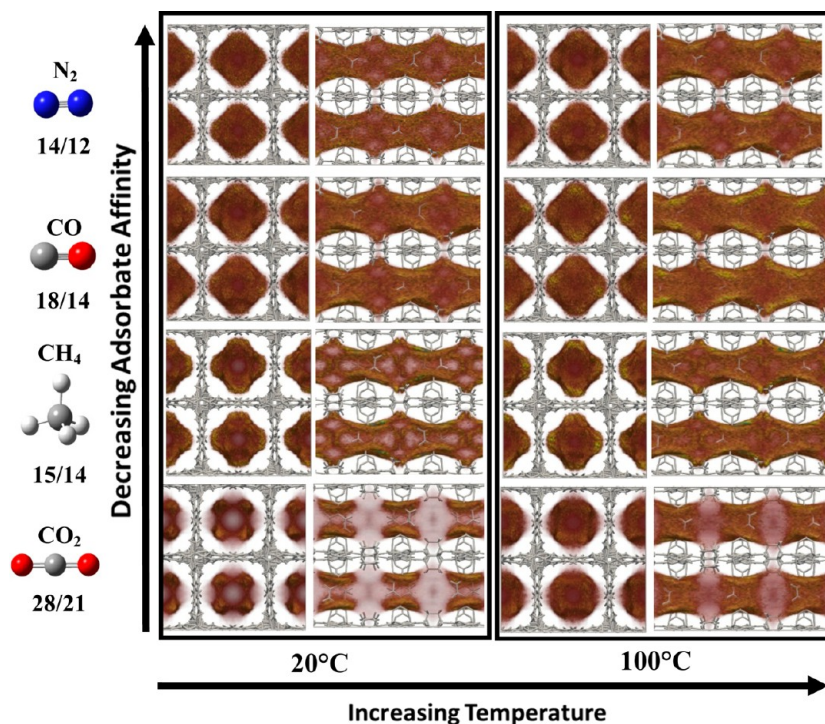
assumption of equal accessible surface areas for adsorbates is no longer valid.<sup>51</sup> The agreement between mixture simulations and experimental IAST predictions show that the simulation methodology and force fields are reliable and that there is no segregation of adsorbates in the system (i.e. the IAST assumptions are valid for this system).

The adsorbate selectivity trends in these structures correlate strongly with their 0 K binding site energetics and degree of adsorbate densities around these sites at the given temperature, providing further validity for the simple yet powerful approach presented in this work for understanding low pressure adsorption behavior. As shown in Figure 8, the difference in adsorbate selectivity between the different structures also diminishes as a function of temperature. The reason for this can be understood from the Figure 9 infinite dilution adsorbate density distributions at 20 and 100 °C. The lowest energy 0 K binding site locations for each adsorbate were similar to those of CO<sub>2</sub> found earlier in the work (i.e., located near the zinc metal cluster). However, as the entropic contributions due to temperature increase in the structures, the adsorbates tend further from these most favorable, lowest energy binding sites and instead toward random, less favorable adsorption sites in the pore. It is also noteworthy that for each of the different adsorbates, the DMOF-DM and DMOF-TM structures show the greatest CO<sub>2</sub> selectivity among the different variations. This finding is of particular importance because it indicates that the increased adsorbate affinity caused by the methyl groups in these structures is most specific toward CO<sub>2</sub> and not a generalized trend that holds for all other adsorbates (i.e., due simply to pore confinement effects). We showed in previous work that the methyl functionalization in DMOF-TM makes the unstable parent DMOF structure kinetically and cyclically stable after adsorbing large amounts of water under humid



**Figure 8.** Selectivity for CO<sub>2</sub> over N<sub>2</sub>, CO, and CH<sub>4</sub> as a function of pressure at 298K in binary, equimolar mixtures (left) and as a function of temperature at infinite dilution (right) in DMOF black ●, DMOF-Cl<sub>2</sub> magenta ◆, DMOF-TF red ▼, DMOF-DM green ■, and DMOF-TM blue ▲. Gray ◆ indicates IAST selectivity values in DMOF from experiment at 294 K.<sup>12</sup>





**Figure 9.** Infinite dilution adsorbate density distributions at 20 and 100 °C for CO<sub>2</sub>, CH<sub>4</sub>, CO, and N<sub>2</sub> in the *x*–*y* and *x*–*z* planes of the parent DMOF structure. The values listed under the adsorbate images are the energies (kJ/mol) at the most favorable 0 K binding sites in the structure.

conditions (near 90% relative humidity),<sup>18</sup> a quality that is seldom observed in MOFs outside of the UiO and MIL series.<sup>52–55</sup> While experimental CO<sub>2</sub> isotherms in this work indicate a reduced CO<sub>2</sub> saturation uptake at higher pressures due to reduced surface area and pore volumes in the methyl functionalized variations, the relatively high CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/CO selectivities and low water adsorption below 30% relative humidity<sup>18,19</sup> indicate that DMOF-TM and methyl functionalized variations of other structures in literature merit further investigation for ambient pressure industrial adsorption applications.

## CONCLUSIONS

In this work, we demonstrate a powerful yet simple approach for gaining quantitative, molecular-level insight into the experimental low pressure CO<sub>2</sub> affinity trends in a series of isostructural, pillared MOFs of the family Zn<sub>2</sub>(BDC-X)<sub>2</sub>(DABCO). This systematic approach for understanding the subtle structural differences which govern the interesting low pressure adsorption trends in this series can easily be applied to other systems, given the method's reliance only on generic force fields and initial quantum mechanics derived charges. After validating the accuracy of our models in the low pressure regime through excellent agreement between experimental and simulated Henry's coefficients and heats of adsorption values, we demonstrate how a detailed analysis of 0 K binding sites and 298 K adsorbate density distributions can be used to obtain a molecular understanding of the key structure–property relationships which govern these interesting results. The experimentally observed increase in low pressure CO<sub>2</sub> affinity as a function of the number of nonpolar functional groups on the BDC ligand can only be understood through an energetic analysis of the contributing van der Waals and Coulombic interactions present at the most favorable 0 K binding site in each structure. In the case of structures with

similar lowest energy binding site energetics, an analysis of the disorder around these lowest energy sites at nonzero temperatures is also necessary. Given the strong agreement between models and experiment, CO<sub>2</sub> selectivity trends were also investigated in the representative structures. These results show that the increased CO<sub>2</sub> adsorption affinity induced by methyl functional groups translates into a higher overall selectivity for CO<sub>2</sub> over CH<sub>4</sub>, CO, and N<sub>2</sub> as well, thus demonstrating a novel case where ligand functionalization can be used to simultaneously improve both the chemical stability<sup>18</sup> and CO<sub>2</sub> selectivity of a MOF relative to its parent structure. Contrary to the behavior of polar functional groups on isolated ligands and free surfaces, CO<sub>2</sub> cannot freely orient itself to obtain the most favorable energetic conformation in the pores of all structures. Our analysis suggests that chemical functionalization changes not only the energetics at the adsorbate binding sites but also the entropic properties of the system. This work presents a powerful method for understanding these effects and will serve as an important approach for predicting the adsorption properties induced by ligand functionalization in next-generation MOFs for CO<sub>2</sub> capture.

## ASSOCIATED CONTENT

### Supporting Information

Further experimental and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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