

Validating the Mechanism Underlying the Slacking of the Gate-Opening Behavior in Flexible Metal–Organic Frameworks Arising from Application of External Force

Homare Arima, Shotaro Hiraide,* Minoru T. Miyahara, and Satoshi Watanabe*

Department of Chemical Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan

E-mail: hiraide@cheme.kyoto-u.ac.jp; nabe@cheme.kyoto-u.ac.jp

Abstract

Flexible metal–organic frameworks (MOFs) are innovative adsorbents expected to revolutionize conventional separation systems, as they exhibit stepwise adsorption arising from structural transitions, commonly known as “gate opening.” However, because MOFs are typically obtained in powder form, they require shaping for industrial applications. In our previous study, we reported that the stepwise uptake observed in the CO₂ gate opening of ELM-11 ([Cu(BF₄)₂(4,4'-bipyridine)₂]) became less distinct when molded with polymer binders and found that this slacking phenomenon could be caused by the polymer binder inhibiting the structural change of the ELM-11 particles. In this study, we aimed to fully validate and generalize the mechanism behind the slacking of gate adsorption from both theoretical and experimental perspectives. First, we conducted grand canonical molecular dynamics simulations for a simplified MOF model to directly calculate free energy profiles of the particle to validate the slacking theory without any assumptions. The results confirmed the fundamental assumption made in

our previous study that the deformation of the flexible motifs within the MOF particles occurs sequentially, which is a key factor contributing to the slacking phenomenon. The second part of the study focused on the relationship between the volume expansion ratio of MOFs and the degree of slacking. The relationship predicted by the theory was experimentally validated by comparing ELM-11, which exhibits 30% volume expansion, to another MOF with a mutually interpenetrating jungle-gym structure, which exhibits 10% volume expansion. These findings strengthened and generalized the understanding of the mechanism underlying the slacking of gate adsorption induced upon the application of external force, which could guide the fabrication of molded MOFs while maintaining a high adsorption efficiency for various industrial applications.

Keywords

metal–organic frameworks, gate adsorption, shape forming, volume expansion, external force, free-energy analysis

1 Introduction

“Ensure access to affordable, reliable, sustainable and modern energy for all”¹ — To achieve this sustainable development goal indicated by the United Nations, increasing the use of renewable energy and decreasing energy consumption by improving energy efficiency are crucial. In the case of the USA, the industrial sector accounts for 32% of domestic energy consumption, approximately half of which is required for traditional thermal-dependent separation processes, represented by distillation.² Therefore, switching to energy-saving methods such as adsorption and membrane separation has become imperative; however, studies on achieving high throughput through these methods are ongoing. Metal–organic frameworks (MOFs) are among the most promising materials for advancing the utilization of adsorbent-based separations. Because of their regular structures and high designability,^{3–8} pore sizes

and host-guest interactions, which determine the gas selectivity and amount adsorbed, can be controlled by customizing the combination of metal ions^{9,10} and organic ligands,^{11,12} making it possible to prepare appropriate MOFs for specific separation systems.^{13,14} In addition, several MOFs possess structural flexibility and exhibit structural deformation in response to external stimuli, such as temperature and pressure changes and light exposure. One notable manifestation of these is the adsorption-induced structural transition, commonly referred to as “gate opening” or “breathing,” which sharply increases the amount adsorbed at a threshold gas pressure (gate pressure).^{15–19} This abrupt change in adsorption renders flexible MOFs useful in various industrial applications. For example, Bonneau et al.²⁰ proposed an acetylene storage system comprising a Zn-based flexible MOF.^{21,22} Because acetylene gas is highly explosive, the separation system must operate within a narrow pressure range to ensure safety. In their study, the gate pressure was deliberately manipulated by substituting NH₂ and NO₂ for the benzene ring of 1,4-benzenedicarboxylate (bdc), an organic ligand for the MOF, thereby enabling acetylene uptake and release within a safe pressure range. Another benefit of using a flexible MOF with a steep S-shaped adsorption isotherm is its exceptional selectivity; each component of the gas mixture has a different gate pressure, which significantly facilitates the separation process. Dong et al.²³ reported that by optimizing the temperature conditions to control the gate pressures, NTU-65²⁴ could be used to separate ethylene gas from a ternary mixture of ethylene, acetylene, and carbon dioxide to a higher purity than the polymer grade. In adsorption separation processes, the large working capacity of flexible MOFs is advantageous because a slight variation in pressure across the gate pressure leads to substantial changes in the amount adsorbed. In our previous study, we found that using elastic layer-structured MOF-11 (ELM-11, [Cu(BF₄)₂(bpy)₂]; bpy = 4,4'-bipyridine)^{25,26} for a CO₂/CH₄ separation process achieved more than twice the CO₂ working capacity of a system using HKUST-1 ([Cu₃(1,3,5-benzenetricarboxylate)₂]).²⁷ Consequently, the column size of the system could be reduced by 69% and the feed gas volume by 62% while maintaining the same yield of product gas.²⁸ Considering the above examples, the superiority of flexible

MOFs apparently relies on the steepness of the abrupt change in adsorption.

Generally, MOFs are obtained in powder form with particle sizes on the micron scale or smaller and thus require shaping for industrial applications. Several studies have discussed shaping methods for rigid types of MOFs, such as compression and pelletization.^{29–34} Although a small portion of MOF crystals becomes amorphous, which decreases the amount that can be adsorbed,³⁰ the shaping itself can be accomplished in a facile manner. However, the shaping of flexible MOFs is more complex than that of regular MOFs because of volume expansion occurring during gate opening. Several studies on the shaping of flexible MOFs have highlighted discrepancies in the gate-opening behavior between powder and molded samples.^{33,35–41} For example, pelletizing MIL-53(Al) ($[\text{Al}(\text{OH})(\text{bdc})]$)⁴² with polyvinyl alcohol as a binder shifted gate opening to higher pressures.^{37,38} We also reported that when ELM-11, which possesses a stacked-layer structure and exhibits gate opening owing to the expansion of the interlayer distance, was molded with polyvinylpyrrolidone (PVP), its original stepwise uptake was smeared.⁴¹ We recognize that these two are the same phenomenon expressed in different ways. In our previous study, we conducted free energy analysis^{43–46} with the aid of the grand canonical Monte Carlo (GCMC) simulations and thermodynamic integration method to elucidate this strange phenomenon and proposed that the smeared gate-opening behavior was caused by the inhibition of structural deformation of ELM-11 particles by forces exerted by the polymer binder.⁴¹ The external force applied to the ELM-11 particles would be nonlinear with the particle thickness, and the force becomes stronger with structural expansion. If it is assumed that the layers in the particle undergo structural deformation sequentially, each layer experiences slight variations in stress, and, therefore, the gate pressure shifts to a higher value to varying degrees, which is believed to be the underlying cause of the smeared gate adsorption. We also demonstrated that ELM-11 pellets with a higher binder content exhibited a greater degree of slacking. This trend supports the aforementioned mechanism because the stress exerted on the MOF particles increases as the number of binder molecules around the MOF particles increases.

Despite the plausible explanation of the slacking phenomenon in our previous study, further theoretical and experimental evidence is required to fully validate and prove the universality of this mechanism. In particular, this mechanism is dependent on the type of structural transition of flexible motifs of the MOF particle, and hence, it must be confirmed. Furthermore, the examination has only been conducted for ELM-11, and the universality of other flexible MOFs is yet to be explored. Referring back to the idea that the slacking is caused by the stress from the polymer binder preventing the volume of the MOF particles from expanding during gate opening, the degree of slacking should be different between MOFs with different volume expansion ratios because decreased MOF particle expansion would cause fewer stresses to be applied. A comprehensive understanding of the slacking phenomenon and its elucidation in all flexible MOFs are crucial for advancing various applications that involve these MOFs, such as adsorption separation processes. Nevertheless, to the best of our knowledge, this objective has not yet been attained.

In this study, the evidence that smeared gate adsorption arises from an external force is provided through both theoretical and experimental approaches. The first part of the study employed a simplified flexible MOF particle model in combination with GCMC and molecular dynamics (MD) simulations, the so-called grand canonical molecular dynamics (GCMD) method. This approach allows for the simultaneous simulation of adsorption and structural transitions as well as the direct calculation of the free energy change of the MOF particle model, without any assumptions regarding how the structural transition proceeds. The obtained results confirmed the mechanism of the slacking phenomenon and showed that the key assumption made in the previous study regarding the deformation type was reasonable, albeit with some discrepancies not significant for the slacking theory. In the second part, a theoretical discussion of the correlation between the degree of slacking and the volume expansion ratio is presented, followed by an experimental investigation of molding a MOF with a mutually interpenetrating jungle-gym structure ($[\text{Cu}_2(\text{bdc})_2(\text{bpy})]$; referred to as JG-MOF),^{47,48} and a comparison with the ELM-11 pellets. The volume expansion ratio

of JG-MOF is only approximately 10% whereas ELM-11 expands by approximately 30% in volume during gate opening, which leads to a noticeable difference in the smearing of the gate opening.

The remainder of this paper is organized as follows. section 2 provides a theoretical background of gate adsorption and the effect of external forces, and explains the gate adsorption and its slacking in terms of free energy. In section 3.1, we report the results of the GCMD simulations conducted with the simplified MOF particle model to validate the slacking gate adsorption through direct calculation of the free energy landscape of the MOF particle. In section 3.2, the relationship between the degree of slacking and the volume expansion ratio is discussed, both theoretically and experimentally. The results are concluded in section 4, and details of the computational methods, material synthesis, and analysis are provided in section 5.

2 Theoretical basis

2.1 Free energy analysis

Gate adsorption behavior can be described based on osmotic free energy analysis, as proposed by Coudert et al.⁴³ Given a unit cell of a stacked-layer-type MOF containing a pair of layers with an interlayer width of h , its osmotic free energy ω_{os} can be expressed as

$$\omega_{\text{os}}(h, P, T) = f_{\text{host}}(h, T) + PV(h) + \omega_{\text{guest}}(h, P, T) \quad (1)$$

where P is the pressure, T is the temperature, V is the system volume, and f_{host} is the Helmholtz free energy of the host framework. ω_{guest} is the grand potential of the guest molecules, calculated by integrating an adsorption isotherm on the unit cell, n_{guest} , as

$$\omega_{\text{guest}}(h, P, T) = -k_{\text{B}}Tn_{\text{guest}}(h, P_{\text{id}}, T) - \int_{P_{\text{id}}}^P n_{\text{guest}}(h, P', T)V_{\text{m}}dP' \quad (2)$$

where k_B is the Boltzmann constant, V_m is the molar volume of the gas ($V_m = (\partial\mu/\partial P)_T$), and μ is the chemical potential of the gas. The first term on the right-hand side of equation 2 is the grand potential at a sufficiently small pressure, P_{id} . The osmotic free energy change due to the expansion of the interlayer space from h_{cl} to h is computed as:

$$\begin{aligned}\Delta\omega_{os}(h, P, T) &= \omega_{os}(h, P, T) - \omega_{os}(h_{cl}, P, T) \\ &= \Delta f_{host}(h, T) + P\Delta V + \Delta\omega_{guest}(h, P, T)\end{aligned}\tag{3}$$

where the $P\Delta V$ term is negligible compared to the other terms and h_{cl} is the interlayer width when the system is in the most stable state at $P = 0$ (closed state).

A typical example of the free energy analysis with the aid of molecular simulations is as follows. Figure 1a shows a schematic of the simplified MOF model that mimics the structure of ELM-11.^{41,45,46} The model consists of a smeared-atom wall sized $10\sigma_{gg} \times 10\sigma_{gg}$, where σ_{gg} is the size parameter of the Lennard–Jones (LJ) potential for a guest molecule, and a pillar molecule positioned at a distance z_p from the smeared-atom wall. The layer is contained in a unit cell sized $10\sigma_{gg} \times 10\sigma_{gg} \times h$, and a simulation box is created by stacking such seven unit cells to meet the potential cutoff length of $5\sigma_{gg}$. Hence, the width of each interlayer space in the simulation box is equal to h . By conducting GCMC simulations using these simulation boxes with varying h (Figure 1b) wherein the positions of the layers are immobilized, n_{guest} can be obtained and then ω_{guest} can be calculated according to equation 2. Approximating that the Δf_{host} is equal to the change in the total interframework potential, the osmotic free energy change of the unit cell, $\Delta\omega_{os}$, is derived from equation 3. Figure 2 shows an example of the $\Delta\omega_{os}$ of the simplified model with $z_p = 0.935\sigma_{gg}$ at various dimensionless pressures, $P^* = P\sigma_{gg}^3/\varepsilon_{gg}$, where ε_{gg} is the depth of the LJ potential for guest molecules. When P^* is zero, no guest molecules are adsorbed at any interlayer width; therefore, $\Delta\omega_{os}$ in vacuo represents the Δf_{host} . At the point where the system achieves the minimum $\Delta\omega_{os}$ ($P^* = 0$), as indicated by the star symbol, the closed state can be defined at $h = h_{cl} = 1.75\sigma_{gg}$. In the range of larger h values, the increase in the amount adsorbed with increasing pressure is

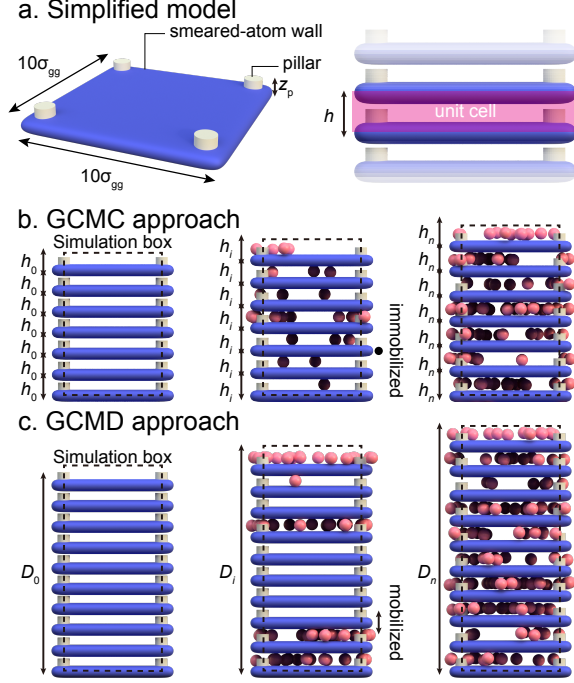


Figure 1: (a) Simplified MOF model that mimics the structure of ELM-11. Simulation boxes used (b) in the GCMC approach wherein the positions of the layers were immobilized and (c) in the GCMD approach wherein these positions were allowed to change in the z -direction. The pink spheres represent adsorbed molecules.

larger, and therefore, ω_{guest} contributes to stabilizing the state encapsulating guest molecules. At $P^* = 3.9 \times 10^{-4}$ (square markers), $\Delta\omega_{\text{os}}$ at $h = 2.00\sigma_{gg}$ becomes equal to that at $h = h_{\text{cl}}$. Because the open state ($h = h_{\text{op}} = 2.00\sigma_{gg}$) continues to be stable over this pressure, the host framework suddenly deforms and exhibits a step-like adsorption isotherm at $P^* = 3.9 \times 10^{-4}$, indicating the gate opening behavior.

2.2 Free energy analysis under external force

The adsorption behavior of pelletized flexible MOFs can be explained by incorporating the effect of the external potential into the free energy analysis described in section 2.1. A key point is that the external potential preventing the structural transition is a function of the entire thickness of a MOF particle, D , and not the interlayer width of a unit cell, h . Therefore, considering a particle with N stacked unit cells, the total free energy along the

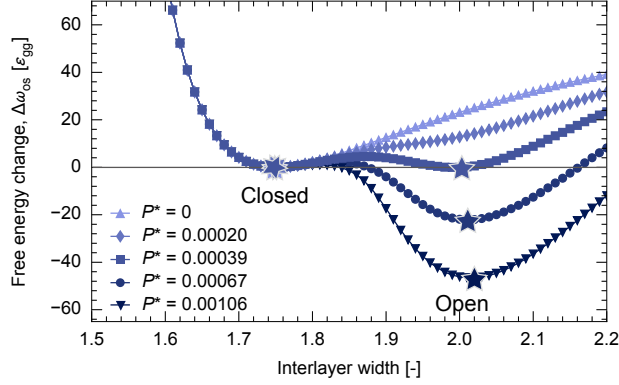


Figure 2: Osmotic free energy change of the unit cell computed using the GCMC approach at several pressures. The star symbols indicate the most stable state at each pressure identified from the point where the free energy reached its minimum value.

particle thickness, $\Delta\Omega_{\text{os}}(D)$, is required to discuss the effect of the external force. If $\Delta\Omega_{\text{os}}$ could be obtained in some way, the free energy change of the system $\Delta\hat{\Omega}_{\text{os}}$, including the external potential ΔW , is expressed as follows:

$$\Delta\hat{\Omega}_{\text{os}}(D, P, T) = \Delta\Omega_{\text{os}}(D, P, T) + \Delta W(D) \quad (4)$$

The amount adsorbed and thickness of the flexible MOF particle in the pellet at each pressure are then determined by the stable state where $\Delta\hat{\Omega}_{\text{os}}$ reaches a minimum. In our previous study,⁴¹ the following equation was found to be suitable for describing the external potential exerted on MOF particles in pellets, as it mimicked the hard-core and soft repulsive-shoulder potential to express the collision of rigid spherical particles in the presence of microgels:⁴⁹

$$W(D) = U_0 \frac{g + \left[\frac{\delta + D_{\text{cl}} - D}{\delta} (g - g^{-1}) - g \right]^{-1}}{g - g^{-1}} \quad (5)$$

where U_0 , g , and δ are parameters for tuning the strength and shape of the external potential, and D_{cl} is the total thickness of the particle when all the layers are in the closed state (Nh_{cl}).

The free energy change of the unit cell $\Delta\omega_{\text{os}}(h)$ should be related to that of the particle

$\Delta\Omega_{\text{os}}(D)$. However, the particle composed of N stacked unit cells has N interlayer widths, $\mathbf{h} = (h_1, h_2, \dots, h_N)$, and the combinations of $\mathbf{h}$ that would lead to the same value of D are impracticably large. To circumvent the difficulty, in our previous study,⁴¹ we took a two-step approach, in which we first calculated $\Delta\omega_{\text{os}}(h)$ using GCMC simulations (see section 2.1) and then converted it to $\Delta\Omega_{\text{os}}(D)$ by assuming the most plausible structural transition, as explained in section 3.1.2. The objective of the first part of this study is to obtain $\Delta\Omega_{\text{os}}(D)$ directly, without making any assumptions, through GCMD simulations, in which the proper state of the system, including the interspaces of all layers, the amount adsorbed, and the free energy, is determined for a given temperature, pressure, and particle thickness. Hereafter, we denote the previous method as the ‘‘GCMC approach’’ and the new method as the ‘‘GCMD approach.’’

3 Results and discussion

3.1 Validating the mechanism of the slacking phenomenon

3.1.1 Direct simulation through GCMD approach

Figure 1c shows the simplified MOF particle model used in the GCMD approach. We placed 10 simplified layers in a simulation box with a size of $10\sigma_{\text{gg}} \times 10\sigma_{\text{gg}} \times D$ and conducted the GCMD method that alternated between the GCMC simulation for the insertion and deletion of gas molecules and the NVT -MD simulation to allow the movement of the layers and gas molecules with various D -sized boxes. Other settings for the model are the same as the example shown in section 2.1.

Figure 3a illustrates the final states of the system at $P^* = 3.9 \times 10^{-4}$ when $D = 17.80\sigma_{\text{gg}}, 18.52\sigma_{\text{gg}},$ and $19.24\sigma_{\text{gg}}$. As this particle model contained 10 layers, h should be $1.78\sigma_{\text{gg}}, 1.85\sigma_{\text{gg}},$ and $1.92\sigma_{\text{gg}},$ respectively, if evenly distributed. However, the layer spacing obtained was bimodal regardless of the D value, i.e., $\sim 1.75\sigma_{\text{gg}}$ and $\sim 2.00\sigma_{\text{gg}},$ corresponding

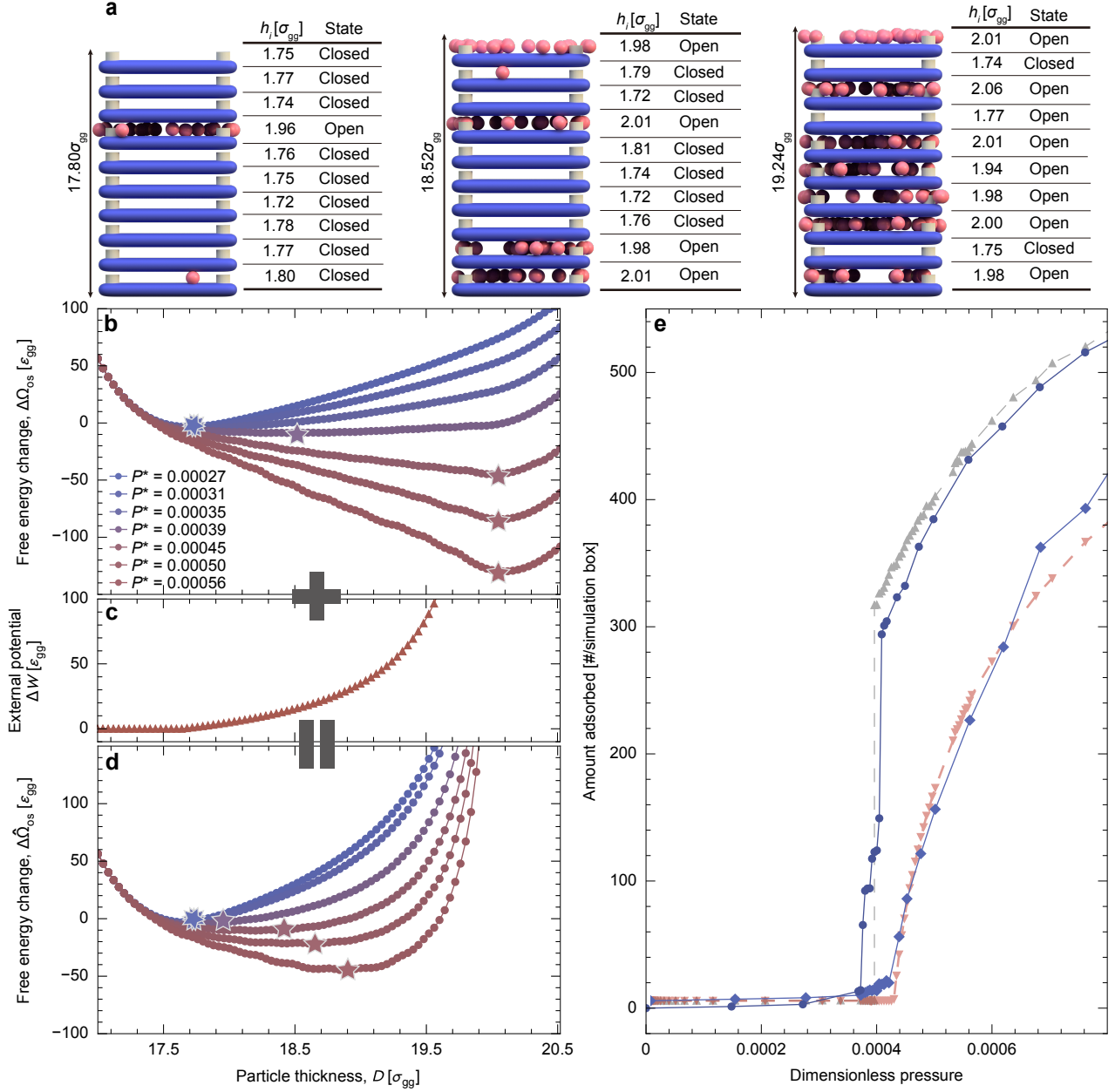


Figure 3: (a) Final states of the simulation box at $P^* = 3.9 \times 10^{-4}$ when $D = 17.80\sigma_{gg}$, $18.52\sigma_{gg}$, and $19.24\sigma_{gg}$. (b) Osmotic free energy profiles of the MOF particle at various dimensionless pressures, (c) hard-core and soft-shoulder potential as an external potential ($U_0^* (= U_0/\sigma_{gg}) = 700$, $g = 0.2$, and $\delta = 2.35\sigma_{gg}$), and (d) total free energy profile of the MOF particle model under the external force. (e) Simulated adsorption isotherms on the MOF particle model with and without the external force. Dashed lines with triangles were obtained from the GCMC approach.

to the closed layer (h_{cl}) and open layer (h_{op}), respectively, as shown in Figure 2. The number of open layers encapsulating gas molecules increased gradually with increasing particle thickness, which indicates that the layers in the particle deform sequentially. Figure 3b shows the free energy landscapes at various pressures calculated by integrating the normal stress in the z -direction, $\sigma_z(D, P)$, over D . Interestingly, a nearly linear profile was obtained in the range between the fully closed state ($D = 17.5\sigma_{\text{gg}}$) and the fully open state ($D = 20.0\sigma_{\text{gg}}$), although it slightly deflected downward and was wavy. The most stable particle thickness at each pressure was identified from the point where the free energy reached its minimum value, as indicated by the star symbols. Tracking the most stable states showed a dramatic change from the fully closed to the fully open with even a small increase in pressure, which is similar to the results shown in Figure 2. As a result, collecting the amount adsorbed at the most stable state yields the characteristic S-shaped adsorption isotherm, which proves that gate opening behavior can be explained by the GCMD approach as well (blue circles in Figure 3e).

By adding an external potential (equation 4 and Figure 3c) to $\Delta\Omega_{\text{os}}$ (Figure 3b), the free energy profile of the particle under the force, $\Delta\hat{\Omega}_{\text{os}}$, can be obtained (Figure 3d). Because the external potential increases nonlinearly with increasing particle thickness, the states at larger D values are more destabilized by the external potential. That is, as indicated by the star symbols in Figure 3d, the external potential makes the intermediate state where the closed and open layers coexist the most stable, and the stable particle thickness (i.e., the ratio of the open layers) gradually increases with increasing pressure, resulting in the unique S-shaped adsorption isotherm becoming less distinct (blue squares in Figure 3e). This should be the mechanism of the slacking phenomenon, and the GCMD approach allowed us to successfully reach this conclusion without relying on any assumptions.

3.1.2 Comparison of $\Delta\Omega_{\text{os}}$ obtained from GCMC and GCMD approaches

In this section, the validity of the assumption made in the previous GCMC approach⁴¹ for converting $\Delta\omega_{\text{os}}$ into $\Delta\Omega_{\text{os}}$ is discussed by comparing with the exact result obtained by the GCMD approach. In the previous study, two extreme modes of structural transition within a particle were considered: the simultaneous mode and the sequential mode. The simultaneous mode assumes that all the layers deform with the same extent, which can be simply formulated as $D = Nh$ and $\Delta\Omega_{\text{os}}(D) = N\Delta\omega_{\text{os}}(h)$. However, this mode resulted in an unnaturally high energy barrier between the closed and open states as well as could not explain the slacking phenomenon: it predicted a higher shift in the gate pressure with maintaining the step shape. Therefore, we concluded that the sequential mode is the most plausible type of structural transition in real systems. Specifically, assuming that one layer has the transitioning ratio, x ($= (h - h_{\text{cl}})/(h_{\text{op}} - h_{\text{cl}})$), and the other layers consist of $n - 1$ open and $N - n$ closed, D and $\Delta\Omega_{\text{os}}$ can be written as⁴¹

$$\begin{cases} D(\mathbf{h}) = D(x, n) = Nh_{\text{cl}} + (h_{\text{op}} - h_{\text{cl}})(n - 1 + x) \\ \Delta\Omega_{\text{os}}(D, P, T) = \Delta\Omega_{\text{os}}(x, n, P, T) = (n - 1)\Delta\omega_{\text{os}}(1, P, T) + \Delta\omega_{\text{os}}(x, P, T) \end{cases} \quad (6)$$

Figures 4a and 4b show the estimated interlayer widths and $\Delta\Omega_{\text{os}}$ at $P^* = 3.9 \times 10^{-4}$ of the simplified MOF particle model used in section 2.1 according to equation 6. Under this assumption, only one layer can be deformed at a time while the other layers remain in the closed or open state. This process is then repeated until all layers are open. Because the transition of each layer induced a change in the free energy by $\Delta\omega_{\text{os}}$, the resulting profile of $\Delta\Omega_{\text{os}}$ exhibited a wavy pattern in which the individual $\Delta\omega_{\text{os}}$ were serially connected. The same plots as Figures 4a and 4b based on the exact results obtained from the GCMD approach yield Figures 4c and 4d. As described in section 3.1.1, sequential deformation was observed in the GCMD simulations, resulting in a similar trend in the development of interlayer widths (Figures 4a and 4c). That is, the sequential-mode assumption made in the previous study was

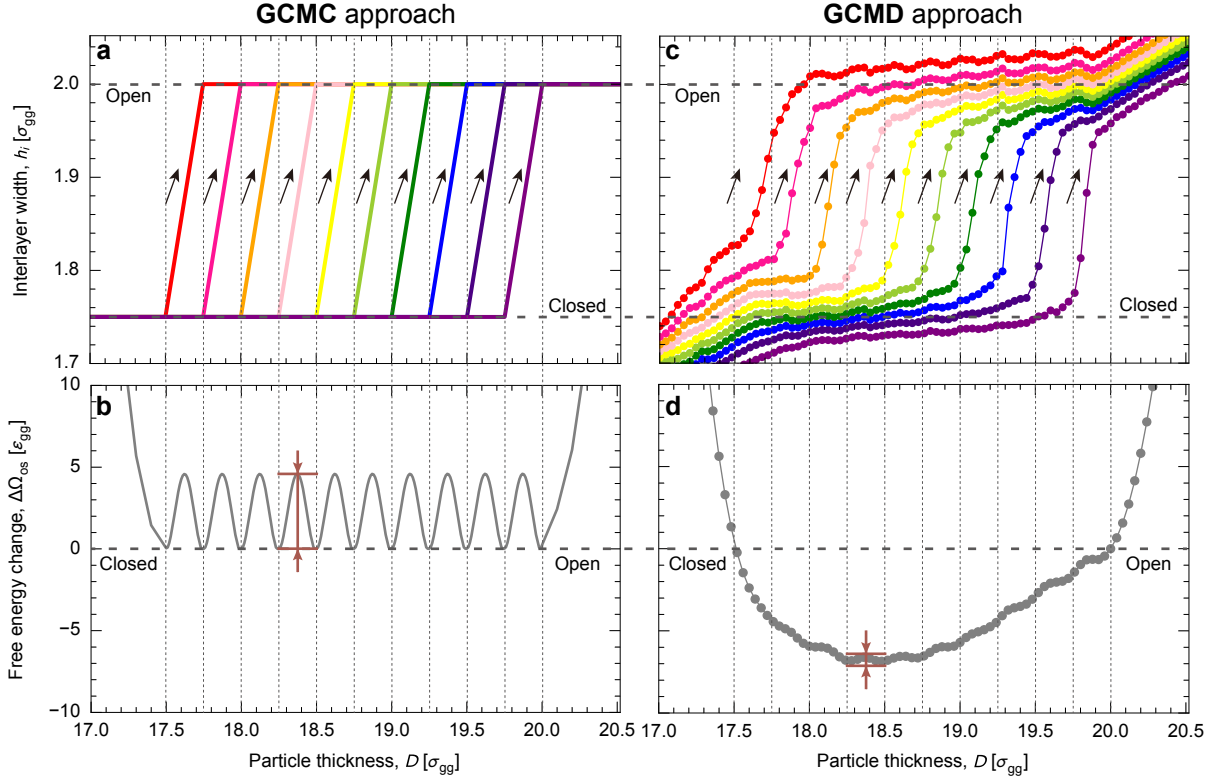


Figure 4: Comparison of schematics representing of equation 6 and the exact results obtained from the GCMD approach. Sequential-mode assumption indicates that the interlayer widths change in turn as shown in (a). The 10 colors indicate 10 interlayer widths in the particle. Notably, the red to violet lines do not correspond to the top-to-bottom interlayer widths of the particle, that is, the correspondence is arbitrary (e.g., the red, magenta, and orange lines may indicate the 3rd, 9th, and 4th interlayer widths from the top of the particle). (b) shows the resulting wavy shape in the osmotic free energy changes of the particle at $P^* = 3.9 \times 10^{-4}$. (c) and (d) are results obtained from the GCMD approach, corresponding to (a) and (b).

largely correct. However, there are two noticeable differences between the estimated $\Delta\Omega_{\text{os}}$ profile and the exact profile obtained from the GCMD approach (Figure 4d, which is an enlargement of Figure 3b), especially regarding the following two factors. First, the obtained profile displays a convex downward curvature. We attribute this behavior to the entropy contribution associated with the placement of the closed and open layers, which is consistent with predictions based on the Boltzmann equation, as elaborated in section S1, Supporting Information. Owing to the convex downward shape, the adsorption isotherm obtained has an S-shaped function with a small width (blue circles in Figure 3e), while a completely discrete function (gray triangles) was obtained from the GCMC approach because a multistable state was established at the gate pressure (Figure 4b). Experimental adsorption isotherms are also known to exhibit less-than-perfect step functions, which may support the convex downward profile of $\Delta\Omega_{\text{os}}$. Second, a difference is noted in the height of the free energy barrier for the transitioning layer as obtained via the GCMC and GCMD approaches. For example, the transition of the fourth layer, where the particle thickness changes from 18.25 to $18.5\sigma_{\text{gg}}$, exhibits a barrier of $4.5\varepsilon_{\text{gg}}$ in the GCMC approach, whereas that in the GCMD approach is below $0.1\varepsilon_{\text{gg}}$. This result stems from the fact that the interlayer widths of the closed and open states obtained via the GCMD approach are not precisely $1.75\sigma_{\text{gg}}$ and $2.00\sigma_{\text{gg}}$, respectively, but a blend of slightly larger and smaller values, respectively (Figures 4a and 4c). In other words, the layers in the closed and open states adopt a slightly unstable state to lower the energy barrier for the transitioning layer (see section S2 for more details). Nevertheless, these discrepancies were found to be insignificant for discussing the slacking phenomenon, as evidenced by the good agreement with the smeared adsorption isotherms obtained using both the GCMC and GCMD approaches, assuming the same external potential (red downward triangles and blue squares in Figure 3e). This is because the effect of the downward convex originating from the entropy is not large compared to pressure-dependence of $\Delta\Omega_{\text{os}}$, resulting in no effect on the relative free energy between the local minima, and the height of energy barriers cannot significantly change the stable state. In summary, the previously

reported GCMC approach and its sequential-mode assumption according to equation 6 are reasonable approximations for discussing the slacking phenomenon, which is advantageous over the exact GCMD approach in terms of computational cost.

3.2 Relationship between degree of slacking and volume expansion ratio

3.2.1 Theoretical results

This section discusses the relation between the ratio of the volume expansion of a MOF particle and the degree of slacking by comparing the two simplified stacked-layer models. The z_p values were set to $0.77\sigma_{gg}$ for model **L** and $0.88\sigma_{gg}$ for model **S**; therefore, the inter-layer widths at which the simplified models adopted their most stable states in a vacuum were different from each other (see section S3). As demonstrated in section 3.1, equation 6 provides a sufficiently accurate estimate for investigating the slacking phenomenon. Therefore, the GCMC approach was employed in this section to obtain the $\Delta\Omega_{os}$ values to reduce computational expenses.

Figures 5a and 5b show the $\Delta\omega_{os}$ values for models **L** and **S**, respectively. Because the closed state is defined as the stable state that has the minimum $\Delta\omega_{os}$ at $P^* = 0$, the h_{cl} value depends exclusively on the interaction between the pillar molecule and layer. Thus, the h_{cl} value of model **L** is smaller than that of model **S**, as model **L** can stack more densely owing to its shorter pillars. Conversely, h_{op} is not significantly influenced by the z_p value because the presence of the pillar does not critically affect the amount adsorbed for these models. Consequently, model **L** exhibited a 30% volume expansion from $h_{cl} = 1.55\sigma_{gg}$ to $h_{op} = 2.01\sigma_{gg}$, while model **S** exhibited a 20% volume expansion from $h_{cl} = 1.68\sigma_{gg}$ to $h_{op} = 2.02\sigma_{gg}$.

The dark blue circles in Figure 5c represent the $\Delta\Omega_{os}$ of model **L** at $P^* = 1.58 \times 10^{-3}$ when considering the MOF particle consisting of five unit cells. At this pressure, $\Delta\Omega_{os}$ reached the

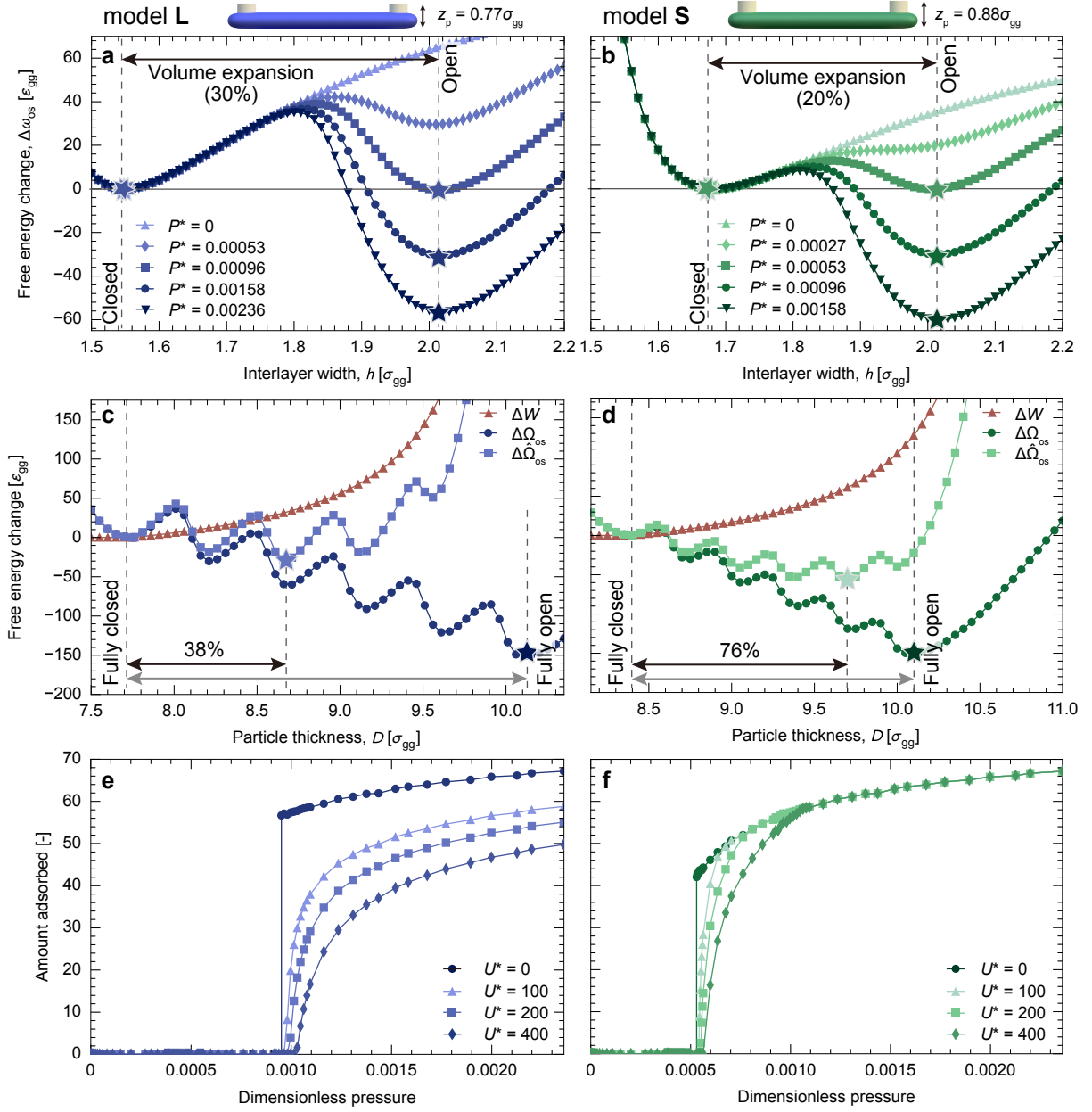


Figure 5: Osmotic free energy profiles along interlayer width of simplified stacked-layer models (a) with $z_p = 0.77\sigma_{gg}$ (model **L**), and (b) with $z_p = 0.88\sigma_{gg}$ (model **S**) at various dimensionless pressures. The free energy profiles along particle thickness of (c) model **L** at $P^* = 1.58 \times 10^{-3}$, and (d) model **S** at $P^* = 9.6 \times 10^{-4}$ considering soft repulsive shoulder potential ($U_0^* = 200$, $g = 0.1$, and $\delta = 2.35\sigma_{gg}$). To clarify the difference in the influence of external forces, the free energy landscape is illustrated with aligned closed states. Simulated adsorption isotherms on (e) model **L** and (f) model **S** under external forces (various U_0^* , $g = 0.1$, and $\delta = 2.35\sigma_{gg}$).

global minimum in the fully open state ($D = 10.05\sigma_{\text{gg}}$). However, when considering the soft repulsive shoulder potential⁴⁹ as an external contribution (red triangles), the system became unstable at this particle thickness (light blue squares). Thus, the stable state changed to an intermediate open state with $D = 8.65\sigma_{\text{gg}}$, and the ratio of structural transition was only 38%. As P^* increased, the stable state shifted to the next open state step-by-step, resulting in a stair-like shape in the adsorption isotherm (see section S4). If an existing MOF particle contains thousands of layers, this stair-like shape is smoothed out, as shown in Figure 5e. In addition, as the external force was increased by increasing the U^* value, the stable particle thickness shifted to an even smaller value, and thus, the slacking effect became more intense.

When the same external potential was applied to model **S**, the exerted force was smaller owing to the nonlinearity of the external potential, resulting in a stable state at $D = 9.70\sigma_{\text{gg}}$ while retaining a high structural transition ratio of 76% (Figure 5d). Therefore, the adsorption isotherm on model **S** could maintain its original steep shape even under an external force (Figure 5f). Furthermore, despite the exerted force becoming stronger, which corresponded to an increase in the binder content in the pellets, the change in the degree of slacking in model **S** was less severe than that in model **L**. This result indicates that for MOFs with small volume expansion, the transition can be completed at the weak part of the nonlinearity in the external force, and therefore, the slacking phenomenon caused by shape formation does not pose a significant issue.

3.2.2 Comparison of pelletized ELM-11 and JG-MOF

ELM-11 has a stacked-layer structure in which the interlayer width expands at gate opening, and a volume expansion ratio that reaches approximately 30% (Figure 6a).²⁶ JG-MOF has an interpenetrating jungle-gym structure in which tilted linkers straighten to generate pores at gate opening, causing a volume expansion of approximately 10% (Figure 6b).⁴⁸ These two MOFs exhibit different types of flexibility; however, the structural transition of JG-MOF is also considered to proceed in a layer-by-layer manner, as the tilted linkers belonging to

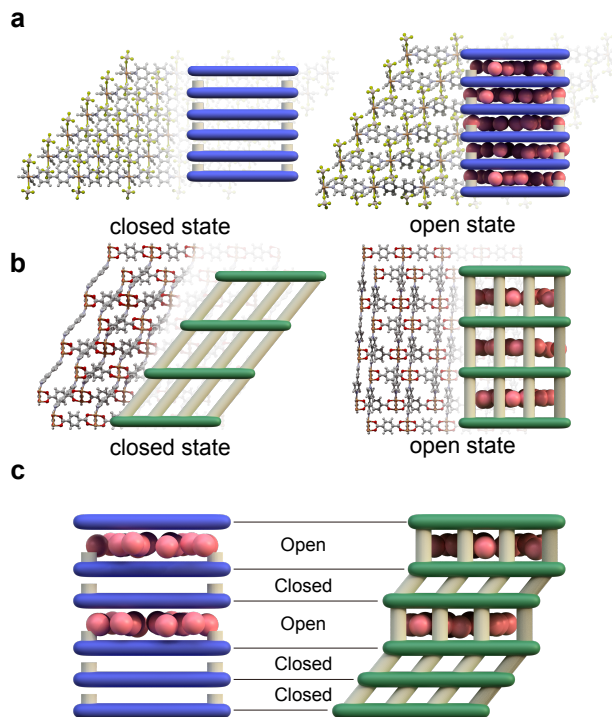


Figure 6: Atomistic structures of (a) ELM-11 and (b) JG-MOF in the closed and open states. (c) Schematics of a layer-by-layer structural transition in the particles.

one floor must cooperate with one other when straightening, as illustrated in Figure 6c. Therefore, ELM-11 and JG-MOF can be regarded as real systems of the models **L** and **S** discussed in section 3.2.1, respectively. Notably, the slacking phenomenon is influenced by the actual degree of volume expansion and not the volume expansion ratio; thus, the particle size is also a determinant of the extent of slacking. Therefore, we prepared two MOFs with similar particle sizes to compare the effects of the volume expansion ratio (see section S5).

Figures 7a and 7b show the CO₂ adsorption isotherms on ELM-11 and JG-MOF in both powder and pellet forms. In this study, the pellets were prepared using PVP as the binder (Figures 8a and 8c); however, the slacking phenomenon was also observed when using polyvinyl alcohol as another binder (see section S6). The vertical axes in Figures 7a and 7b represent the amount adsorbed per gram of MOF, not per gram of pellets. While the stepwise change in the ELM-11 pellet became more heavily smeared compared to that of the

powder sample owing to its higher w_{PVP} [g-MOF/(g-PVP+g-MOF)], the JG-MOF pellet maintained most of its original step shape, regardless of the PVP content. For example, comparing pellets with $w_{\text{PVP}} = 0.3$, the amount adsorbed on the ELM-11 pellet at 100 kPa was less than half of the original capacity, whereas the JG-MOF pellet captured the same amount of CO_2 as the powder. This result indicates that owing to the external force from the binder molecules, the ELM-11 particles in the pellets were in an intermediate open state consisting of both closed and open layers. In fact, the in-situ X-ray diffraction (XRD) measurements for the ELM-11 pellet at 100 kPa of CO_2 and 273 K revealed that its pattern contained peaks belonging to the open and closed states (Figure 7c). In contrast, the in-situ XRD pattern of the JG-MOF pellet at 100 kPa of CO_2 and 263 K was almost identical to that of the powder form, exhibiting peaks in the fully open state (Figure 7d).

Comparing the pellets with $w_{\text{PVP}} = 0.1$, while the ELM-11 pellet spontaneously collapsed during the adsorption measurements, the JG-MOF pellet retained its form (Figure 8). This outcome implies that the force required to maintain the pellet morphology against the volume expansion of internal particles diminishes as the PVP content decreases. Furthermore, the critical threshold of PVP content for sustaining the pellet shape is dependent on the volume expansion ratio of the enclosed MOFs.

A previous study reported that the second adsorption measurement for the ELM-11 pellet resulted in a sharper step than the first measurement, as shown in Figure 9a.⁴¹ This implies that the significant volume expansion ratio of ELM-11 causes PVP molecules to be displaced, which do not completely return to their initial locations even as ELM-11 undergoes shrinkage owing to gate closing. Consequently, a smaller force was exerted on ELM-11 during the gate opening for the second time. In contrast, the adsorption isotherm on the JG-MOF pellet was found to have perfect reproducibility in the repeated measurement (Figure 9b). This suggests that the small volume expansion ratio causes the external force to be retained in the region of elastic deformation, allowing the polymer molecules to return to their original positions.

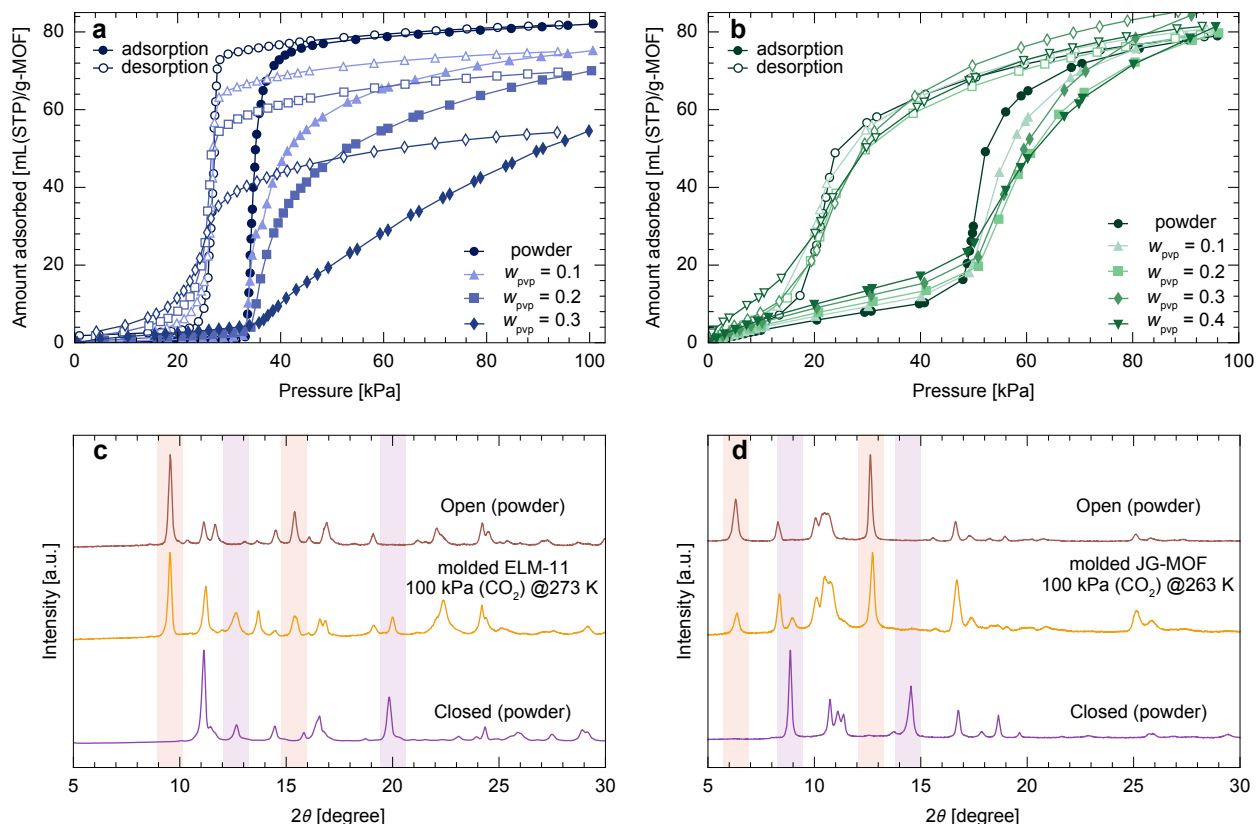


Figure 7: CO₂ adsorption isotherms (a) on molded ELM-11 at 273 K and (b) on molded JG-MOF at 263 K. (c) In situ XRD patterns of the ELM-11 powder in vacuo (closed) and at 100 kPa of CO₂ (open) at 273 K and that of the ELM-11 pellet at 100 kPa of CO₂ and 273 K.⁴¹ The peaks originating from the open state are highlighted in red, and those from the closed state in purple. (d) In-situ XRD data of JG-MOF corresponding to (c), where the temperature was set to 263 K.

Additionally, we investigated the adsorption isotherms on pellets crushed by milling. Although the slight decrease in the amount adsorbed suggests amorphization of the crystalline structure by milling, the adsorption performance of ELM-11 increased owing to the release of the polymer binders surrounding the ELM-11 particles (see section S7). The negligibly small effect of this for JG-MOF confirms that the slacking of the gate adsorption is not because of some chemical effect of PVP, but because of a physical effect depending on the volume expansion ratio of the MOFs. These observations are consistent with the theoretical analysis in section 3.2.1, thereby leading to the conclusion that the slacking of gate adsorption is

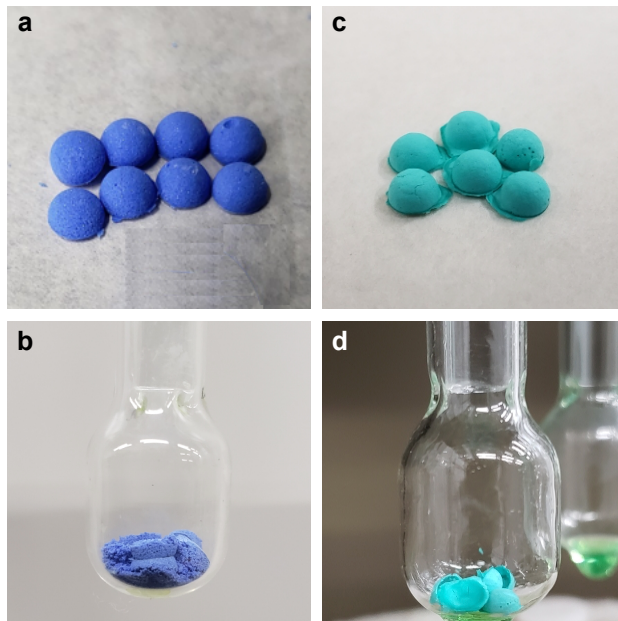


Figure 8: Images of the ELM-11 pellet with $w_{\text{PVP}} = 0.1$ (a) before and (b) after the CO_2 adsorption measurement. Images of the JG-MOF pellet with $w_{\text{PVP}} = 0.1$ (c) before and (d) after the CO_2 adsorption measurement.

indeed induced by the external force and that the extent of slacking is contingent upon the volume expansion ratio.

4 Conclusion

This study utilized a combination of molecular simulations and experimental investigations to elucidate the mechanism behind the slacking of gate adsorption on flexible MOFs and explore the effect of external forces on their adsorption performance. The first part of this study involved performing GCMD simulations and directly calculating the free energy profile of the MOF particle model to explain the slacking phenomenon without any assumptions. The simulations revealed that equation 6, which is a simplified expression proposed under the plausible sequential mode, contains two primary flaws; however, their impact on the discussion of the slacking phenomenon is insignificant. The results confirm that the assumption about the structural transition of flexible motifs within the MOF particle was validated and

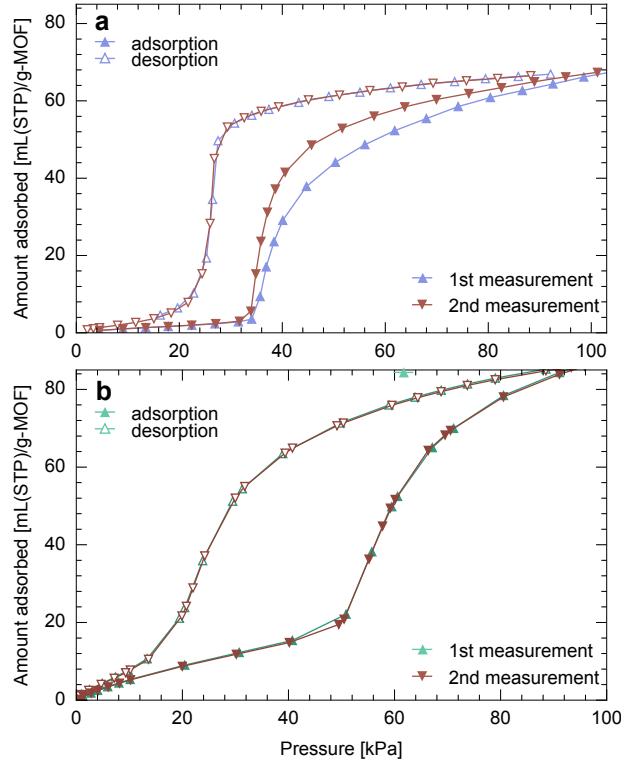


Figure 9: (a) First and second CO_2 adsorption isotherms on the ELM-11 pellet with $w_{\text{PVP}} = 0.2$ at 273 K and (b) those on the JG-MOF pellets with $w_{\text{PVP}} = 0.31$ at 263 K .

that the GCMC approach is useful to explain the slacking phenomenon.

The second part of the study examined the impact of external forces on the adsorption performance of flexible MOFs using two different particle models with varying volume expansion ratios. The results showed that slightly deformed flexible MOFs could effectively suppress smeared gate adsorption when in pellet form. Additionally, two types of flexible MOFs, ELM-11 and JG-MOF with volume expansion ratios of 30% and 10%, respectively, were fabricated into pellets, and their adsorption characteristics were thoroughly investigated. The findings indicated that the JG-MOF pellets with a smaller volume expansion ratio could mitigate the slacking of gate adsorption. These observations are consistent with the theoretical discussion, which concluded that the slacking of gate adsorption is indeed caused by external forces and that the degree of slacking is influenced by the volume expansion ratio of the MOF.

Notably, this study does not claim the superiority of JG-MOF or other MOFs that show small expansions. This is because the structural deformability of flexible MOFs is also related to their unique intrinsic thermal management capabilities: flexible MOFs can deform their structures by absorbing the heat of adsorption, allowing their adsorption performances to be maintained at an elevated level even under non-isothermal conditions which can be found in pressure swing adsorption processes.^{50–52} The impact is more noticeable in a MOF that demonstrates large structural deformation. Therefore, in some instances, it may be beneficial to permit some extent of slacking and prioritize the inherent thermal management capability. In other words, striking a balance between their sharp increases in adsorption and innate thermal management ability is vital when considering the industrial application of flexible MOFs. The development of sophisticated pelletizing methods to reduce the forces on MOF particles in the pellets is also vital; for instance, this can be achieved by loading the MOF particles onto a support.

Although this study regarded external force as having a negative effect on the adsorption performance, this effect can be positively utilized in a potential application of gate closing induced by an external force, as proposed by Mason et al.⁵⁰ The findings of this study can also provide guidance for this gate-enclosing process. For example, although MOFs with larger volume expansion can desorb more guest molecules with a smaller force, desorption of all guest molecules is challenging.

Overall, this study provides crucial insights into the mechanism behind smeared gate adsorption and highlights the importance of considering external forces and volume expansion when shaping MOFs for practical applications. In an industrial process, such powder samples should receive an external force not only by polymer binders in a pellet but also as vertical stresses from the column wall or loads on the sample itself. The findings of this study can guide the use of MOFs while maintaining high adsorption performance and efficiency, bringing us closer to maximizing the properties of these materials for various industrial applications.

5 Experimental and Computational Methods

5.1 Simplified stacked-layer model

We used a toy model that simplifies the stacked-layer structure developed in our previous studies.^{45,46} In this model, the square-grid structure of ELM-11, consisting of copper and bpy, was represented by a smeared-atom wall, and the pillar molecule (BF_4) was expressed as a single atom with a position offset, z_p , in the stacking direction from the center of the layer (Figure 1a). The density of the pillars was set to $0.01\sigma_{\text{gg}}^{-2}$, meaning that each unit cell contained one pillar. The layer–layer, layer–pillar, and pillar–pillar interaction potentials were derived from area integrals of the LJ 10-4, LJ 10-4, and LJ 12-6 potentials, respectively. The guest–layer and guest–guest interaction potentials were derived from the LJ 10-4 and LJ 12-6 potentials, respectively. All potentials were cut and shifted by a distance of $5\sigma_{\text{gg}}$. The LJ parameters (σ_{gg} , $\varepsilon_{\text{gg}}/k_{\text{B}}$) for the layer, pillar, and guest were set to (0.34 nm, 28 K), (0.341 nm, 119.8 K), and (0.341 nm, 119.8 K), respectively, and the cross parameters were calculated according to the Lorentz–Berthelot mixing rules. Further details of the simplified model can be found elsewhere.^{41,45,46}

5.2 Free energy calculations

5.2.1 GCMC approach

GCMC simulations were conducted to obtain the adsorption isotherms for the simulation boxes depicted in Figure 1b with various interlayer widths ($1.70\sigma_{\text{gg}}\text{--}2.05\sigma_{\text{gg}}$) in steps of $0.01\sigma_{\text{gg}}$. Periodic boundary conditions were applied in all directions, and three trial moves, that is, displacement, insertion, and deletion of guest molecules, were performed with the same probabilities. The temperature was set to 119.8 K ($= \varepsilon_{\text{gg}}/k_{\text{B}}$). The lengths of the simulation runs were at least 2.5×10^7 steps and 2×10^8 steps for equilibrium and sampling, respectively. The relationship between the bulk gas pressure and chemical potential was obtained from the Johnson–Zollweg–Gubbins (JZG) equation of state for the LJ fluid.⁵³

According to equation 2, the stabilization factor due to guest adsorption, ω_{guest} , was evaluated by integrating the adsorption isotherms obtained from GCMC simulations. The Δf_{host} can be divided into two terms; the internal energy change Δu_{host} and the entropy change Δs_{host} . In this study, we considered Δf_{host} as only Δu_{host} for simplicity and calculated it as the sum of the potential energies between the simplified layers. Subsequently, $\Delta \omega_{\text{os}}$ was evaluated using equation 3, and $\Delta \Omega_{\text{os}}$ was estimated using equation 6. The simulations were performed using our in-house code.

5.2.2 GCMD approach

GCMD simulations^{54,55} were performed for the simulation boxes depicted in Figure 1c, where periodic boundary conditions were applied in all directions. This simulation is similar to the GCMC simulation described in section 5.2.1 but includes an *NVT*-MD simulation as a trial move of the Monte Carlo simulation. In the *NVT*-MD trial, 1000 MD steps with a time interval of 1 fs were performed to allow the movement of the layers and guest molecules by controlling the temperature using a Nose–Hoover thermostat. The ratios for each trial move were set as follows: 0.4995 for insertion, 0.4995 for deletion, and 0.001 for the *NVT*-MD trial. A 1×10^7 MC step was conducted to equilibrate the system (see section S8). Subsequently, in the last 5×10^6 MD steps, a long-term (3×10^5 steps) MD simulation was conducted every 10,000 MC steps to sample the normal stress in the *z*-direction (σ_z), the amount of gas adsorbed in each interlayer ($n_{\text{ads},i}$), and the interlayer widths as functions of the particle thickness (D) and bulk gas pressure (P) which was in turn derived from μ according to the JZG equation. σ_z was computed by

$$\sigma_z = \frac{1}{100\sigma_{\text{gg}}^2 D} \langle \sum_i m_i v_{zi} \rangle_D + \frac{1}{100\sigma_{\text{gg}}^2 D} \langle \sum_{i>j} z_{ij} F_{zij} \rangle_D \quad (7)$$

where m_i is the mass of atom i , v_{zi} is the velocity in the z -direction of atom i , z_{ij} is the distance in the z -direction between atoms i and j , F_{zij} is the force exerted in the z -direction

between atoms i and j , and $\langle \rangle$ is the ensemble average of the values. $\Delta\Omega_{\text{os}}$ is then computed as

$$\Delta\Omega_{\text{os}} = -100\sigma_{\text{gg}}^2 \int_{D_i}^{D_j} \langle P_z \rangle_D dD \quad (8)$$

Our in-house code was used to perform the simulations.

5.3 Preparation of MOFs

Pre-ELM-11 (hydrated form of ELM-11) was purchased from Tokyo Chemical Industry Co, Ltd. JG-MOF was synthesized by the following procedures.^{48,56} First, 0.21 g of terephthalic acid (98.0%, Sigma-Aldrich Co. LLC.) and 1.50 mL of formic acid (98%, Sigma-Aldrich Co. LLC.) were dissolved in 200 mL of methanol (99.8%, Kishida Chemical Co., Ltd.) and mixed at 313 K in a hot bath. After complete dissolution (approximately 30 min to 1 h), 0.31 g of copper(II) sulfate pentahydrate ($\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$, 98.5%, Kanto Chemical Co., Inc.) dissolved in 10 mL of methanol was mixed with the prepared solution using a magnetic stirrer, and the mixture was allowed to react for 72 h at 313 K. The supernatant was then removed by centrifugation at 3500 rpm, affording greenish blue particles, which are precursors of JG-MOF with a two-dimensional molecular structure.^{57,58} The precursor particles were again distributed in 50 mL of methanol and then mixed with 0.10 g of 4,4'-bipyridine (98.0%, Tokyo Chemical Industry Co., Ltd.) dissolved in 8 mL of methanol for 48 h at 313 K. Centrifugation and washing of the precipitate with methanol were repeated three times, and the collected yellow green particles were dried under vacuum. Notes on the synthesis are given in section S9. All chemicals were used as received.

5.4 Shaping of MOF

ELM-11 and JG-MOF were molded using PVP (average molecular weight: 360,000, Sigma-Aldrich Co. LLC.) as a binder. PVP was dissolved in solvents (ELM-11: deionized water prepared using an arium[®] mini plus (Sartorius) water purification system; JG-MOF:

methanol) by hand-stirring slowly on a hot plate at approximately 333 K to ensure no bubbles in the slurry. After the PVP slurry cooled down to room temperature (approximately 297 K), MOF powder was added to the corresponding slurry. The mixture was injected into hemispherical molds (diameter = 6 mm) on a silicone sheet and dried in a thermostatic oven at 308 K for 12 h. The weight fractions of PVP were varied (w_{PVP}) and their influence on gate adsorption was observed. The amount of solvent was approximately 0.4 mL per 250 mg of the mixture of PVP and MOFs.

5.5 CO₂ adsorption isotherm measurement

The adsorption isotherms of CO₂ on ELM-11 pellets at 273 K and JG-MOF pellets at 263 K were measured using the BELSORP-mini and BELSORP-max (Microtrac BEL Co.) equipped with a chiller (CL-80R, Taitec). Before the measurements, pelletized samples were heated under a pressure of less than 0.1 Pa (ELM-11, at 373 K for 12 h; JG-MOF, at 423 K for 2 h) to transform into guest-free MOFs. When remeasuring the adsorption isotherms on the same samples, the samples were pretreated under the same conditions.

5.6 Characterization

We analyzed the sizes and thicknesses of the MOFs using a 3D laser scanning microscope (VK-X100) and the observation/analysis software VK-H1XM (Keyence). The in-situ XRD patterns of ELM-11 and JG-MOF pellets in vacuo and under CO₂ pressure were measured using a SmartLab instrument with Cu K α radiation (Rigaku Co.), which had a cryostat equipped with a single-stage Gifford–McMahon refrigerator connected to a BELSORP-18 volume adsorption apparatus (Microtrac BEL Co.). The pellets were molded into a sheet shape for application in Bragg–Brentano optics. The sample cell temperature was maintained within ± 0.01 K during the XRD measurements.

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Supporting Information Available

The Supporting Information is available free of charge on the ACS Publications website.

- Configurational entropy; Comparison of the energy barrier between the GCMC approach and the GCMD approach; Simulation details; Effect of external potential on a few layers-particle; Synthesis results of JG-MOF; Adsorption isotherm on pellets with different binders; Adsorption isotherm on crushed pellets; Simulation results to confirm the equilibrium; Notes on the synthesis of JG-MOF (PDF)

References

- (1) Nations, U. THE 17 GOALS | Sustainable Development (accessed 27 November 2022). <https://sdgs.un.org/goals>.
- (2) Sholl, D. S.; Lively, R. P. Seven Chemical Separations to Change the World. *Nature* **2016**, *532*, 435–437.
- (3) Kondo, M.; Yishitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. Three-Dimensional Framework with Channeling Cavities for Small Molecules: [M₂(4,4'-

- bpy) $_3$ (NO $_3$) $_4$] $_x$ H $_2$ O $_n$ (M = Co, Ni, Zn). *Angew. Chem. Int. Eng. Engl.* **1997**, *36*, 1725–1727.
- (4) Kitagawa, S.; Kondo, M. Functional Micropore Chemistry of Crystalline Metal Complex-Assembled Compounds. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739–1753.
 - (5) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. Synthetic Strategies, Structure Patterns, and Emerging Properties in the Chemistry of Modular Porous Solids. *Acc. Chem. Res.* **1998**, *31*, 474–484.
 - (6) Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. Design and Synthesis of an Exceptionally Stable and Highly Porous Metal–Organic Framework. *Nature* **1999**, *402*, 276–279.
 - (7) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal—Organic Frameworks. *Science* **2013**, *341*, 1230444.
 - (8) Gu, C.; Hosono, N.; Zheng, J.-J.; Sato, Y.; Kusaka, S.; Sakaki, S.; Kitagawa, S. Design and Control of Gas Diffusion Process in a Nanoporous Soft Crystal. *Science* **2019**, *363*, 387–391.
 - (9) Ehrling, S.; Mendt, M.; Senkovska, I.; Evans, J. D.; Bon, V.; Petkov, P.; Ehrling, C.; Walenszus, F.; Pöppl, A.; Kaskel, S. Tailoring the Adsorption-Induced Flexibility of a Pillared Layer Metal–Organic Framework DUT-8(Ni) by Cobalt Substitution. *Chem. Mater.* **2020**, *32*, 5670–5681.
 - (10) Miura, H.; Bon, V.; Senkovska, I.; Ehrling, S.; Bönisch, N.; Mäder, G.; Grünzner, S.; Khadiev, A.; Novikov, D.; Maity, K.; Richter, A.; Kaskel, S. Spatiotemporal Design of the Metal-organic Framework DUT-8(M). *Adv. Mater.* **2023**, *35*, 2207741.
 - (11) Macreadie, L. K.; Babarao, R.; Setter, C. J.; Lee, S. J.; Qazvini, O. T.; Seeber, A. J.; Tsanaktsidis, J.; Telfer, S. G.; Batten, S. R.; Hill, M. R. Enhancing Multicomponent

- Metal–Organic Frameworks for Low Pressure Liquid Organic Hydrogen Carrier Separations. *Angew. Chem. Int. Ed.* **2020**, *59*, 6090–6098.
- (12) Macreadie, L. K.; Idrees, K. B.; Smoljan, C. S.; Fahra, O. K. Expanding Linker Dimensionality in Metal-organic Frameworks for sub-Angstrom Pore Control for Separation Applications. *Angew. Chem. Int. Ed.* **2023**, *e202304094*.
- (13) Fan, W.; Wang, Y.; Xiao, Z.; Huang, Z.; Dai, F.; Wang, R.; Sun, D. Two-Dimensional Cobalt Metal-Organic Frameworks for Efficient C₃H₆/CH₄ and C₃H₈/CH₄ Hydrocarbon Separation. *Chin. Chem. Lett.* **2018**, *29*, 865–868.
- (14) Zhao, M.; Huang, S.; Fu, Q.; Li, W.; Guo, R.; Yao, Q.; Wang, F.; Cui, P.; Tung, C.-H.; Sun, D. Ambient Chemical Fixation of CO₂ Using a Robust Ag₂₇ Cluster-Based Two-Dimensional Metal–Organic Framework. *Angew. Chem. Int. Ed.* **2020**, *59*, 20031–20036.
- (15) Horike, S.; Shimomura, S.; Kitagawa, S. Soft Porous Crystals. *Nature Chem.* **2009**, *1*, 695–704.
- (16) Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R. A. Flexible Metal–Organic Frameworks. *Chem. Soc. Rev.* **2014**, *43*, 6062.
- (17) Chang, Z.; Yang, D.-H.; Xu, J.; Hu, T.-L.; Bu, X.-H. Flexible Metal–Organic Framework: Recent Advances and Potential Applications. *Adv. Mater.* **2015**, *27*, 5432–5441.
- (18) Krause, S.; Hosono, N.; Kitagawa, S. Chemistry of Soft Porous Crystals: Structural Dynamics and Gas Adsorption Properties. *Angew. Chem. Int. Ed.* **2020a**, *59*, 15325–15341.
- (19) Li, Y.; Wang, Y.; Fan, W.; Sun, D. Flexible Metal–Organic Frameworks for Gas Storage and Separation. **2022**, *51*, 4608.

- (20) Bonneau, M.; Lavenn, C.; Zheng, J.-J.; Legrand, A.; Ogawa, T.; Sugimoto, K.; Coudert, F.-X.; Reau, R.; Sakaki, S.; Otake, K.-i.; Kitagawa, S. Tunable Acetylene Sorption by Flexible Catenated Metal–Organic Frameworks. *Nature Chem.* **2022**, *14*, 816–822.
- (21) Chen, B.; Liang, C.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yagji, O. M.; Dai, S. A Microporous Metal–Organic Framework for Gas–Chromatographic Separation of Alkanes. *Angew. Chem. Int. Ed.* **2006**, *45*, 1390–1393.
- (22) Gu, Y.; Zheng, J.-J.; Otake, K.-i.; Sugimoto, K.; Hosono, N.; Sakaki, S.; Kitagawa, S. Structural-Deformation-Energy-Modulation Strategy in a Soft Porous Coordination Polymer with an Interpenetrated Framework. *Angew. Chem.* **2020**, *132*, 15647–15651.
- (23) Dong, Q.; Zhang, X.; Liu, S.; Lin, R.-B.; Guo, Y.; Ma, Y.; Yonezu, A.; Krishna, R.; Liu, G.; Duan, J.; Matsuda, R.; Jin, W.; Chen, B. Tuning Gate-Opening of a Flexible Metal–Organic Framework for Ternary Gas Sieving Separation. *Angew. Chem. Int. Ed.* **2020**, *59*, 22756–22762.
- (24) Song, B.-Q.; Yang, Q.-Y.; Wang, S.-Q.; Vandichel, M.; Kumar, A.; Crowley, C.; Kumar, N.; Dong, C.-H.; GasconPerez, V.; Lusi, M.; Wu, H.; Zhou, W.; Zaworotko, M. J. Reversible Switching between Nanoporous and Porous Phases of New SIFSIX Coordination Network Induced by a Flexible Linker Ligand. *J. Am. Chem. Soc.* **2020**, *142*, 696–6901.
- (25) Li, D.; Kaneko, K. Hydrogen Bond-Regulated Microporous Nature of Copper Complex-Assembled Microcrystals. *Chem. Phys. Lett.* **2001**, *335*, 50–56.
- (26) Kondo, A.; Noguchi, H.; Ohnishi, S.; Kajiro, H.; Tohdoh, A.; Hattori, Y.; Xu, W.-C.; Tanaka, H.; Kanoh, H.; Kaneko, K. Novel Expansion/Shrinkage Modulation of 2D Layered MOF Triggered by Clathrate Formation with CO₂ Molecules. *Nano Lett.* **2006**, *6*, 2581–2584.

- (27) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. A Chemically Functionalizable Nanoporous Material $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$. *Science* **1999**, *283*, 1148–1150.
- (28) Hiraide, S.; Sakanaka, Y.; Kajiro, S.; Kawaguchi, S.; Miyahara, M. T.; Tanaka, H. High-Throughput Gas Separation by Flexible Metal–Organic Frameworks with Fast Gating and Thermal Management Capabilities. *Nat. Commun.* **2020**, *11*, 3867.
- (29) Peterson, G. W.; DeCoste, J. B.; Glover, T. G.; Huang, Y.; Jasuja, H.; Walton, K. S. Effect of Pelletization Pressure on the Physical and Chemical Properties of the Metal–Organic Frameworks $\text{Cu}_3(\text{BTC})_2$ and UiO-66. *Microporous Mesoporous Mater.* **2013**, *179*, 48–53.
- (30) Bazer-Bachi, D.; Assié, V.; Harbuzaru, B.; Falk, V. Towards Industrial Use of Metal–Organic Framework: Impact of Shaping on the MOF Properties. *Powder Technol.* **2014**, *255*, 52–59.
- (31) Zhu, H.; Zhang, Q.; Zhu, S. Alginate Hydrogel: A Shapeable and Versatile Platform for in Situ Preparation of Metal–Organic Framework–Polymer Composites. *ACS Appl. Mater. Interfaces* **2016**, *8*, 17395–17401.
- (32) Valizadeh, B.; Nguyen, T. N.; Stylianou, K. C. Shape Engineering of Metal–Organic Frameworks. *Polyhedron* **2018**, *145*, 1–15.
- (33) Tsalaporta, E.; Macelroy, J. D. A Comparative Study of the Physical and Chemical Properties of Pelletized HKUST-1, ZIF-8, ZIF-67 and UiO-66 Powders. *Heliyon* **2020**, *6*, e04883.
- (34) Wang, Z.; Liu, L.; Li, Z.; Goyal, N.; Du, T.; He, J.; Li, G. K. Shaping of Metal–Organic Frameworks: A Review. *Energy Fuels* **2021**, *36*, 2927–2944.

- (35) Finsy, V.; Ma, L.; Alaerts, L.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. Separation of CO₂/CH₄ Mixtures with the MIL-53(Al) Metal–Organic Framework. *Microporous Mesoporous Mater.* **2009**, *120*, 221–227.
- (36) Kajiro, H.; Kondo, A.; Kaneko, K.; Kanoh, H. Flexible Two-Dimensional Square-Grid Coordination Polymers: Structures and Functions. *Int. J. Mol. Sci.* **2010**, *11*, 3803–3845.
- (37) Remy, T.; Ma, L.; Maes, M.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. Vapor-Phase Adsorption and Separation of Ethylbenzene and Styrene on the Metal–Organic Frameworks MIL-47 and MIL-53(Al). *Ind. Eng. Chem. Res.* **2012**, *51*, 14824–14833.
- (38) Kristen, M.; Schmitz, J. V.; Siegel, J.; Smith, C. E.; Kaspereit, M.; Hartmann, M. Shaping of Flexible Metal–Organic Frameworks: Combining Macroscopic Stability and Framework Flexibility. *Eur. J. Inorg. Chem.* **2019**, 4700–4709.
- (39) Kundu, T.; Shah, B. B.; Bolinois, L.; Zhao, D. Functionalization-Induced Breathing Control in Metal–Organic Frameworks for Methane Storage with High Deliverable Capacity. *Chem. Mater.* **2019**, *31*, 2842–2847.
- (40) Ohsaki, S.; Nakahara, Y.; Nakamura, H.; Watano, S. Flowability Improvement of Soft Metal–Organic Framework Particles by Wet Granulation. *Microporous Mesoporous Mater.* **2020**, *293*, 109785.
- (41) Hiraide, S.; Arima, H.; Tanaka, H.; Miyahara, M. T. Slacking of Gate Adsorption Behavior on Metal–Organic Frameworks under an External Force. *ACS Appl. Mater. Interfaces* **2021**, *13*, 30213–30223.
- (42) Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Férey, G. A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration. *Chem. Eur. J.* **2004**, *10*, 1373–1382.

- (43) Coudert, F.-X.; Jeffroy, M.; Fuchs, A. H.; Boutin, A.; Mellot-Draznieks, C. Thermodynamics of Guest-Induced Structural Transitions in Hybrid Organic-Inorganic Framework. *J. Am. Chem. Soc.* **2008**, *130*, 14294–14302.
- (44) Watanabe, S.; Sugiyama, H.; Adachi, H.; Tanaka, H.; Minoru, M. T. Free Energy Analysis for Adsorption-Induced Lattice Transition of Flexible Coordination Framework. *J. Chem. Phys.* **2009**, *130*, 164707.
- (45) Numaguchi, R.; Tanaka, H.; Watanabe, S.; Miyahara, M. T. Simulation Study for Adsorption-Induced Structural Transition in Stacked-Layer Porous Coordination Polymers- Equilibrium and Hysteretic Adsorption Behaviors. *J. Chem. Phys.* **2013**, *138*, 054708.
- (46) Numaguchi, R.; Tanaka, H.; Watanabe, S.; Miyahara, M. T. Dependence of Adsorption-Induced Structural Transition on Framework Structure of Porous Coordination Polymers. *J. Chem. Phys.* **2014**, *140*, 044707.
- (47) Seki, K.; Takamizawa, S.; Mori, W. Design and Gas Adsorption Property of a Three-Dimensional Coordination Polymer with a Stable and Highly Porous Framework. *Chem. Lett.* **2001**, *30*, 332–333.
- (48) Sakata, Y.; Furukawa, S.; Kondo, M.; Horike, N.; Takashima, Y.; Uehara, H.; Louvain, N.; Meilikhov, M.; Tsuruoka, T.; Isoda, S.; Kosaka, W.; Sakata, O.; Kitagawa, S. Shape-Memory Nanopores Induced in Coordination Frameworks by Crystal Downsizing. *Science* **2013**, *339*, 193–196.
- (49) Jagla, E. A. Minimum Energy Configurations of Repelling Particles in Two Dimensions. *J. Chem. Phys.* **1999**, *110*, 451.
- (50) Mason, J. A.; Oktawiec, J.; Taylor, M. K.; Hudson, M. R.; Rodriguez, J.; Bachman, J. E.; Gonzalez, M. I.; Cervellino, A.; Guagliardi, A.; Brown, C. M.;

- Llewellyn, P. L.; Masciocchi, N.; Long, J. R. Methane Storage in Flexible Metal–Organic Frameworks with Intrinsic Thermal Management. *Nature* **2015**, *527*, 357.
- (51) Hiraide, S.; Tanaka, H.; Ishikawa, N.; Miyahara, M. T. Intrinsic Thermal Management Capabilities of Flexible Metal–Organic Frameworks for Carbon Dioxide Separation and Capture. *ACS Appl. Mater. Interfaces* **2017**, *46*, 41066–41077.
- (52) Peng, J.; Lie, Z.; Wu, Y.; Xian, S.; Li, Z. High-Performance Selective CO₂ Capture on a Stable and Flexible Metal–Organic Framework via Discriminatory Gate-Opening Effect. *ACS Appl. Mater. Interfaces* **2022**, *14*, 21089–21097.
- (53) Johnson, J. K.; Zollweg, J. A.; Gubbins, K. E. The Lennard Jones Equation of State Revisited. *Mol. Phys.* **1993**, *78*, 591–618.
- (54) Ghoufi, A.; Maurin, G. Hybrid Monte Carlo Simulations Combined with a Phase Mixture Model to Predict the Structural Transitions of a Porous Metal–Organic Framework Material upon Adsorption of Guest Molecules. *J. Phys. Chem. C* **2010**, *114*, 6496–6502.
- (55) Goeminne, R.; Krause, S.; Kaskel, S.; Verstraelen, T.; Evans, J. D. Charting the Complete Thermodynamic Landscape of Gas Adsorption for a Responsive Metal–Organic Framework. *J. Am. Chem. Soc.* **2021**, *143*, 4143–4147.
- (56) Seki, K. Dynamic Channels of a Porous Coordination Polymer Responding to External Stimuli. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1968–1971.
- (57) Mori, W.; Inoue, F.; Yoshida, K.; Nakayama, H.; Takamizawa, S.; Kishita, M. Synthesis of New Adsorbent Copper(II) Terephthalate. *Chem. Lett.* **1997**, *26*, 1219–1220.
- (58) Carson, C. G.; Hardcastle, K.; Schwartz, J.; Liu, X.; Hoffmann, C.; Gehardt, R. A.; Tannenbaum, R. Synthesis and Structure Characterization of Copper Terephthalate Metal–Organic Framework. *Eur. J. Inorg. Chem.* **2009**, *16*, 2338–2343.

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