

Atomic Force Microscopy Strategies for Capturing Guest-Induced Structural Transitions in Single Flexible Metal–Organic Framework Particles

Homare Arima,[†] Shotaro Hiraide,^{*,†,‡} Hiroyuki Nagano,[†] Leila Abylgazina,[¶] Irena Senkovska,[¶] Günter K. Auernhammer,[§] Andreas Fery,^{§,||} Stefan Kaskel,[¶] and Satoshi Watanabe^{*,†}

[†]*Department of Chemical Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan*

[‡]*Institute for Aqua Regeneration, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan*

[¶]*Inorganic Chemistry I, Technische Universität Dresden, Bergstrasse 66, 01069 Dresden, Germany*

[§]*Division of Physical Chemistry and Polymer Physics, Leibniz Institut f. Polymerforschung Dresden, Hohe Str. 6, 01069 Dresden, Germany*

^{||}*Physical Chemistry of Polymeric Materials, Technische Universität Dresden, Bergstrasse 66, 01062 Dresden, Germany*

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

Abstract

Flexible metal–organic frameworks (MOFs) exhibit stepped adsorption isotherms due to structural transitions between narrow-pore (np) and large-pore (lp) states. This

characteristic stepwise uptake at a certain pressure results in adsorptive high working capacities, making these materials highly effective for energy-efficient gas storage and separation processes. The transition pressure, which is key to enhancing separation efficiency, can be tuned by varying the particle size of flexible MOFs. However, a comprehensive understanding of size-dependent effects has been limited due to particle size distribution in samples. Conventional adsorption measurements provide only averaged isotherms for powder samples, and analyzing the size effect at the single-particle level requires experimental techniques that can capture transition behavior of individual particles separately. This study utilized atomic force microscopy coupled with thermodynamic analysis to investigate guest-induced structural transitions. Force application to a MOF particle triggered a structural change from the lp to np state, generating force profiles that were analyzed to uncover the underlying transition mechanisms and calculate transition pressures using free energy analysis. The evaluation revealed distinct transition mechanisms for two flexible MOFs: ELM-12 exhibited a step-by-step mechanism, while DUT-8(Ni) displayed an all-at-once transition. Force profile analysis enabled precise determination of the free energy changes and transition pressures for individual particles. This approach provided detailed insights into the transition mechanisms and their impact on overall adsorption isotherms, offering a novel perspective on how single-particle behavior influences bulk material performance.

Introduction

Since the international union of pure and applied chemistry (IUPAC) first addressed adsorption in gas/solid systems and introduced the categorization of adsorption isotherms,¹ the past four decades have witnessed remarkable advancements in adsorption technology, particularly with the development of innovative adsorbents such as metal-organic frameworks (MOFs).^{2,3} MOFs are characterized by well-defined structures and high design flexibility, enabling large adsorption capacities and exceptional selectivity. These properties can be tailored by vary-

ing the combination of metal and organic components, allowing for the design of MOFs optimized for specific separation systems.⁴ The significant progress in adsorption technology prompted the IUPAC to revisit and update its categorization of adsorption isotherms.⁵ In its report, the IUPAC noted that structural transformations are observed in some MOFs and their sorption behavior is not easy to interpret. Such MOFs, referred to as flexible MOFs, undergo structural transitions from narrow-pore (np) to large-pore (lp) states and vice versa in response to guest molecule adsorption/desorption, respectively.^{6–8} This guest-induced structural transition, known as “gate adsorption” or “breathing,” occurs at specific guest pressures, resulting in stepped adsorption isotherms. The high working capacity near the transition pressure positions flexible MOFs as promising materials for energy-efficient processes. While understanding their sorption behavior is crucial for industrial applications, it remains challenging to interpret and continues to be a subject of active research and debate.

Transition pressures are critical variables in separation processes involving flexible MOFs and must be optimized based on the gas composition of the target system. These pressures vary depending on the gas type and the specific combination of metal and organic components. Coudert et al.⁹ proposed a thermodynamic theory of guest-induced structural transitions, where host-framework deformation creates pore spaces capable of adsorbing guest molecules, providing a comprehensive understanding of these phenomena. The transition occurs when the destabilization caused by the structural change is balanced by the stabilization due to guest adsorption. This theory has been extensively applied to elucidate the distinctive transitions observed in various flexible MOF systems during the adsorption and desorption of guest molecules.^{10–16}

Despite the well-established and widely accepted thermodynamic theory, other factors influencing adsorption behavior remain inadequately understood. One of the most studied factors is the particle size of flexible MOFs;^{17–26} however, these studies primarily relied on adsorption isotherm measurements. Adsorption isotherms are typically measured on pow-

der samples comprising an ensemble of particles with a size distribution, and as such, they represent averaged behaviors across this distribution. Discussing particle-size dependence requires careful observation of transition behavior at the single-particle level. Some researchers have attempted to reveal the transition mechanism within a single MOF particle through computational studies. Triguero et al.²⁷ developed a one-dimensional particle model mimicking the structure of the MIL-53 series and simulated the cooperative transition involving structural distortion. Schaper et al.²⁸ used all-atomic models of breathing-type MOFs to investigate the transition pathways. Vandenhoute et al.²⁹ performed molecular dynamics (MD) simulations of structural deformation in $37 \times 10 \times 37$ unit cells, at a scale comparable to real particles. Notably, all of these studies focused on transitions without guest molecules as an elementary consideration. In contrast, we developed a simplified particle model of elastic layer-structured MOFs (ELMs) to simulate both adsorption and structural transitions simultaneously, using grand canonical Monte Carlo simulation combined with MD simulation.³⁰ The computed free energy profiles validated that the transition within an ELM particle occurs layer by layer, rather than all at once. Zhang et al.^{31,32} also proposed a step-by-step transition (referred to as an aperiodic manner) undergone in various flexible MOF particles with the aid of MD simulations. Despite advances in simulation studies, there is currently no experimental evidence to support the fundamental question of whether guest-induced structural transitions in a single MOF particle occur step by step or all at once. To identify the molecular structures of single MOF crystals, techniques, such as environmental transmission electron microscopy,³³ single crystal X-ray diffraction (XRD) analysis,³⁴ optical microscopy,³⁵ and Raman spectroscopy³⁶ have been proposed for in-situ measurements under increasing guest pressure. However, these methods could not answer the fundamental question regarding transition mechanisms. In this study, we propose using atomic force microscopy (AFM), as an innovative and distinct approach, to probe the individual transition behaviors of submicron MOF particles, combined with thermodynamic analysis of force profiles. A colloidal probe³⁷ applies force to a MOF particle, inducing a structural transition

and producing a corresponding force profile. AFM techniques have been widely used to measure interaction forces,^{38,39} with force profiles revealing not only the mechanical properties of materials but also providing valuable insights into phenomena at the atomic scale. Lim et al.⁴⁰ used AFM to measure solvation forces between two surfaces, quantitatively capturing the force magnitude associated with solvent molecule ordering, thereby shedding light on the underlying phenomenon. Inspired by such pioneering research, this study is the first to apply AFM techniques to capture guest-induced structural transitions. Other researchers have reported the effect of mechanical pressure on MOFs;^{41,42} however, these experiments were conducted on powders, which differ significantly from our focus. The objective of this study is to probe the structural transitions of single particles using AFM, specifically targeting the ethanol (EtOH)–ELM-12 ($[\text{Cu}(\text{bpy})_2(\text{CF}_3\text{SO}_3)_2]_n$; bpy = 4,4'-bipyridine)⁴³ and guest-free DUT-8(Ni) ($[\text{Ni}_2(2,6\text{-ndc})_2(\text{dabco})]_n$; 2,6-ndc = 2,6-naphthalenedicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane)^{44,45} systems. Consequently, the transition behaviors of individual particles were identified.

This paper provides the thermodynamic interpretation of force profiles obtained by AFM, using the gate-type transition theory proposed by Coudert et al.⁹ before showing experimental results. In the following experimental section, we compare the obtained profiles between the ELM-12 and DUT-8(Ni) systems to verify that the profiles represent their respective structural transition behaviors. Good agreement between the theoretical and experimental results confirms that the force profiles accurately reflect the distinct transition mechanisms within the particles, validating the hypothesized mechanisms for both systems. Finally, the transition pressures upon adsorption and desorption of an ELM-12 particle with a specific size are identified at the single-particle level.

Experimental Procedure

Synthesis of MOF materials

ELM-12 was synthesized following the procedure described in prior research.⁴⁶ 0.33 g of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (98.0%, Sigma-Aldrich Co. LLC) was dissolved in 30 mL of deionized water, prepared using an arium[®] mini plus (Sartorius) water purification system. Meanwhile, 0.70 g of 4,4'-bipyridine (98.0%, Tokyo Chemical Industry Co., Ltd.) was dissolved in 30 mL of EtOH (99.5%, Kishida Chemical Co., Ltd.). A central collision-type microreactor⁴⁷ was used to facilitate rapid mixing of the solutions. The two solutions were pumped into the microreactor at a flow rate of 20 mL/min at 278 K, and the reaction solution from the outlet was collected. The precipitate was subjected to suction filtration, washed with EtOH, and the collected blue particles were dried under vacuum. Before adsorption measurements, ELM-12 was heated at 363 K under a pressure of less than 0.1 Pa for 2 h to be activated by transforming into np-state ELM-12.

DUT-8(Ni) was synthesized by modifying the method proposed for submicron-sized particles.²² 0.18 g of 2,6- H_2ndc (99%, Sigma-Aldrich Co. LLC) was dissolved in 25 mL of *N,N*-dimethylformamide (DMF, reagent grade, Fisher Chemical) and the solution was treated in an ultrasonic bath to completely dissolve the solids. Next, 0.24 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (97.0%, Sigma-Aldrich Co. LLC) was added to the solution, followed by 0.30 g of dabco (99%, Sigma-Aldrich Co. LLC). The mixed solution was treated in the ultrasonic bath for 30 min. To obtain the particles of defined shape, the solution was placed in an autoclave at 393 K for 72 h. After cooling, the mother solution was removed by centrifugation, and the resultant particles were washed with DMF several times. Finally, green particles were collected. DUT-8(Ni) was activated using the supercritical CO_2 method.⁴⁸ The synthesized samples were soaked in acetone for two days to replace DMF with acetone, then treated with supercritical CO_2 . The removal of guest molecules from DUT-8(Ni) typically leads to its transformation into the np state, but the gentle activation method preserves the lp state

even without guest molecules. The adsorption behavior of DUT-8(Ni) activated in such a way was compared to that obtained by heating at 373 K overnight. To maintain the guest-free lp state, the sample was stored in a glove box with an Ar flow. All chemicals were used as received.

Characterization

In-situ powder XRD patterns of ELM-12 powder in vacuo and at EtOH partial pressures were measured using a SmartLab instrument with Cu K α radiation (Rigaku Co.). The instrument was equipped with a cryostat containing a single-stage Gifford–McMahon refrigerator, connected to a BELSORP-18 volumetric gas adsorption apparatus (Microtrac BEL Co.). The temperature in the sample cells was maintained within ± 0.01 K during the XRD measurements. XRD patterns of DUT-8(Ni) were collected on an STOE STADI P diffractometer, using Cu K α radiation and a 2D detector (Mythen, Dectris) in transmission geometry using a rotating flatbed sample holder. Scanning electron microscopy (SEM) images were obtained using SU8020 and SU8220 field emission SEMs (Hitachi High-Tech Corp., Japan). EtOH adsorption isotherms on ELM-12 at 298 K and N₂ adsorption on DUT-8(Ni) at 77 K were measured using a BELSORP-max (Microtrac BEL Co.) apparatus equipped with a chiller (CL-80R, Taitec) and a Quadrasorb (Anton Paar GmbH, Austria) apparatus, respectively.

AFM measurement

Force applications were performed using an MFP-3D Origin (Oxford Instruments, UK) with a colloidal probe³⁷ fabricated by attaching a silica microsphere (~ 20 μm , SP-25B Quatron, Fuso Chemical Co., Ltd., Japan) to a cantilever (AD-450-AS, spring constant ~ 450 N/m, Adama Innovations Ltd., Ireland) with epoxy/polyamide reactive adhesive (CA-149, Cemedine Co., Ltd., Japan). The spring constants of each cantilever were accurately calibrated before attaching the silica particle by applying force on the substrate at a rate of 2 $\mu\text{m}/\text{sec}$ for 50 cycles, followed by averaging the spring constant over a 3-minute period using the thermal

noise method.⁴⁹ The colloidal probe was plasma-treated (PDC-32G, Harrick Plasma, USA) prior to use to remove potential contaminants from the silica surface. ELM-12 particles were dispersed in EtOH, and the dispersion was dropped onto a mica substrate and left under vacuum overnight. All measurements were performed in a closed fluid cell (Oxford Instruments, UK) under EtOH partial pressures controlled by a vapor-pressure regulator (me-40DP-2PLW, micro equipment Inc., Japan) and mass flow controllers (CP-SP-1461, Azbil Corp.) at room temperature ($\sim 25^\circ\text{C}$). During the AFM procedure, the ELM-12 particles were desolvated and activated by flowing N_2 through the closed cell containing the sample and colloidal probe for 1 h, instead of heating the sample. Successful desolvation of ELM-12 was confirmed through thermogravimetric analysis conducted at room temperature (see Section S1, Supporting Information). A gas mixture with a fixed EtOH/ N_2 ratio was then introduced into the closed cell for 1 h to induce EtOH adsorption on the ELM-12 particles. EtOH partial pressures were calibrated using gas chromatography (GC-2014, Shimadzu Corp.) before the first measurement each day. After scanning the substrate surface to locate an isolated ELM-12 particle, the operation mode was switched to force measurement, and the colloidal probe was approached toward the particle. The approach speed was set to 20 nm/sec, the lowest possible speed for the AFM apparatus used in this study. To ensure uniform pressing of the ELM-12 particle surface, AFM measurements were conducted exclusively on particles smaller than 600 nm, which are significantly smaller than the silica particles ($\sim 20\ \mu\text{m}$, detailed consideration is presented in Section S2).

For the AFM measurements on DUT-8(Ni), the powder sample and a glass substrate were placed in a petri dish and shaken to adhere the DUT-8(Ni) particles to the substrate. Afterward, the closed cell was assembled with the substrate and a colloidal probe (HQ:NS35/Al BS, $\sim 16\ \text{N/m}$, MikroMasch[®] Bulgaria; a silica particle size is $\sim 20\ \mu\text{m}$) in it. DUT-8(Ni) samples were activated as described in the Synthesis section and were handled under a N_2 atmosphere throughout the preparation process to prevent exposure to air. The other procedures were the same as those used in the ELM-12 system, but the force applications were

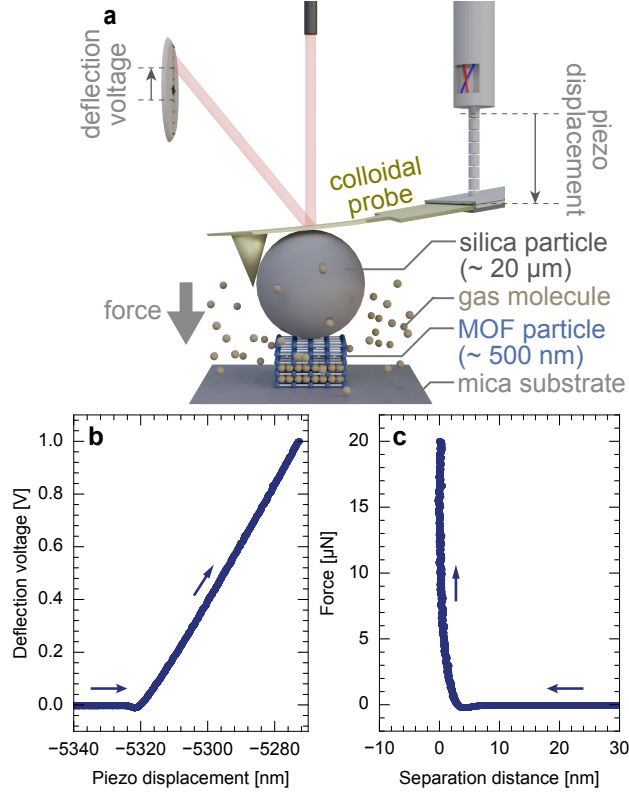


Figure 1: (a) Schematics of the AFM measurement principle. The AFM apparatus detects only piezo expansion/contraction and changes in the laser detection point caused by probe bending, as shown in (b) with a piezo displacement vs. deflection voltage profile as raw data. This is converted to (c) a separation distance vs. force profile by using the general method outlined in Section S3. (b) and (c) represent specific results of pressing a mica substrate under an EtOH/N₂ atmosphere.

conducted under a N₂ atmosphere.

Figure 1 depicts the AFM measurement method. The colloidal probe, which directly applies force to a MOF particle, is connected to a piezoelectric element (piezo) that expands and contracts in response to an applied voltage. Its position is fine-tuned via a feedback loop controlling piezo displacement. When the probe encounters attractive or repulsive forces, it bends, and this bending is detected by a laser diode and split photodetector. The degree of bending, called “deflection voltage,” is measured by the shift in the laser detection point from the reference. The relationship between piezo displacement and deflection voltage, obtained as raw data (Figure 1b), is converted to a force profile (separation distance vs. force, Figure 1c). In principle, the separation distance is measured from the sample surface.

However, because our target systems (MOF particles) shrink their volume to move the surface position, we shifted the terminal position to zero and redefined the separation distance. This conversion method from raw data, based on the physical properties of individual probes, is validated³⁷ and detailed in Section S3.

Theoretical Interpretations

Thermodynamics of guest-induced structural transition

During the transition, host-framework deformation and guest adsorption occur nearly simultaneously, but thermodynamics allows them to be considered separately. Host deformation destabilizes the entire system, while guest adsorption stabilizes it. Since these two contributions represent ΔF_{host} and $\Delta \Omega_{\text{guest}}$, respectively, the total free energy change of the entire system from the np state, $\Delta \Omega_{\text{os}}$, is expressed as follows:⁹

$$\Delta \Omega_{\text{os}}(P, T, X) = \Delta F_{\text{host}}(T, X) + \Delta \Omega_{\text{guest}}(P, T, X) \quad (1)$$

where P is the pressure, T is the temperature, and X is the degree of the transition progress (at $X = 1$, the system is in the lp state). At lower pressures, $\Delta F_{\text{host}}(> 0)$ dominates, fixing the system in the np state. As the pressure increases, $\Delta \Omega_{\text{guest}}(< 0)$ stabilizes the entire system, eventually making the lp state more stable than the np state ($\Delta \Omega_{\text{os}}(X = 1) < 0$) and driving the equilibrium transition. Although many studies have analyzed the transitions thermodynamically using equation 1, fully elucidating the relationship between the free energy profiles and force profiles to be obtained by AFM requires a careful understanding of the formulation based on fundamental thermodynamic principles. The osmotic free energy is defined as^{9,50}

$$\Omega_{\text{os}} = U - TS - \mu_{\text{guest}}N_{\text{guest}} + PV_{\text{host}} \quad (2)$$

where U is the internal energy, S is the entropy, μ_{guest} is the chemical potential of the guest molecule, N_{guest} is the amount of adsorbed guests, and V_{host} is the volume of the host framework. The total differential of the osmotic free energy is expressed as follows:

$$d\Omega_{\text{os}} = -SdT + V_{\text{host}}dP - N_{\text{guest}}d\mu_{\text{guest}} \quad (3)$$

where the fundamental thermodynamic relation, $dU = TdS - PdV_{\text{host}} + \mu_{\text{guest}}dN_{\text{guest}} + \mu_{\text{host}}dN_{\text{host}}$ (μ_{host} : the chemical potential of the host, N_{host} : the number of hosts), and $dN_{\text{host}} = 0$ were used. Discussing phase transitions requires the introduction of an order parameter that represents the phase characteristics. For example, the order parameter for the gas-liquid transition was determined to be the density.⁵¹ Guest-induced structural transition occurs involving individual transitions of flexible motifs composing the entire particle; thus, the number of transitioned motifs should be defined as the order parameter, X .

$$X = \sum_{j=1}^M x_j \quad (4)$$

where $0 \leq x_j \leq 1$ is the degree of transition progress in the j -th motif and M is the total number of motifs composing the particle. The equation has been commonly used to elucidate the cooperative transition of smallest cells consisting macroscopic models, such as ferromagnet.⁵² For the ELM series, including ELM-12, x_j corresponds to the interlayer width of the j -th motif and these motifs control the transition of entire particles and the X value.²⁶ Here, the conjugate intensive variable is defined as π , which physically represents the force applied to a particle to hold X at a specific value. π is commonly known as the adsorption stress proposed by Neimark et al.,¹¹ when X is defined as the MOF system volume. The osmotic free energy, Ω_{os} , is defined as a function of P, T , and X , and the total differential is

the following.

$$\begin{aligned} d\Omega_{\text{os}}(P, T, X) = & -S(P, T, X)dT + V_{\text{host}}(P, T, X)dP \\ & - N_{\text{guest}}(P, T, X)d\mu_{\text{guest}} - \pi(P, T, X)dX \end{aligned} \quad (5)$$

Transforming equation 5 yields equation 1 by considering the transition from $(P, T, 0)$ to (P, T, M) via the following separate paths:

$$\begin{aligned} \int_{(P,T,0)}^{(P,T,M)} \Omega_{\text{os}} d\mathbf{s} = & \int_{(P,T,0)}^{(0,T,0)} \Omega_{\text{os}} d\mathbf{s} + \int_{(0,T,0)}^{(0,T,M)} \Omega_{\text{os}} d\mathbf{s} + \int_{(0,T,M)}^{(P,T,M)} \Omega_{\text{os}} d\mathbf{s} \\ = & - \int_0^M \pi(P=0) dX + P\Delta V_{\text{host}} - \int_0^P \Delta N_{\text{guest}} V_{\text{m}} dP \end{aligned} \quad (6)$$

where $\mathbf{s}$ represents the system status, and $d\mu_{\text{guest}} = V_{\text{m}}dP$ (V_{m} is the molar volume of the gas). The detailed transformation is presented in Section S4. The first term in the last line is obtained by integrating the force on the particle along the transition progress, which represents the work required to advance the transition at $P = 0$, namely, ΔF_{host} . As $P\Delta V_{\text{host}}$ is negligibly small compared to the other terms and the third term is $\Delta\Omega_{\text{guest}}$, equation 6 is identified as equation 1. In contrast, equation 5 establishes an important relationship by considering the direct path from $(P, T, 0)$ to (P, T, M) :

$$\Delta\Omega_{\text{os}} = - \int_0^M \pi(P, T, X) dX \quad (7)$$

where $\Delta\Omega_{\text{os}} = \Delta\Omega_{\text{os}}(P, T, X = M)$ for simplicity. Consequently, when π and X are measured at constant temperature and pressure, the free energy change can be determined. Conversely, differentiating $\Delta\Omega_{\text{os}}(P, T, X)$ with respect to X provides the X vs. π profile. Force application on a MOF particle by AFM yields both the force magnitude, π , and the displacement in particle thickness corresponding to X . Therefore, force profiles can be theoretically predicted from the free energy profiles of guest-induced structural transitions.

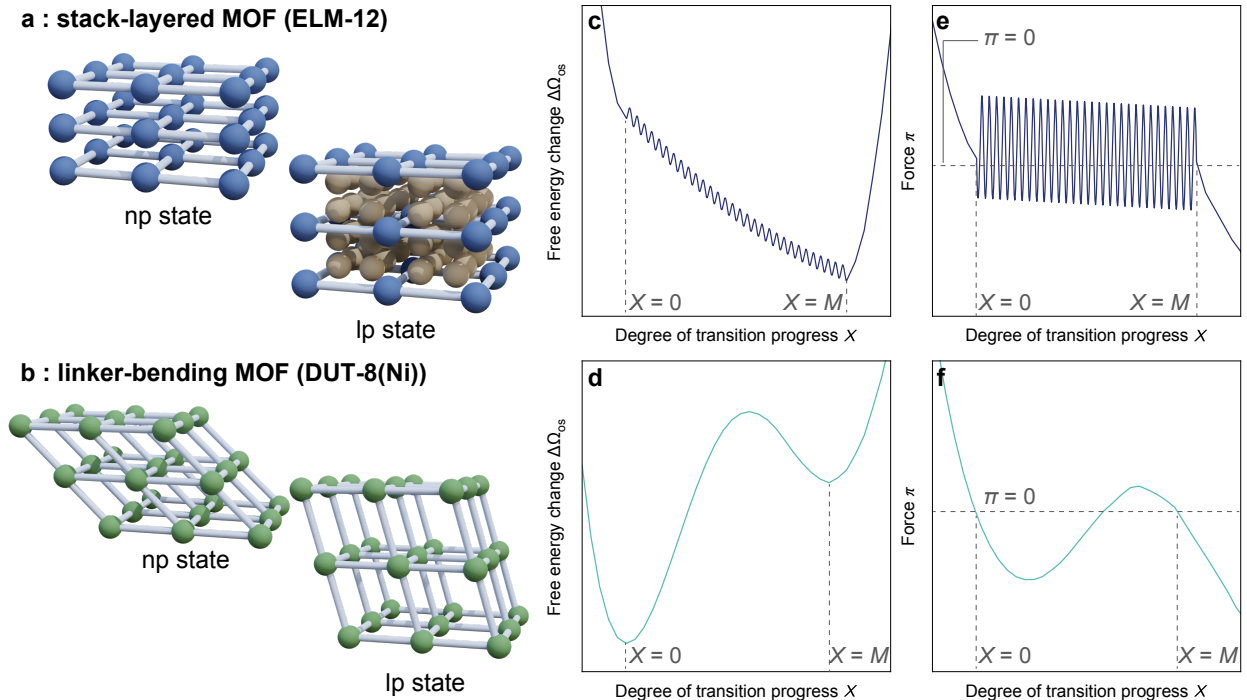


Figure 2: Schematic structures of (a) ELM-12 and (b) DUT-8(Ni) showing their corresponding free energy profiles (c) and (d), respectively. Differentiating (c) and (d) yields the theoretically predicted force curves (e) and (f).

Free energy profiles of ELM-12 and DUT-8(Ni) particles

Our previous study developed toy models that mimic the structures of smallest periodic unit cells (UCs) and concluded that their free energy profiles are bell-shaped, with an energy barrier between the np and lp states^{10,13} (the free energy profiles are presented in Section S5). However, this approach is insufficient to determine the free energy profiles of entire MOF particles, which are governed by cooperative transition mechanisms of multiple UCs. ELM-12 undergoes the transition with interlayer expansion, while DUT-8(Ni) undergoes cluster-linker bond bending (Figures 2a and 2b). At the particle scale, the interactions between layers of ELM-12, which originate from the van der Waals interaction, are significantly weaker than the coordinate bond forming two-dimensional layers, allowing for sequential layer-by-layer transitions (the structure detail is present in Section S6). As each interlayer transition forms a single bell-shaped profile, the layer-by-layer transitions repeat the bell shape as many times as there are layers. Additionally, our previous studies have shown that the entire profile

exhibits an overall downward deflection due to the entropic effect^{26,30} (Figure 2c). Notably, Figure 2c shows the profile for a particle with 30 layers as an example. However, actual particles contain 10^2 layers, resulting in finer wavy lines with the same number of oscillations as the layers. In contrast, DUT-8(Ni) has coordinate bonds in three-dimensional space with comparable magnitudes, causing all UCs to undergo the transition simultaneously⁵³ (the structure detail is present in Section S6). As each UC forms a single bell-shaped profile, the all-at-once transition produces the same bell shape but with a magnitude multiplied by the number of UCs. It was hypothesized that the profile shape remains even when the lp state contains no guest molecules (Figures 2b and 2d).⁵⁴ Because of the high energy barrier, the metastable guest-free lp state of DUT-8(Ni) can be preserved. Differentiating the free energy profiles (X vs. $\Delta\Omega_{\text{os}}$) yields the theoretically predicted force profiles (X vs. π , Figures 2e and 2f), which can be obtained by AFM. Notably, the layer-by-layer transition for ELM-12 and the all-at-once transition for DUT-8(Ni), as shown in Figures 2c and 2d, have been considered reasonable in previous studies,^{15,26,30,53} though without experimental evidence. This study aims to validate the distinct transition mechanisms between the two types of flexible MOFs by experimentally obtaining force profiles.

Results and Discussion

Synthesis results

The ELM-12 sample exhibited a double-step, S-shaped behavior for EtOH adsorption at 298 K (Figure 3a). Figure 3b shows in-situ XRD patterns of the ELM-12 sample at $P_{\text{EtOH}}/P_0 = 0.005, 0.045$, and 0.727 (P_0 represents the saturated vapor pressure of EtOH at 298 K) to compare the structures before and after the steps. The states at the three pressures display different peaks, indicating adsorption-induced structural transitions; we called their frameworks as narrow-pore (np), large-pore (lp), and super-large-pore (slp) states, respectively. As the transitions between them underwent within a narrow pressure variation,

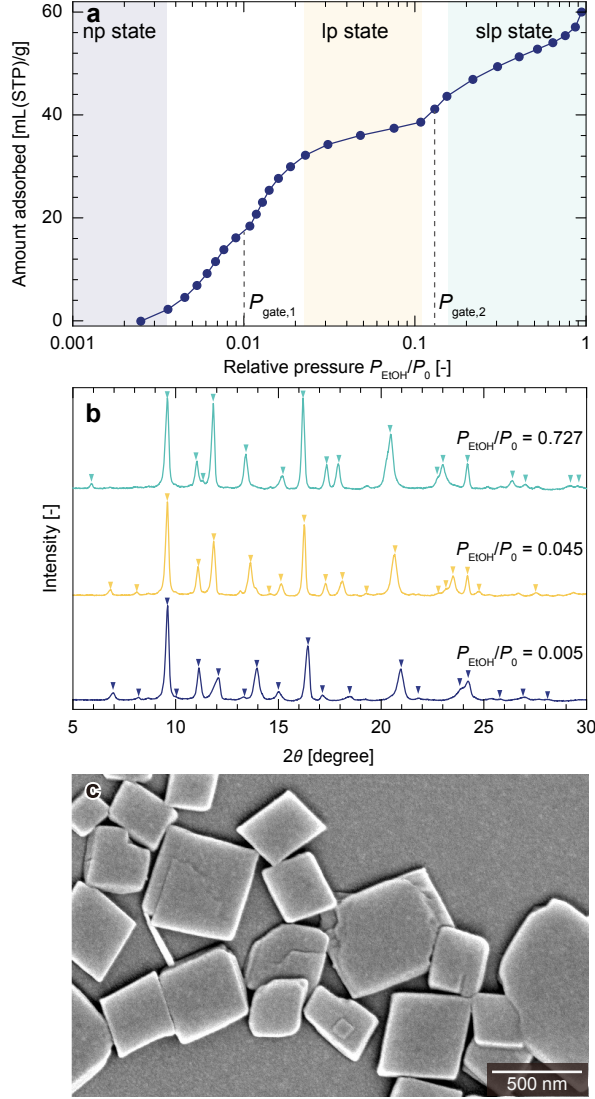


Figure 3: ELM-12: (a) EtOH adsorption isotherm showing double-step gate adsorption behavior at 298 K. (b) In-situ XRD patterns at $P_{\text{EtOH}}/P_0 = 0.005$, 0.045, and 0.727, corresponding to np, lp, and slp states, respectively. Triangle markers highlight peaks used for indexing. (c) SEM image.

the transition pressures were defined to be $P_{\text{gate},1}/P_0 \sim 0.01$ and $P_{\text{gate},2}/P_0 \sim 0.13$ as representative values. Indexing the peaks to calculate lattice constants confirmed an increase in interlayer width with each structural deformation (np: 6.37 Å, lp: 6.48 Å, and slp: 6.60 Å; the lattice constants are presented in Section S7). Additionally, gate desorption occurred at lower pressures, resulting in hysteresis, a characteristic of guest-induced structural transitions (see Section S8). Figure 3c shows an SEM image of the resulting ELM-12 platelet

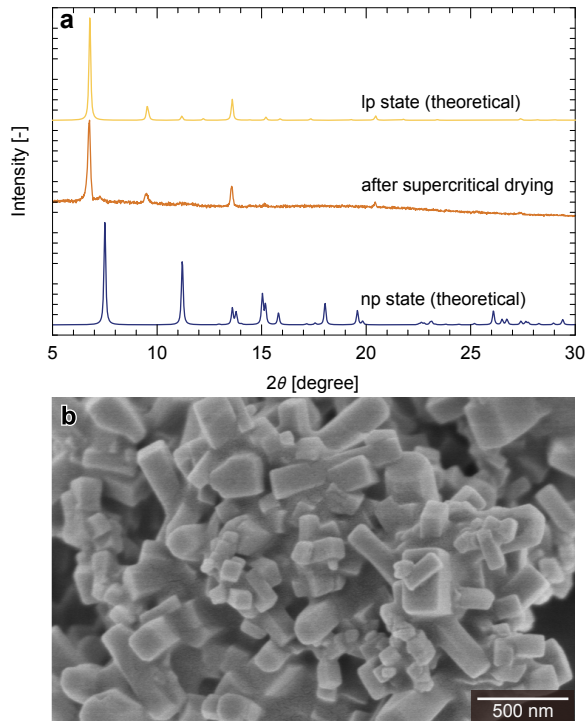


Figure 4: DUT-8(Ni): (a) XRD patterns under an Ar atmosphere and the theoretical patterns²² and (b) an SEM image.

particles, which have a lateral size of 720 ± 338 nm.

After supercritical drying, DUT-8(Ni) displayed an XRD pattern with peaks corresponding to the lp state only (Figure 4a) and exhibited a type-I N_2 adsorption isotherm at 77 K with no structural transition (see Section S9). This behavior differed from the stepwise uptake observed in the sample after evacuation and heating, confirming that the desolvation process may control the guest-free state and that the supercritically dried sample remained in the metastable lp state without guests. Figure 4b shows an SEM image of the synthesized DUT-8(Ni) as rectangular-shaped particles, with a length of 316 ± 216 nm and a width of 162 ± 74 nm.

Elucidation of transition mechanisms within single particles

The AFM measurement was first performed on an ELM-12 particle at $P_{\text{EtOH}}/P_0 = 0.016$. Scanning the mica substrate with a colloidal probe confirmed that the particle had the

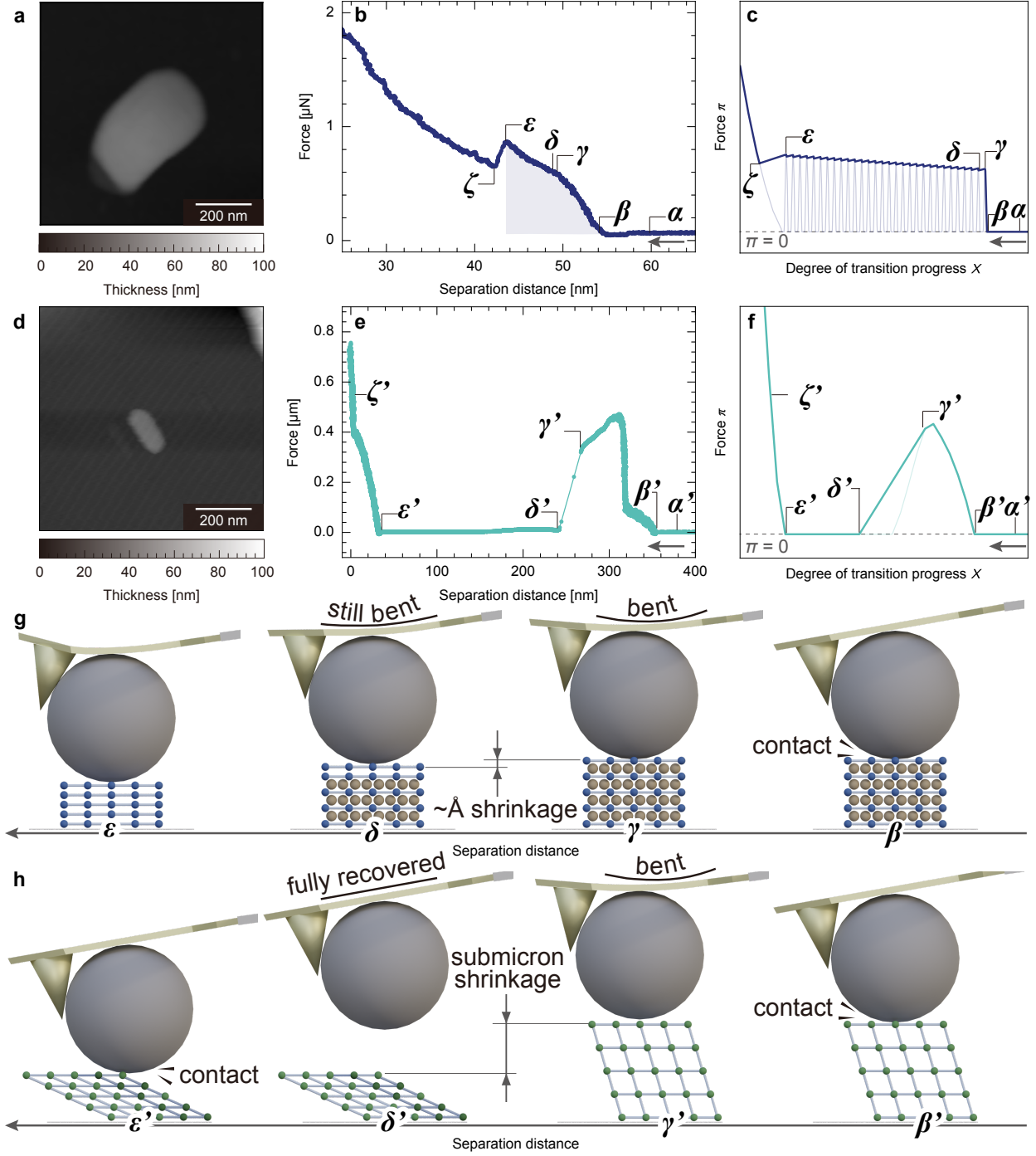


Figure 5: (a) AFM scan image of an ELM-12 particle using a colloidal probe. (b) Experimental data from force application on an ELM-12 particle at $P_{\text{EtOH}}/P_0 = 0.016$. (c) Theoretically expected force profile, modified to account for experimental limitations. (d), (e) and (f) show a scan image of a DUT-8(Ni) particle, an experimental force profile on the particle under a N_2 atmosphere, and its theoretical profile, respectively. Predicted transition mechanisms for (g) ELM-12 and (h) DUT-8(Ni).

same shape and size as shown in the SEM image (Figures 3c and 5a). Additionally, the thickness change of the ELM-12 particles due to EtOH uptake was detected (see Section S10). All ELM-12 particles on the mica substrate expanded their thickness vertically from the substrate, increasing the distance between the two-dimensional (2D) layers, which indicated that the 2D layers were oriented parallel to the substrate. Thus, the direction of pressure applied by the colloidal probe corresponds to the direction of particle contraction during gate desorption. Figure 5b shows the force profile for the ELM-12 particle. After the initial force detection (β), the force gradually increased, passed through a point of slope change (γ), abruptly decreased ($\varepsilon \rightarrow \zeta$), and then increased again. This behavior differed from that on a flat substrate (Figure 1c), confirming successful force application on the soft MOF particle. However, it also deviated from the theoretically predicted profile shown in Figure 2e. The discrepancy between the experimental and theoretical profiles stemmed from different interpretations of “force”: the experiment measured the force detected by the colloidal probe, while the theory considered it as the force exerted on the MOF particle. To predict the force profile accurately, the theoretical profile was converted to the force profile of a colloidal probe by considering the following two points: First, a negative force theoretically arises when the MOF particle spontaneously contracts (Figure 2e). Experimentally detecting such a negative force requires pulling the probe down by the MOF particle, which is impossible. Therefore, the measurable force in this setup is primarily $\pi \geq 0$, represented by the semi-transparent thin line in Figure 5c, where the $\pi \geq 0$ region from Figure 2e is applied. Second, the probe detects force by bending, with the force magnitude uniquely determined by the degree of bending. When the MOF particle contracts and separates from the probe tip, the probe recovers toward its original straight configuration from an upward-bent one. Both the separation distance and applied force decrease at a slope equal to the probe’s spring constant. If the MOF contraction naturally exhibits a steeper slope (i.e., a larger speed), the probe cannot follow the contraction motion. As a result, the force decreases with the slope of the probe’s spring constant ($\gamma \rightarrow \delta$ and $\varepsilon \rightarrow \zeta$ in Figure 5c). This process continues until

all UCs complete their transitions (ϵ), and the overall force profile ultimately resembles the experimental result (Figure 5b).

The good agreement (Figures 5b and 5c) allowed for elucidating the transition mechanism by referring to the theoretical illustrations (Figure 5g; detailed mechanisms are present in Section S11): As the probe approached the MOF particle, the force remained zero (α) until they made contact (β in Figure 5g). Once the force was applied, it increased until the transition began (γ). The ELM-12 particle underwent a layer-by-layer transition, with a single interlayer displacement on the order of Å ($\gamma \rightarrow \delta$). This slight displacement was insufficient to fully return the upward-bent probe to its straight configuration. As a result, the force continued to be exerted and remained non-zero (δ). When all layers completed their transitions (ϵ), the particle reached the np state, and further pressing resulted in another structure with a slightly narrower interlayer distance (ζ). Beyond this point, other factors, such as particle breakage, affected the force profile, leading to behaviors that could not be theoretically predicted. Notably, the theory assumed a quasi-static process in which, during the MOF contraction, probe recovery occurred immediately and piezo expansion paused. However, in the actual process, the expansion continued and made the probe tip closer to the MOF particle, inhibiting the probe recovery and applying an extra force. Thus, the slopes of $\gamma \rightarrow \delta$ and $\epsilon \rightarrow \zeta$ differed from the spring constant, thereby obscuring the force reductions (Figure 5b). This effect depended on the spring constant of cantilevers and shrinkage degree of MOF particles. It is also noted that the scanned particle thickness was sometimes smaller than that estimated from the force profile. This discrepancy may be due to the less precise measurement of thickness with the colloidal probe, as other particles around the target could interfere. However, these nearby particles did not obstruct the force application or analysis (quantitative details are provided in Section S12).

A force application on DUT-8(Ni) resulted in a different-shaped force profile (Figure 5e). The most notable difference was that the force decreased to zero and remained there until the subsequent force detection for the DUT-8(Ni) system ($\gamma' \rightarrow \epsilon'$). In contrast, the decrease

for the ELM-12 system terminated at a positive value (ζ in Figure 5b), which stemmed from differences in their transition mechanisms. Converting the theoretical force profile for the DUT-8(Ni) particle (Figure 2f) to that of a colloidal probe (Figure 5f) revealed the transition mechanism (Figure 5h), as it closely matched the experimentally observed profile (Figure 5e). The DUT-8(Ni) particle underwent an all-at-once inelastic transition, with a thickness displacement on the submicron scale ($\gamma' \rightarrow \epsilon'$ in Figure 5e). This large displacement was sufficient to fully straighten the probe, where the $\gamma' \rightarrow \delta'$ slope equaled the probe's spring constant, and the force ultimately reached zero (δ'). Once the probe was fully recovered, the force remained zero until the probe contacted and pushed down the DUT-8(Ni) particle again, which was in the np state (ϵ'). The underlying reason for this starkly contrasting characteristic is the metastable lp state of DUT-8(Ni) without guests, which is preserved after supercritical drying in particular for particles smaller than 500 nm. An irreversible thermally induced transformation from the lp to np state was also observed in a range of 508 to 538 K, corroborating the metastability.⁵⁵ Hence, the lp–np transformation is highly inelastic and cooperative in this case. In conclusion, the obtained force profiles highlighted the significant difference between the two MOF types, which was elucidated and supported by the theory based on their respective transition mechanisms. Although previous studies have conducted single-particle analyses to trace transitions at the single-particle level,^{33–36} they basically monitored the structural variation of particles through, e.g., diffraction patterns and direct microscopy observation. In contrast, this study focuses on the transition mechanisms undergone within a MOF particle to provide the first experimental evidence distinguishing the transition manners of ELM-12 and DUT-8(Ni): layer by layer and all at once, respectively.

Free energy change for the imposed transition

Because the theoretical force profile was derived by differentiating the free energy profile, the free energy change for the gate desorption of the ELM-12 particle, $\Delta\Omega_{\text{os}}$, can, con-

versely, be calculated by integrating the corresponding part of the force profile, as outlined in equation 7. The particle was subjected to a force for the imposed transition ($\beta \rightarrow \epsilon$ in Figure 5b). β represented the point where the force started to exert and became non-zero for the first time, while ϵ represented the point where gate desorption was complete, resulting in the np-state particle. At this point, the slope changed dramatically, followed by a force reduction with decreasing separation distance until ζ . To experimentally confirm the end-of-transition point, repeated force applications were conducted on an identical ELM-12 particle with varying force magnitudes (the force profiles are presented in Section S13). When the force measurements (approach and withdrawal) were repeated in the region where the force monotonically increased ($\beta \rightarrow \epsilon$) with a 50-sec interval, the same force profiles were reproduced. These reversible responses demonstrated that the pressed ELM-12 particle, which included several np-state layers, reformed to the lp state while adsorbing EtOH during the measurement interval. Further pressing caused a force reduction ($\epsilon \rightarrow \zeta$) and the subsequent force profiles displayed patterns similar to those on the mica substrate (Figure 1c), rather than on the particle. This indicated that further pressing beyond the point ϵ distorted the np-state structure, inhibiting its retransformation to the lp state. Accordingly, the imposed transition from the lp to np state concluded at the point where the force began to decrease (ϵ). The force reduction was identified using a unified criterion based on a differentiated force profile (the detailed calculation procedure is provided in Section S14). As a result, the work required to impose the transition was calculated by integrating the $\beta \rightarrow \epsilon$ region (the shaded area in Figure 5b): yielding a value of 5.9 fJ/particle. Strictly speaking, integrating force profiles must exclude discrete ranges where the probe recovered ($\gamma \rightarrow \delta$), because the herein detected force did not exert on the separate MOF particle. However, the overvalued work is independent of the adsorptive pressure and becomes negligible at higher pressures (see Section S15); therefore, the calculated work can be regarded as the free energy change for the transition. To facilitate discussion, the obtained value was converted to the free energy change per UC ($[\text{Cu}(\text{bpy})_2(\text{CF}_3\text{SO}_3)_2]_{n=1}$), resulting in $-\Delta\Omega_{\text{os}} = 0.414 \text{ kJ/mol-UC}$,

where the total number of UCs was calculated from the particle size. Although the $\Delta\Omega_{\text{os}}$ values varied with gas pressure, as discussed below, they were comparable to values obtained through detailed simulations for other systems,^{9,14,16} suggesting that the work done by the probe is fully converted into the free energy change rather than being partially dissipated as heat.

Pressure dependence of the free energy change

Figure 6 depicts the EtOH adsorption isotherms and force profiles on ELM-12 particles at various partial pressures of EtOH (GC results were present in Section S16), all of which had a similar particle size (~ 500 nm). Because the gate pressures of the system were $P_{\text{gate},1}/P_0 \sim 0.01$ and $P_{\text{gate},2}/P_0 \sim 0.13$, the ELM-12 particles at the force measurements were identified as the np, lp, lp, and slp states, respectively (Figure 6a). The force applied on the ELM-12 particles encapsulating EtOH molecules exhibited characteristic profiles showing a gradual increase, which corresponded to the $\beta \rightarrow \varepsilon$ region, and the force reduction (Figures 6c to 6e). Integrating the shaded areas corresponding to $\beta \rightarrow \varepsilon$ provided the free energy changes for gate desorption. At $P_{\text{EtOH}}/P_0 = 0$, where the ELM-12 particle was in the np state, the force profile resembled that of the mica substrate; however, the unified criterion identified an obscured force reduction (Figure 6b and see Figure S18). As the np-state particle does not undergo transitions associated with shrinkage, the detected point represented its compression limit, and the calculated work reflected its inherent elasticity (0.15 kJ/mol-UC). The force applied to the slp-state particle at $P_{\text{EtOH}}/P_0 = 0.14$ resulted in the largest free energy change, as it involved an additional transition from the slp to lp states (Figure 6e, $-\Delta\Omega_{\text{os}} = 2.10$ kJ/mol-UC). Most notably, the free energy change was larger at higher P_{EtOH} , even though the particles were in the same lp state and encapsulated nearly identical amounts of EtOH (Figures 6a, 6c and 6d, $-\Delta\Omega_{\text{os}} = 1.00$ and 1.66 kJ/mol-UC). This trend aligned with the thermodynamic interpretation of adsorption. Under constant temperature and $\pi = 0$ conditions, the free energy change associated with the transition is derived from

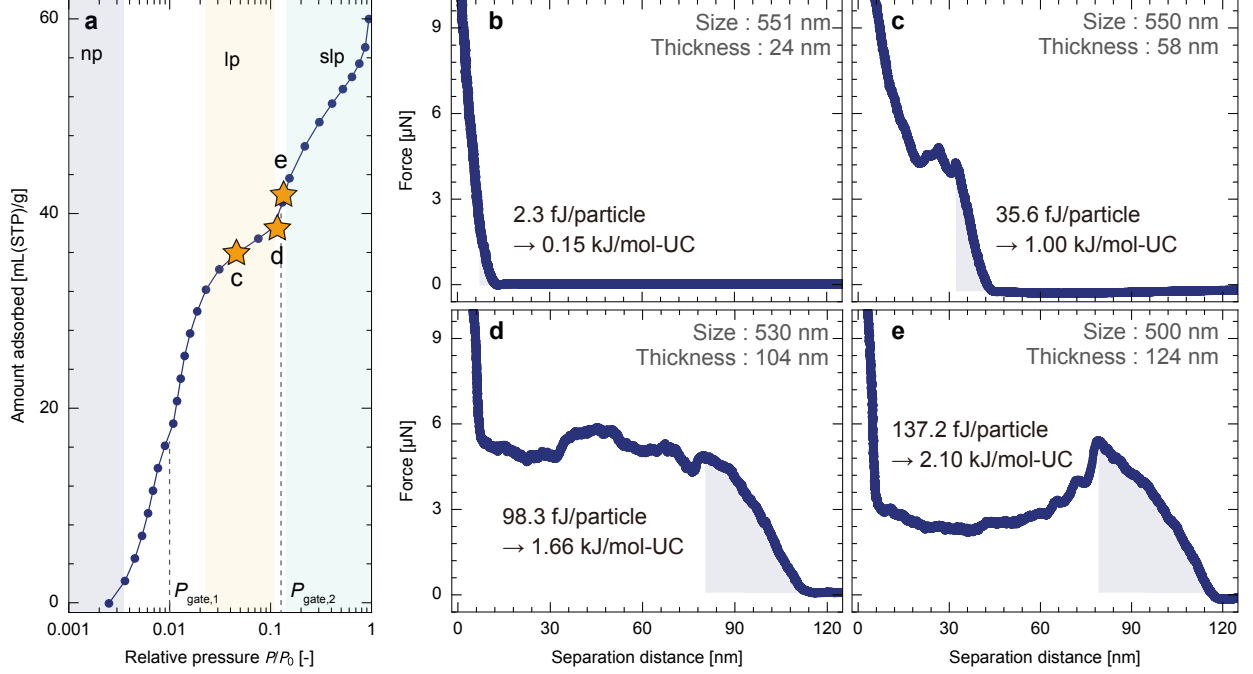


Figure 6: (a) EtOH adsorption isotherm on the ELM-12 sample (reprint of Figure 2a). Force profiles on ELM-12 particles (b) at $P_{\text{EtOH}}/P_0 = 0$ (np state), (c) $P_{\text{EtOH}}/P_0 = 0.04$ (lp state), (d) $P_{\text{EtOH}}/P_0 = 0.11$ (lp state), (e) $P_{\text{EtOH}}/P_0 = 0.14$ (slp state), where the pressures are highlighted as star symbols in (a).

equation 5, where the $V_{\text{host}}dP$ term is negligible, as

$$\Delta\Omega_{\text{os}} = -k_{\text{B}}T \int_{P_{\text{gate}}}^{P_{\text{measured}}} \Delta N_{\text{guest}} d \ln P \quad (8)$$

where P_{measured} and P_{gate} represent the measurement and gate pressures, respectively, and the ideal gas approximation was considered. Equation 8 indicates that the $\Delta\Omega_{\text{os}}$ value can be calculated as the area obtained by integrating a semilogarithmic adsorption isotherm between P_{measured} and P_{gate} , and its absolute value increases with adsorptive pressure (P_{measured}) regardless of the amount adsorbed. In summary, the pressure-dependent results obtained are thermodynamically plausible, demonstrating that the AFM measurement and analysis methods are capable of probing the gate desorption of individual ELM-12 particles.

Identifying the transition pressures of individual particles

Successfully probing the transition behaviors provided insights into particle-size dependence at the single-particle level. AFM measurements of several ELM-12 particles at $P_{\text{EtOH}}/P_0 \sim 0.04$, where all particles were in the lp state, revealed a size effect: the calculated work decreased with particle size (yellow circles in Figure 7a). All corresponding force profiles are provided in Section S17. Modeling N_{guest} with the Langmuir equation, characterized by n_∞ and K , yielded:

$$\Delta\Omega_{\text{os}} = -n_\infty k_B T \ln \frac{1 + K P_{\text{measured}}}{1 + K P_{\text{gate}}} \quad (9)$$

and thus,

$$P_{\text{gate}} = \frac{1}{K} \left\{ (1 + K P_{\text{measured}}) \exp \left(\frac{\Delta\Omega_{\text{os}}}{n_\infty k_B T} \right) - 1 \right\} \quad (10)$$

was obtained, where amount adsorbed on the np state was assumed zero. Equation 10 indicates that when the free energy change, $\Delta\Omega_{\text{os}}$, and the measurement pressure, P_{measured} , are known, the gate pressures of individual particles are determined. By fitting the EtOH adsorption and desorption isotherms of ELM-12 at 298 K, the parameters were determined as $n_\infty = 1.11$ mol-EtOH/mol-UC and $K = 99.23$ kPa $^{-1}$ (the fitted results are presented in Section S18). As the analysis focused on the gate desorption process, the P_{gate} value represented the gate desorption pressure, P_{des} . By substituting the calculated work into $-\Delta\Omega_{\text{os}}$ in equation 10, the P_{des} values were obtained, as shown in Figure 7b. The results revealed that P_{des} increases with particle size, a trend consistent with observations in numerous other systems.^{19,22,24,26} Indeed, at $P_{\text{EtOH}}/P_0 = 0$, where all ELM-12 particles are in the np state, all calculated values are almost zero, indicating that the inherent elasticity of the particles is negligible (blue squares in Figure 7a). Therefore, it was concluded that the size dependence observed at $P_{\text{EtOH}}/P_0 \sim 0.04$ is related to the varied transition pressures of the particles. Notably, the P_{des} values were higher than that observed in the desorption isotherm (Figure S6). This discrepancy primarily arose from the thermodynamic analysis relying on simple Langmuir fitting of the isotherms, which may lack precision. Because the transition

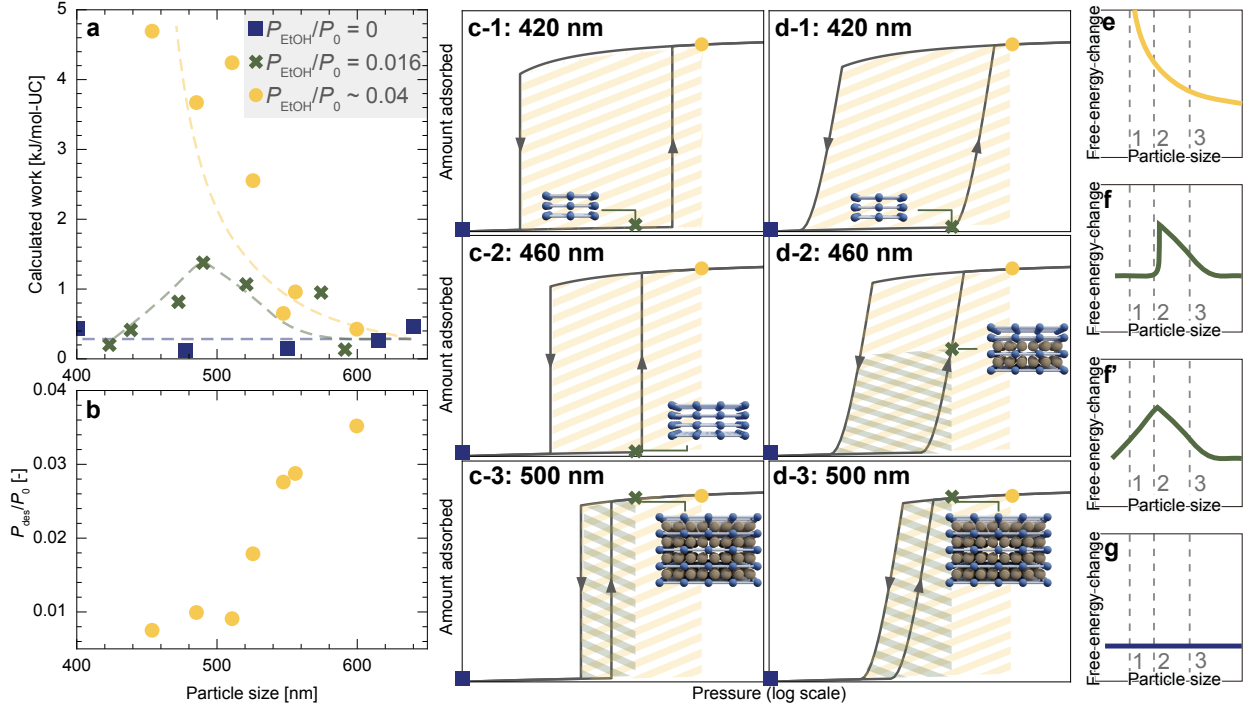


Figure 7: Calculated work (a) at $P_{\text{EtOH}}/P_0 = 0$ (blue squares), 0.016 (green X symbols), and 0.04 (yellow circles). (b) Gate desorption pressures of individual particles obtained by the thermodynamic analysis of the AFM results at $P_{\text{EtOH}}/P_0 \sim 0.04$. Schematics of free energy calculations using (c) stepwise adsorption/desorption behaviors and (d) S-shaped ones within narrow pressure ranges of various-sized particles, where shaded areas correspond to the free energy changes, $-\Delta\Omega_{\text{os}}$, at each pressure, where the symbols correspond to (a). The snapshots represent the particle state at $P_{\text{EtOH}}/P_0 = 0.016$, highlighted by green X symbols. Both calculations yield the same tendencies in particle size vs. free energy profiles at (e) $P_{\text{EtOH}}/P_0 \sim 0.04$ and (g) $P_{\text{EtOH}}/P_0 = 0$, but distinct tendencies at $P_{\text{EtOH}}/P_0 = 0.016$. (c) shows the abrupt change at the threshold size (f), while (d) demonstrates the gradual change (f'), which was observed in (a). The numbers in (e)–(g), 1, 2, and 3, correspond to the particle size termed in (c) and (d)

begins at very low pressure, accurately fitting the amount adsorbed on the np state was not possible. In this study, it was assumed that this amount adsorbed was zero across the entire pressure range, which overestimated the transition pressures. When the limited adsorption data was forcibly fitted, the values of transition pressures were reduced to become closer to that obtained from the desorption isotherm (see Section S19). Nevertheless, the quantitative trend of the gate desorption pressures among the particles remained invariable, accurately reflecting the tendencies of the individual particle properties. Statistical errors

may be present in the AFM results. However, according to Matei et al.,⁵⁶ the accuracy of the relevant measurement method is within 10%, which is unlikely to be significant enough to distort the observed quantitative trend.

The AFM analysis identified not only the gate desorption pressures but also the gate adsorption pressures. The two tendencies obtained at $P_{\text{EtOH}}/P_0 = 0$ and 0.04 are representative of the typical behaviors exhibited by np-state and lp-state ELM-12, respectively. The calculated works for lp-state particles equal to the $-\Delta\Omega_{\text{os}}$ values obtained by integrating the amount adsorbed with $\ln P$ between P_{measured} and P_{des} (equation 8, yellow shaded area in Figure 7c-1). As the P_{des} values increase with particle size, the required work decreases (Figures 7c and 7e). On the other hand, np-state particles showed nearly constant works (Figure 7g). Thus, the similarity with these reference profiles can serve as an indicator of the particle state, specifically whether it is in the np or lp state. The green X symbols in Figure 7a represent the AFM results at $P_{\text{EtOH}}/P_0 = 0.016$, which are close to the gate adsorption pressure (np $\rightarrow$ lp) in the adsorption isotherm $P_{\text{gate},1}$. The particles larger than 490 nm showed a decrease in work with particle size, exhibiting the same trend as observed for the lp-state particles. However, the opposite trend was observed for smaller particles below 490 nm: the required work decreased with smaller particle sizes. This is attributed to the combination of two key points: First, the smaller particles remained in the np state before the force was applied and did not undergo any transitions under the exerted force, as the gate adsorption pressures decrease with the particle size (green shaded areas in Figure 7c). This situation assumes that all particles smaller than 490 nm are in the fully np state and exhibit minimal work values, consistent with the result at $P_{\text{EtOH}}/P_0 = 0$ (Figure 7f). However, the assumption does not completely account for the gradual change observed in particle sizes of 400–490 nm (green X symbols in Figure 7a), leaving room for further explanation. Second, each of the small ELM-12 particles partially underwent a transition before the force application, meaning that each particle was not defined as the fully np or lp state but can be an intermediate structure containing both np and lp layers. This demonstrates

that the transition occurred layer by layer even in the absence of external forces. Our previous study showed that the layer-by-layer transition exhibits the S-shaped uptake within a narrow pressure range, rather than a stepwise uptake (Figure 7d-1).^{26,30,57} As the S-shaped adsorption branches shift to lower pressures with particle size, the proportion of lp-state layers gradually increases, thereby enhancing the $-\Delta\Omega_{\text{os}}$ values (green shaded areas in Figure 7d-2). The particles larger than the threshold size are in the fully lp state at this pressure (Figure 7d-3); thus, the $-\Delta\Omega_{\text{os}}$ values turn to the decreasing trend due to increasing P_{des} (Figure 7f). Therefore, particles at the boundary between the increasing and decreasing trend in Figure 7a completed the transition exactly at the pressure, and the measurement pressure ($P_{\text{EtOH}}/P_0 = 0.016$) was identified as the gate adsorption pressure for 490-nm particles. Because the gate desorption pressure was calculated as $P_{\text{EtOH}}/P_0 = 0.010$ (Figure 7b), the transition pressures upon both the adsorption and desorption of a single particle (490 nm) were successfully identified.

Conclusion

This study proposed a method for individually probing guest-induced structural transitions in flexible MOFs by combining AFM with thermodynamic analysis. The approach provided experimental evidence that ELM-12 and DUT-8(Ni) exhibit distinct force profiles due to their differing transition mechanisms: layer-by-layer and all-at-once, respectively. Thermodynamic analysis of the obtained force profiles enabled the characterization of gate desorption behaviors for individual particles. The pressure-dependent results for ELM-12 aligned with theoretical predictions, demonstrating the effectiveness of the AFM method for probing gate behaviors. Analysis of multiple particles at identical pressures revealed that gate adsorption/desorption pressures vary with particle size, and that each isotherm exhibits a distinct slope rather than a stepwise shape, experimentally supporting our theoretical discussion.^{26,30,57} While size-controlled transition behaviors have been reported for many

flexible MOF systems,^{17–26} this study represents the first instance of such observations at the single-particle level. Specifically, Figure 7b shows that the P_{des} value for 500-nm particles is approximately one-quarter of that for 600-nm particles, demonstrating how significantly the particle size distribution in samples reduces the steepness of the S-shaped adsorption isotherms. This indicates the importance of uniform particle size to achieve clearly defined stepwise adsorption isotherms for industrial use. Notably, the AFM analysis was limited to particles smaller than 600 nm due to the size of the silica particles attached to the cantilevers; however, this limitation could be overcome by using larger silica particles. Although the size effect has already been investigated through multiscale simulations combined with thermodynamic analysis,²⁶ experimentally probing individual particle behaviors will deepen the understanding of size-dependent phenomena. Moreover, the AFM approach can address not only particle size but also other properties, such as particle shape,^{58,59} metal substitution,⁶⁰ and ligand mixing.⁶¹ This advancement opens new avenues for exploring the diverse possibilities of flexible MOFs.

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Supporting Information Available

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

- Thermogravimetric analysis of ELM-12 powder; The threshold size of the AFM measurements; Conversion from piezo displacement vs. deflection voltage profiles into force profiles; Derivation of equation 6; Free energy profiles of the single UC; Atomistic structures; Crystal lattice data for ELM-12 with adsorbed EtOH molecules; EtOH adsorption and desorption branches of ELM-12; N₂ adsorption isotherms on DUT-8(Ni); Thickness change while increasing the EtOH partial pressure; Detailed transition mechanisms; Nearby particles reducing the scanned thickness; Confirming the end-of-transition point by repeating force applications; Calculation method of the work required to induce transitions per UC; Overvalued work by discrete ranges in force profiles; Gas chromatograph results; All measured force profiles for ELM-12; Langmuir fitting result for the EtOH adsorption isotherm on ELM-12; Fitting adsorption isotherms on the np-state ELM-12 (PDF)

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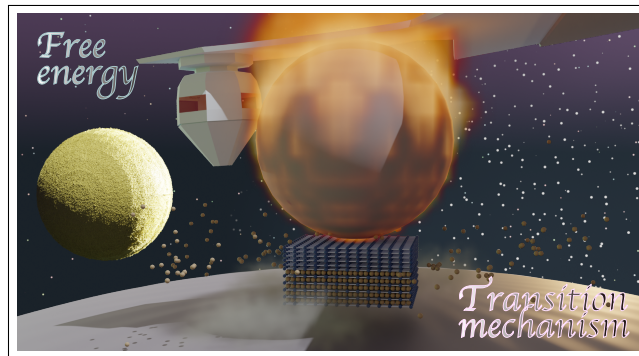
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TOC Graphic



Supporting Information:

Atomic Force Microscopy Strategies for Capturing Guest-Induced Structural Transitions in Single Flexible Metal–Organic Framework Particles

Homare Arima,[†] Shotaro Hiraide,^{*,†,‡} Hiroyuki Nagano,[†] Leila Abylgazina,[¶] Irena Senkovska,[¶] Günter K. Auernhammer,[§] Andreas Fery,^{§,||} Stefan Kaskel,[¶] and Satoshi Watanabe^{*,†}

[†]*Department of Chemical Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan*

[‡]*Institute for Aqua Regeneration, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan*

[¶]*Inorganic Chemistry I, Technische Universität Dresden, Bergstrasse 66, 01069 Dresden, Germany*

[§]*Division of Physical Chemistry and Polymer Physics, Leibniz Institut f. Polymerforschung Dresden, Hohe Str. 6, 01069 Dresden, Germany*

^{||}*Physical Chemistry of Polymeric Materials, Technische Universität Dresden, Bergstrasse 66, 01062 Dresden, Germany*

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

S1. Thermogravimetric analysis of ELM-12 powder

Since we used the AFM system that was not equipped with a heating device, the desolvation of the MOF samples was achieved by flowing non-adsorbed gas for 1 h at room temperature. Figure S1 depicts thermogravimetric analysis results of the ELM-12 samples while switching non-adsorbed gas (N_2) to adsorbed gas (EtOH/ N_2) flows at room temperature. During the N_2 flow, the sample weight decreased to reach a plateau in 30 min (1800 sec), indicating that the N_2 flow had completed the desolvation of the ELM-12 powder within the time frame. Subsequently, the EtOH/ N_2 flow provided ELM-12 powder with EtOH molecules to be adsorbed, leading to an increase in weight. The higher P_{EtOH} condition allowed the ELM-12 to adsorb more EtOH molecules, further increasing the weight. The increased weights were comparable to the values calculated from adsorption isotherms (7.3 wt% at $P_{\text{EtOH}}/P_0 \sim 0.04$ and 9.5 wt% at $P_{\text{EtOH}}/P_0 \sim 0.2$, which were calculated from Figure 3a), validating that the powder had been activated and involved EtOH molecules by an EtOH/ N_2 flow. Therefore, we introduced N_2 gas for 1 h (30 min plus extra 30 min) and afterward EtOH/ N_2 mixture gas at the target pressure for 1 h before starting the AFM measurement.

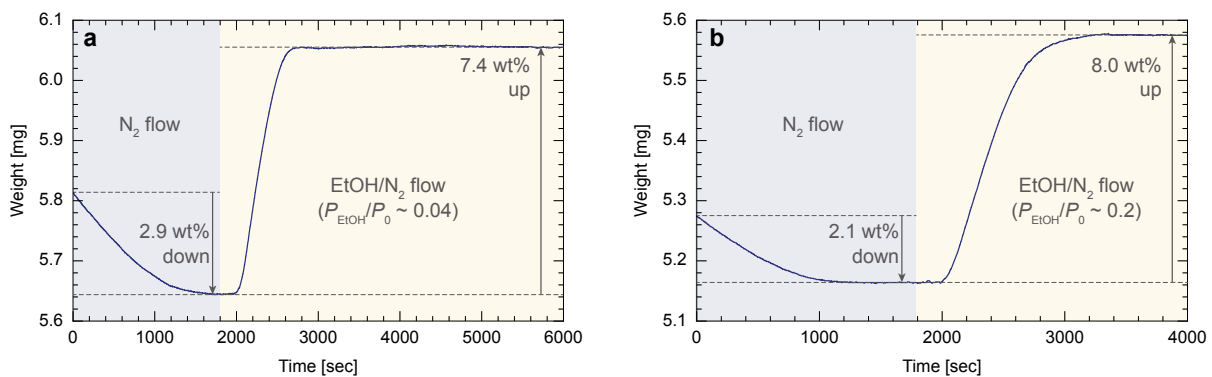


Figure S1: Thermogravimetric analysis on the ELM-12 powder while switching a N_2 flow to an EtOH/ N_2 flow at two conditions, (a) $P_{\text{EtOH}}/P_0 \sim 0.04$ and (b) $P_{\text{EtOH}}/P_0 \sim 0.2$.

S2. The threshold size of the AFM measurements

Uniformly pressing down the particle surface is one of the most important factors in the AFM measurements to simultaneously induce a structural transition of UCs within single layers. This is evaluated by the height difference of the silica particle between the positions at the center and edge of the MOF particle, Δh_{silica} , which is calculated as:

$$\Delta h_{\text{silica}} = D_{\text{silica}}/2 - \sqrt{D_{\text{silica}}^2/4 - d_{\text{MOF}}^2/4}$$

where D_{silica} and d_{MOF} are the diameter of the silica particle and the lateral size of the MOF particle, respectively (Figure S2). As d_{MOF} increased, the height difference exponentially increased. When $D_{\text{silica}} = 20 \mu\text{m}$ and $d_{\text{MOF}} = 600 \text{ nm}$, $\Delta h_{\text{silica}} = 4.5 \text{ nm}$ was obtained (Table S1), which is a difference of less than 10 % of the particle thickness. When $d_{\text{MOF}} = 800 \text{ nm}$, $\Delta h_{\text{silica}} = 8.0 \text{ nm}$ was considered non-negligible, leading to inaccuracies in the force profile. We considered the difference to be crucial for ensuring uniform force application. Therefore, the AFM measurements were performed exclusively on smaller MOF particles than 600 nm.

Table S1: The height difference between the center and edge of a pressed MOF particle.

d_{MOF} [nm]	400	600	800	1000
Δh_{silica} [nm]	2.0	4.5	8.0	12.5

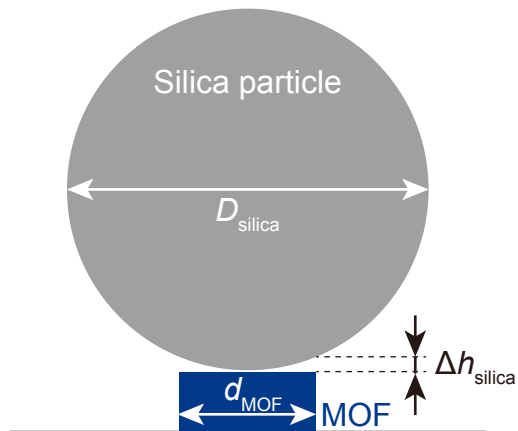


Figure S2: Illustration of the size relationship between the silica and MOF particle.

S3. Conversion from piezo displacement vs. deflection voltage profiles into force profiles

The AFM system is capable of detecting only the two values: piezo displacement, z_{piezo} , and deflection voltage, V_{defl} (Figure 1a). These values are output as raw data, which is transformed to a separation distance (h_{sep}) vs. force (F) profile. All of the variables are related and obtained from the other variable set. First of all, from the V_{defl} [V] value, which is a change in the laser detection point from the reference, a deflection of the cantilever tip, h_{defl} [nm], is obtained as follows:

$$h_{\text{defl}} = \text{InvOLS} \times V_{\text{defl}}$$

where InvOLS [nm/V] is a correction factor, the derivation of which is shown below. The exerted force is obtained by multiplying the cantilever's spring constant, k , and the h_{defl} value as

$$F = k \times h_{\text{defl}}$$

Second, z_{piezo} is converted into the change in the height of the cantilever tip, h_{sep} . The change in h_{sep} is reduced by a bend of the cantilever; thus, the value is obtained as

$$h_{\text{sep}} = z_{\text{piezo}} - h_{\text{defl}}$$

Therefore, the force (h_{sep} vs. F) profile is obtained from the raw data.

Note that the InvOLS [nm/V] value depends on multiple factors that change when setting up the AFM system and thus must be known before the force applications. The value is obtained from the slope of a force profile while pushing a standard sample that is flat and solid. We performed force applications 50 times on the mica substrate and obtained the averaged InvOLS [nm/V] value. For example, in the force profile shown in Figure 1b,

the cantilever pressed down the substrate from $z_{\text{piezo}} = -5230$ to -5272 nm, and then, *InvOLS* was calculated as 44.4 nm/V. Unless the laser position is changed, the *InvOLS* value remains the same.

Due to technical problems, the V_{def} value may change even though the cantilever is not in contact with the sample, the so-called “virtual deflection” problem, which was calibrated before *InvOLS* was obtained.

S4. Derivation of equation 6

$$\begin{aligned}
\int_{(P,T,0)}^{(P,T,M)} \Omega_{\text{os}} d\mathbf{s} &= \int_{(P,T,0)}^{(0,T,0)} \Omega_{\text{os}} d\mathbf{s} + \int_{(0,T,0)}^{(0,T,M)} \Omega_{\text{os}} d\mathbf{s} + \int_{(0,T,M)}^{(P,T,M)} \Omega_{\text{os}} d\mathbf{s} \\
&= \int_P^0 V_{\text{host}}(P, T, X=0) dP - \int_P^0 N_{\text{guest}}(P, T, X=0) V_{\text{m}} dP \\
&\quad - \int_0^M \pi(P=0, T, X) dX \\
&\quad + \int_0^P V_{\text{host}}(P, T, X=M) dP - \int_0^P N_{\text{guest}}(P, T, X=M) V_{\text{m}} dP \\
&= - \int_0^M \pi(P=0) dX + \int_0^M [V_{\text{host}}(X=M) - V_{\text{host}}(X=0)] dP \\
&\quad - \int_0^P [N_{\text{guest}}(X=M) - N_{\text{guest}}(X=0)] V_{\text{m}} dP \\
&= - \int_0^M \pi(P=0) dX + P \Delta V_{\text{host}} - \int_0^P \Delta N_{\text{guest}} V_{\text{m}} dP
\end{aligned}$$

S5. Free energy profiles of the single UC

We have developed toy models mimicking the UC structure to compute the free energy change along displacement from the np state. The left stable point is in the np state and the right one is in the lp state. The profile shape changes depending on the adsorptive pressures: increasing the pressure stabilized the lp state, resulting in the transition from the np to lp state at the equilibrium transition pressure.

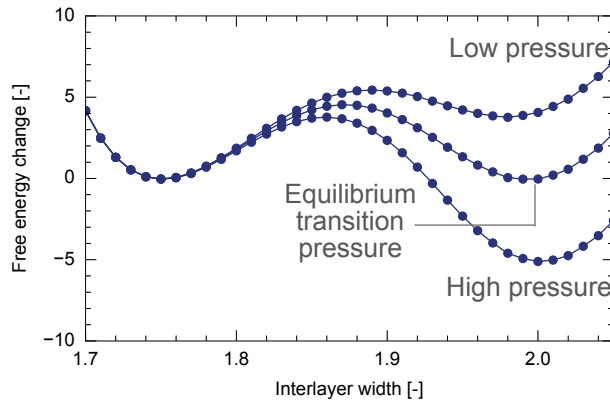


Figure S3: Free energy profiles of the toy model developed mimicking the UC of ELM series.^{S1}

S6. Atomistic structures

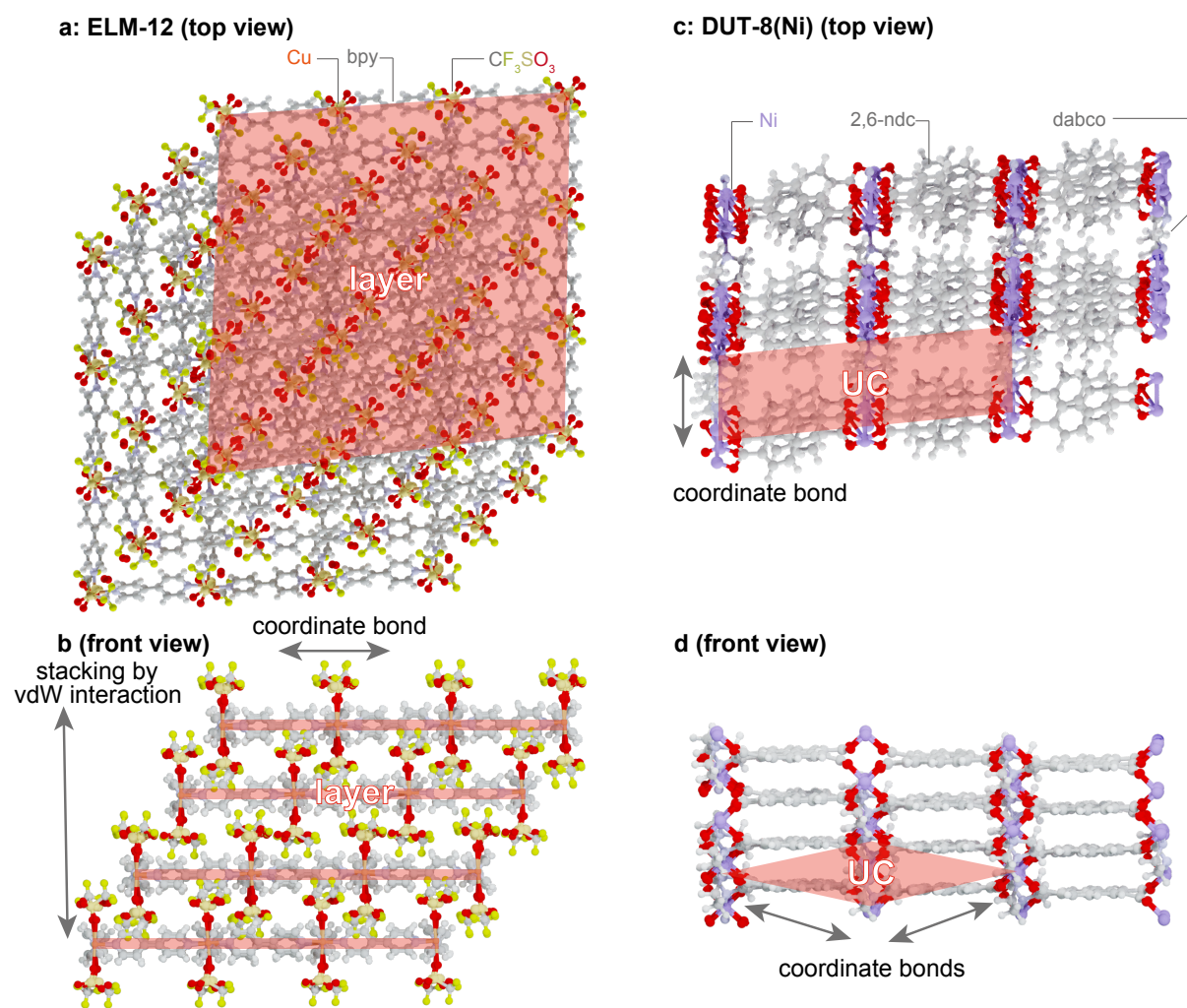


Figure S4: Atomistic structures of np-state ELM-12 (a: top view and b: front view) and np-state DUT-8(Ni) (c: top view and d: front view).

S7. Crystal lattice data for ELM-12 with adsorbed EtOH molecules

By indexing the highlighted peaks in Figure 3b using CONOGRAPH software, the crystal lattice data for the ELM-12 sample with EtOH was obtained (Table S2). The interlayer width at $P_{\text{EtOH}}/P_0 = 0.005$ was a bit wider than the reference,^{S2} indicating that the transition already started at that pressure. The obtained results were refined by the Pawley method using the GSAS-II software (Figure S5).

Table S2: Crystal lattice data for ELM-12 samples obtained by the XRD patterns shown in Figure 3b.

P_{EtOH}/P_0	0.005	0.045	0.727
state	np	lp	slp
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P1$ (no. 1)	$C2/m$ (no.12)	$P2/m$ (no.10)
a [Å]	11.084(6)	16.564(7)	9.3395(22)
b [Å]	16.627(16)	14.9537(12)	14.9859(11)
c [Å]	26.139(24)	13.475(6)	11.920(4)
α [°]	99.16(9)	90	90
β [°]	101.60(3)	105.613(18)	101.478(9)
γ [°]	94.981(3)	90	90
Interlayer distance [Å]	6.37	6.48	6.60
R_{wp} [%]	4.58	7.70	6.99

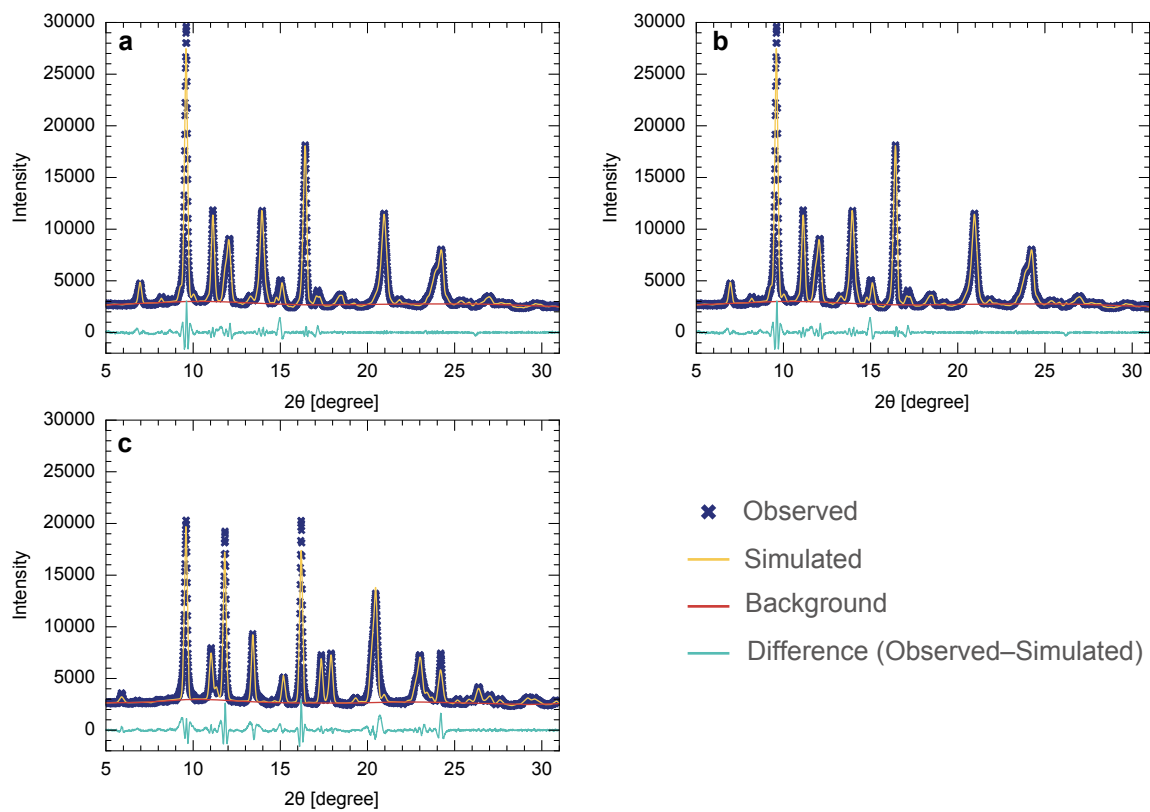


Figure S5: Pawley refinement results of (a) $P_{\text{EtOH}}/P_0 = 0.005$, (b) 0.045, and (c) 0.727, in which blue plots (observed) are replicated from Figure 3b.

S8. EtOH adsorption and desorption branches of ELM-12

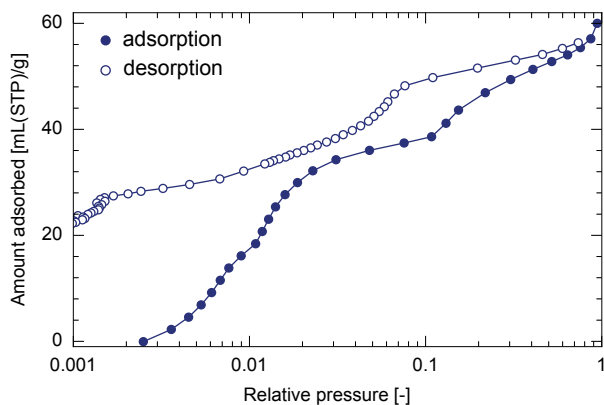


Figure S6: EtOH adsorption (closed symbols) and desorption (open symbols) isotherms on ELM-12 at 298 K.

S9. N₂ adsorption isotherms on DUT-8(Ni)

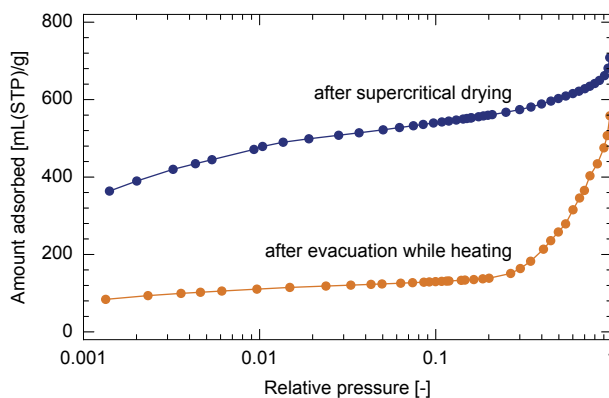


Figure S7: Semilogarithmic N₂ adsorption isotherms on DUT-8(Ni) at 77 K.

S10. Thickness change while increasing the EtOH partial pressure

Scanning by a cantilever without a silica particle attached produced height images to demonstrate thickness changes of ELM-12 particles while increasing EtOH partial pressure. All the pressures were confirmed by gas chromatography. Figure S8a depicts the thickness change of an ELM-12 particle. The abrupt increase around $P_{\text{EtOH}}/P_0 = 0.1$ originates from the transition from the lp to slp state. Additionally, the transition from the np to lp state also expands the thickness ($P_{\text{EtOH}}/P_0 = 0 \rightarrow 0.06$). The tendency was observed for other ELM-12 particles as well (Figure S8b).

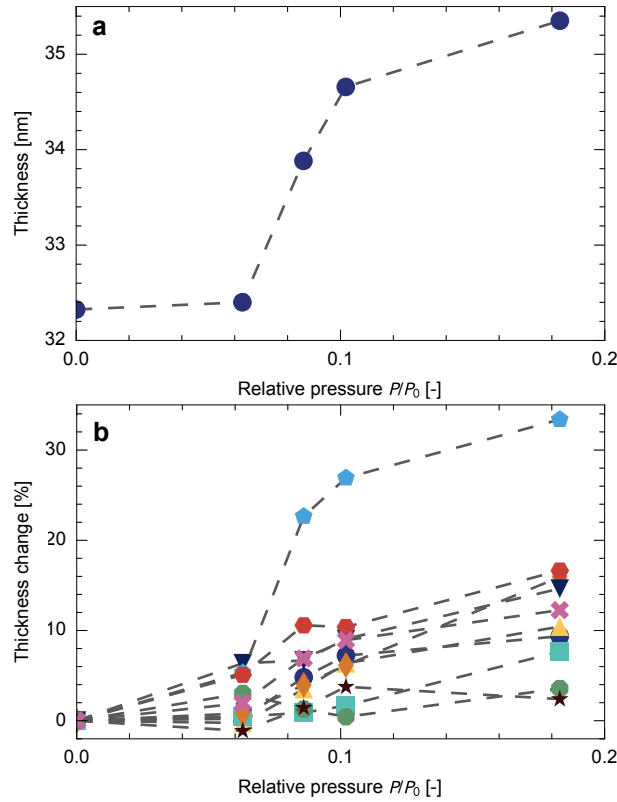


Figure S8: (a) The thickness change for an ELM-12 particle with increasing P_{EtOH} and (b) the expansion degrees of the thickness for ten different particles.

S11. Detailed transition mechanisms

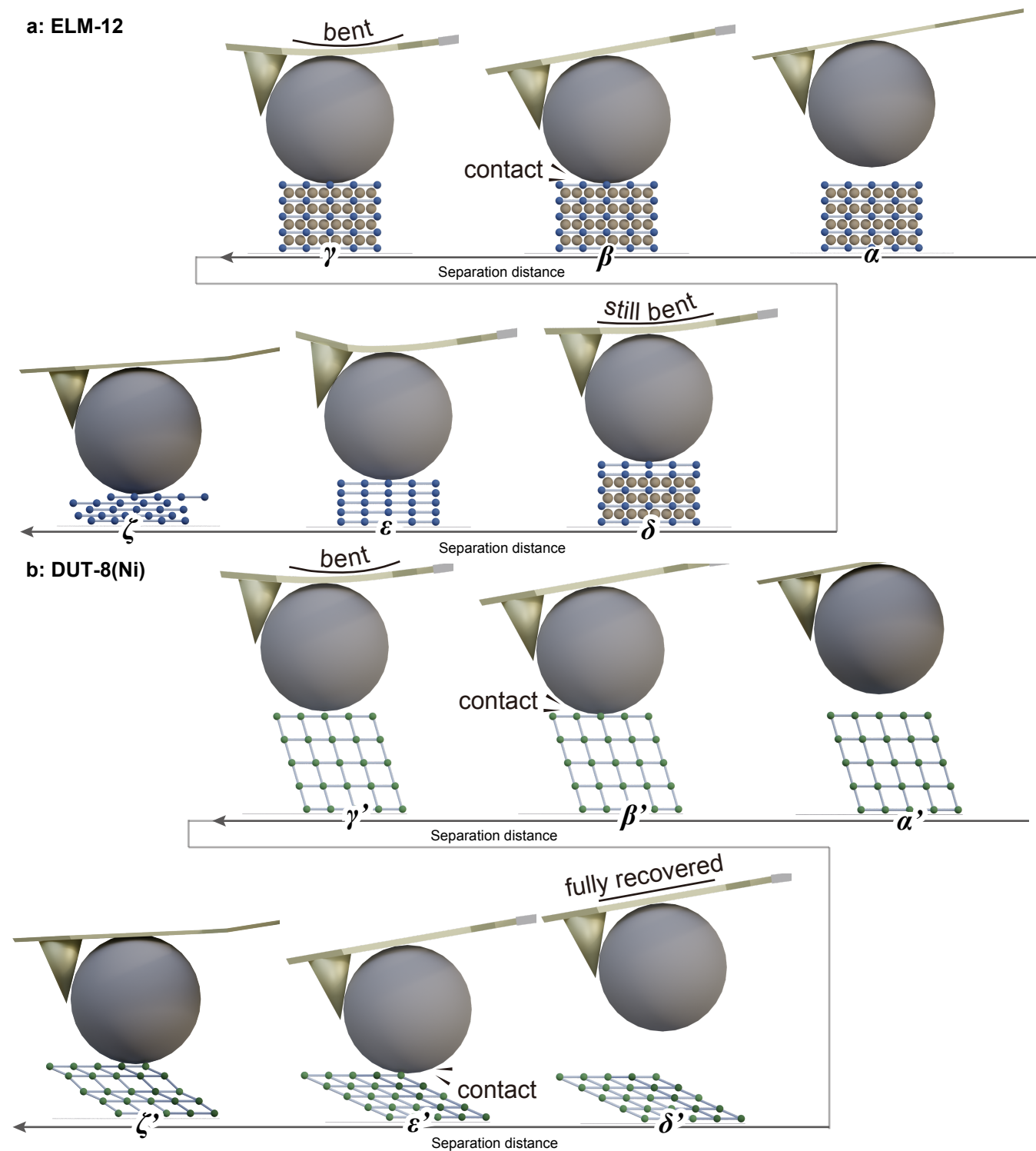


Figure S9: Detailed transition mechanisms within an (a) ELM-12 and (b) DUT-8(Ni) particle, induced by force applications.

S12. Nearby particles reducing the scanned thickness

Scanning a substrate with a colloidal probe is technically challenging because the attached silica particle is large, regarding the scan resolution. Especially, if there are other particles nearby, the thickness of the target particle will not be correctly imaged. As an example, considering that two MOF particles, whose thicknesses both are h_{MOF} , are located l_{nearby} apart (Figure S10), the scanned thickness is different from the true one as:

$$\Delta h_{\text{scan}} = h_{\text{MOF}} - \left[D/2 - \sqrt{D_{\text{silica}}^2/4 - l_{\text{nearby}}^2/4} \right]$$

where D_{silica} is the diameter of the silica particle. When $D_{\text{silica}} = 20 \mu\text{m}$ and $h_{\text{MOF}} = 60 \text{ nm}$, the relationship between l_{nearby} and Δh_{scan} was obtained as Table S3. This demonstrated that when any other particle exists $1.5 \mu\text{m}$ apart, the scanned thickness is only half of the true one. The effect of nearby particles might not be eliminated due to the difficulty of preparing the substrate and scanning. Areas with high particle concentration were avoided as much as possible, and the highest particle was selected in a scan image. Nonetheless, the nearby particles cannot inhibit the force application and the imposed transition.

Table S3: Relationship between distance apart and reduced height.

$l_{\text{nearby}} [\mu\text{m}]$	0.5	1	1.5	2.2
$\Delta h_{\text{scan}} [\text{nm}]$	57	47	32	0

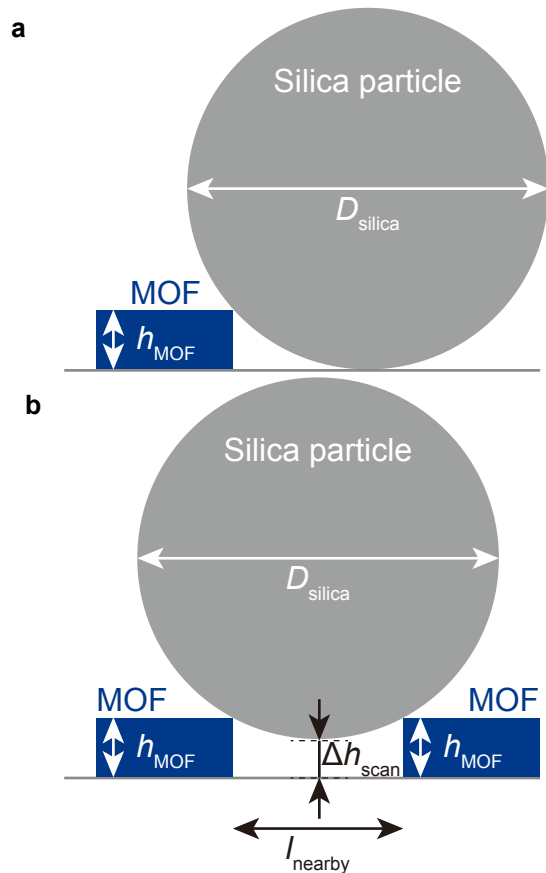


Figure S10: Schematics of scanning MOF particles on the mica substrate using a colloidal probe attached with a $20\ \mu\text{m}$ silica particle under the conditions where (a) the particle is independent and (b) a nearby particle exists.

S13. Confirming the end-of-transition point by repeating force applications

From the theoretical point of view, at the slope-changing point, the imposed transition is terminated. Repeating force application experimentally identified the end-of-transition point as below. The main feature is that the transition is reversible. We fixed the maximum force, $F_{\max}$, on the ELM-12 particle (Figure S11a), performed the application, and increased $F_{\max}$ (Figures S11c to S11f). The first and second measurements with $F_{\max} = 4.2 \mu\text{N}$ illustrated identical force profiles which show gradual increase in the force. The gradual increase indicated the partially imposed transition to the np state and the reproducibility indicated a reversible event: between the first and second applications, the ELM-12 particle underwent re-transition to the lp state with adsorbed EtOH. The third measurement with $F_{\max} = 10.2 \mu\text{N}$ showed a slope-changing point ($\sim 4 \text{ nm}$) considered as the end of transition, and the fourth and fifth measurements illustrated different profiles without negative slopes. This indicated the occurrence of an irreversible event. Additionally, the third force profile until the slope-changing point had the same shape as the first and second ones, demonstrating the range corresponding to the imposed transition. After the point, the ELM-12 particle was broken by further pressing, which was scanned after the force applications (Figure S11b). The breaking behavior depended on the ELM-12 particles, and thus, the responses after the point were varied.

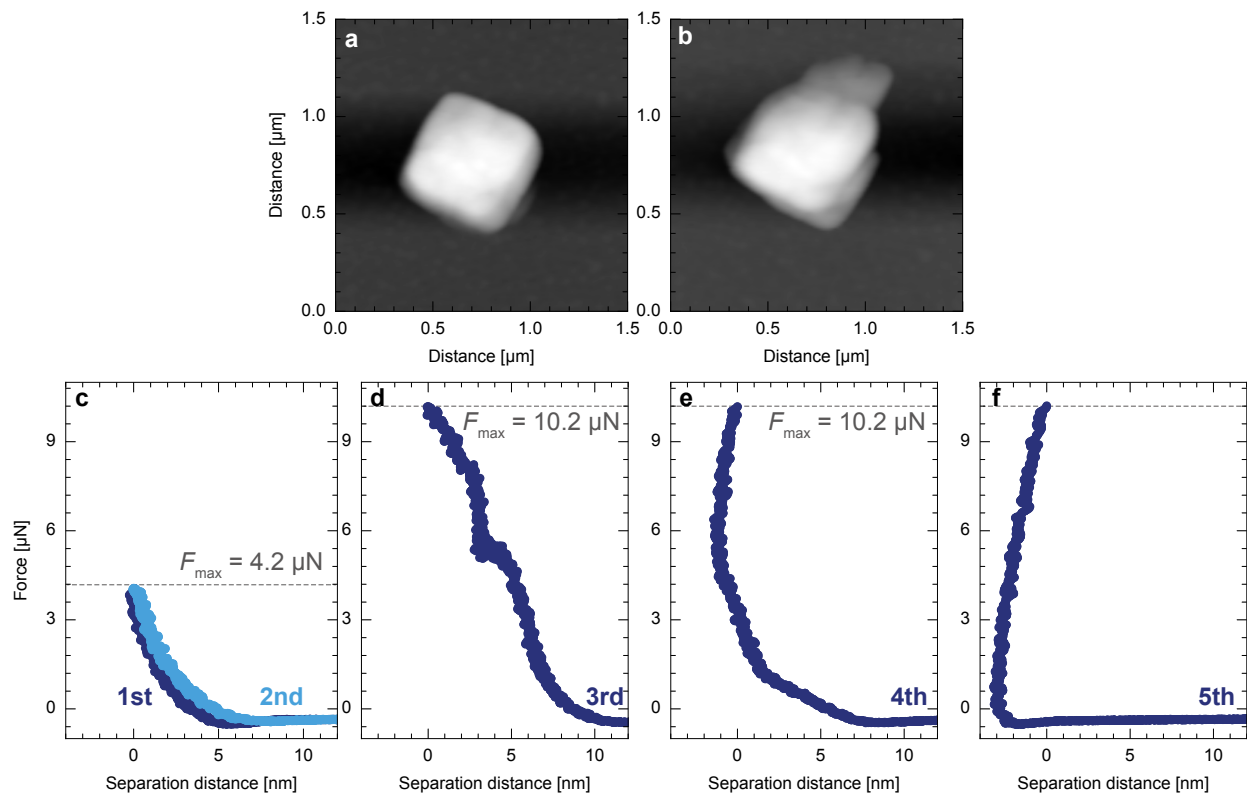


Figure S11: A scanned ELM-12 particle (a) before and (b) after repeated force applications (c)–(f), which were obtained with fixed maximum forces at each measurement.

S14. Calculation method of the work required to induce transition per UC

Calculating the work per single UC necessitated two factors: the work of the entire particle, and the particle size and thickness.

First, the work was calculated by integrating the obtained force profile until the force started to decrease; however, identifying this point is sometimes challenging due to a kinetic problem and measurement noise. For example, force reductions were invisible in Figure S12a, but the slope-changed point was observed at a separation distance of approximately 6 nm. The point seemed the end-of-transition point, but it was obscured. Therefore, we set a unified criterion for judging the occurrence of the transition as follows:

- Smooth the x - and y -values using 100 points (a pink dashed line in Figure S12a).
- Differentiate the smoothed line (Figure S12b).
- Identify a local maximum that showed a great change from the immediately preceding local minimum as the end-of-transition point.

Second, the particle size and thickness were obtained from scanned images in four directions (Figure S13). The thickness was measured from the direction along and perpendicular to the scan direction. The size was measured as the side lengths of the rectangle shape.

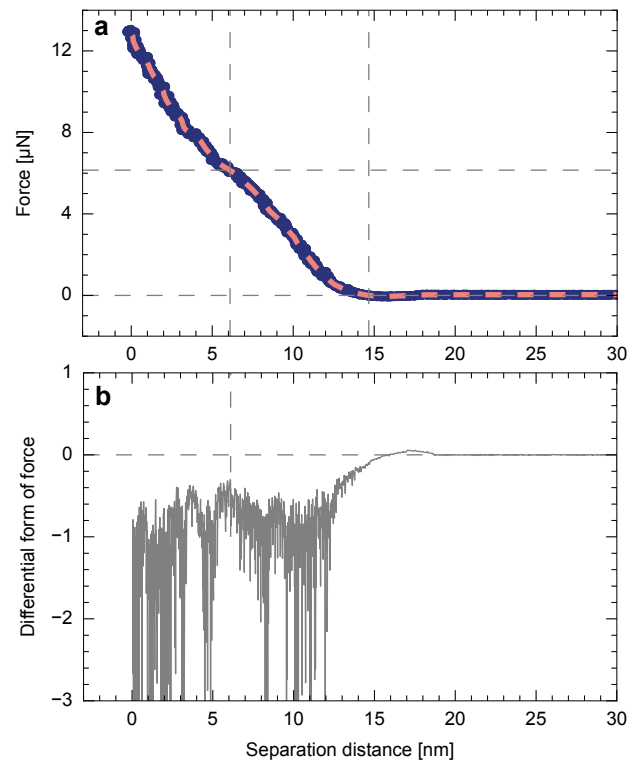


Figure S12: (a) A force curve on ELM-12 with EtOH and (b) the differential form.

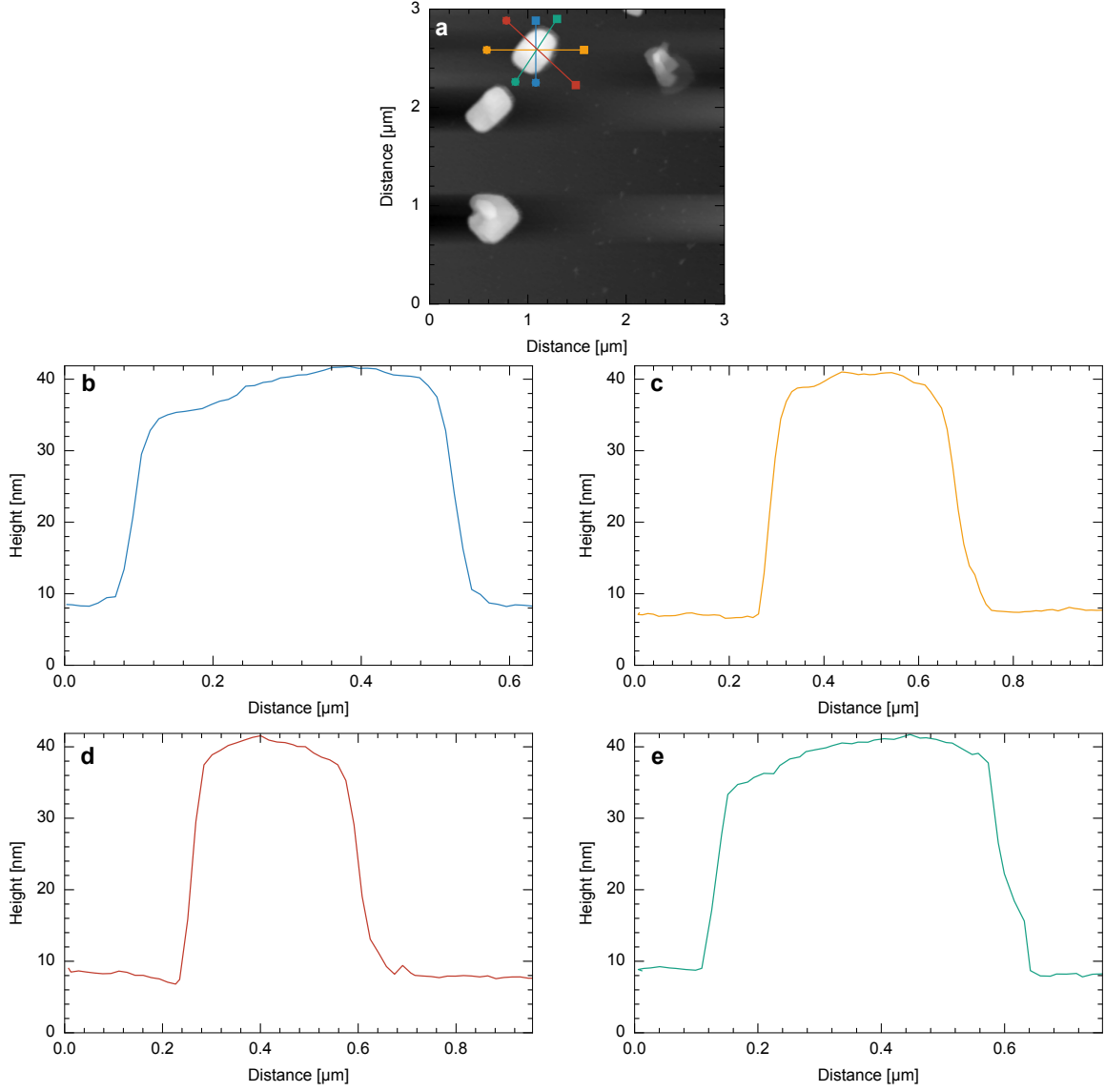


Figure S13: (a) A scanned image of ELM-12 particles and colored lines for measuring the particle size and thickness. (b)–(e) two-dimensional images for measuring thickness (b,c) and size (d,e), whose colors correspond.

S15. Overvalued work by discrete ranges in force profiles

In this study, by integrating force profiles obtained with a colloidal probe in AFM, the free energy change for gate desorption, $-\Delta\Omega_{\text{os}}$, was calculated as work. Strictly speaking, the calculations were not accurate, because of discrete ranges where the probe recovered. Figure S14 depicts schematics of overvalued works in the free energy calculations for the five-layer ELM-12 particles as a model case. Figures S14a to S14c illustrate the free energy profiles of an ELM-12 particle with increasing adsorptive pressure. Differentiating the profiles results in the theoretical X vs. π profiles; thus, the free energy change from the lp to np state can be calculated by integrating the X vs. π profiles (Figures S14d to S14f). However, as mentioned in Figure 5, the AFM techniques cannot completely trace the profiles due to technical limitations, and exhibit the modified profiles (Figures S14g to S14i). The integrated area in the experimental force profiles equals the work exerted by a colloidal probe, W , not that subjected to the ELM-12 particles; therefore, these values differ from the $-\Delta\Omega_{\text{os}}$ ones. Nevertheless, these relationships between the W and $\Delta\Omega_{\text{os}}$ values are close, because the $-\Delta\Omega_{\text{os}}$ values equal to the W values minus the pink-shaded areas with diagonal lines plus the remaining areas highlighted by green and purple (Figure S14j). The remaining area would be negligible, considering hundreds-layered particles. Notably, the pink-shaded areas are consistent irrespective of the adsorptive pressures and thus become relatively smaller at higher pressures than the gate pressure (Figure S14i). As the AFM experiments were conducted at the higher pressures, $-\Delta\Omega_{\text{os}}$ was approximated as W , derived by integrating the measured force profiles. This approach provided a reliable estimation.

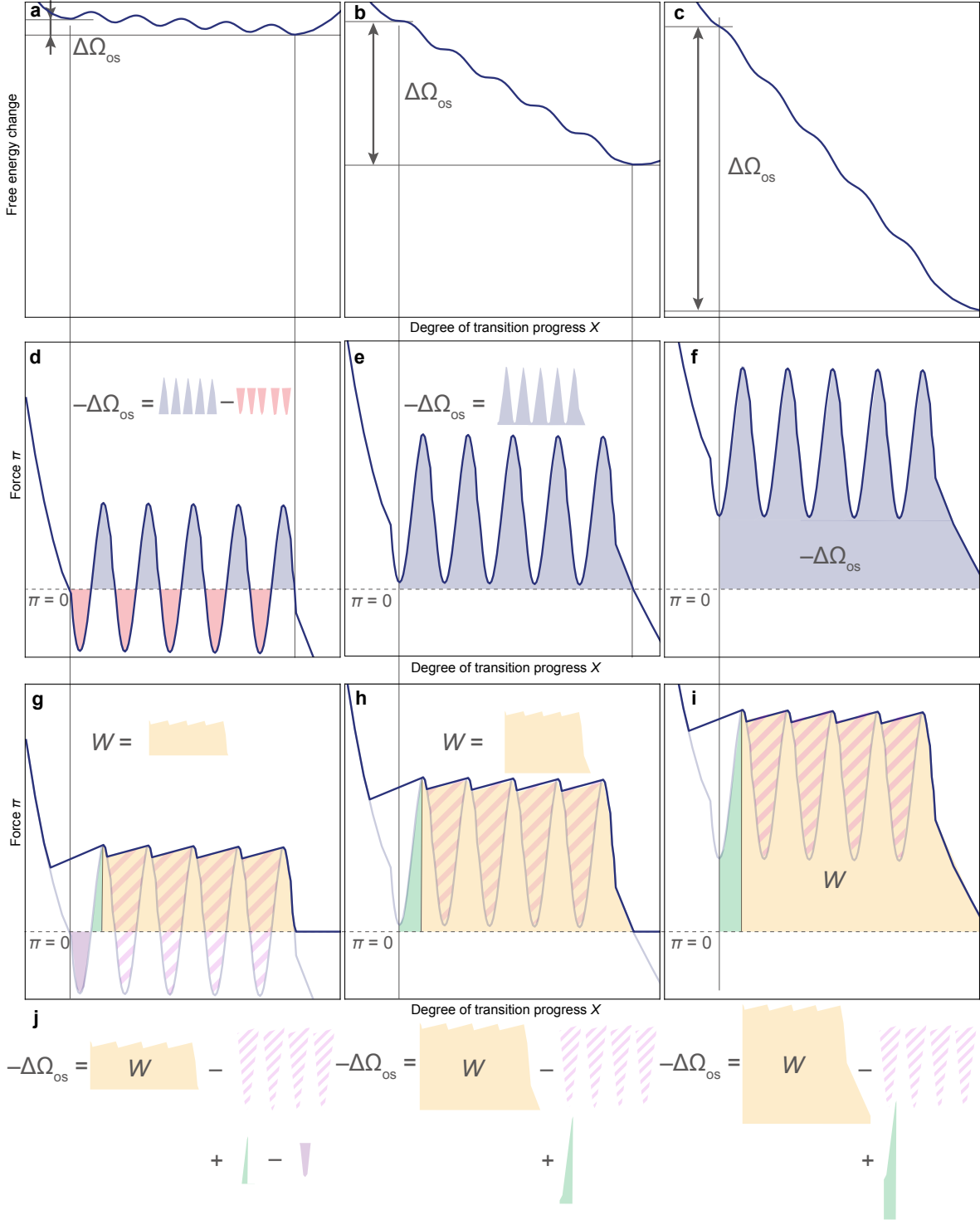


Figure S14: (a)–(c) Schematics of free energy profiles for an ELM-12 particle composed of five layers with increasing adsorptive pressures. (d)–(f) Corresponding force profiles obtained by differentiating (a)–(c), and (g)–(h) theoretically expected force profiles, respectively. (j) Accurate calculation to obtain the free energy change.

S16. Gas chromatograph results

Before each AFM measurement, the EtOH partial pressure was measured by gas chromatography. First of all, we used gas bags and a mass flow controller to create the calibration curve. N₂ was introduced for a certain time and liquid EtOH was dropped in fixed amounts by a microsyringe to arrange target atmospheres with different conditions ($P_{\text{EtOH}}/(P_{\text{EtOH}} + P_{\text{N}_2}) = 0.005, 0.01, 0.015, 0.02$, which equal to $P_{\text{EtOH}}/P_0 = 0.064, 0.129, 0.193, 0.257$) (Figure S15a). The calibration curve was drawn along the area ratio for EtOH and N₂, as illustrated in Figure S15b. By interpolating or extrapolating the calibration curve, the P_{EtOH}/P_0 values were determined for each AFM measurement, which were averaged over three gas chromatography measurements (Figure S15c). In principle, the absolute position of each peak is always the same though the strength is different, but it was not so due to differences in the flow rate or the gas amount. Calculating the ratio of areas within certain ranges avoided the error caused by experimental limitations.

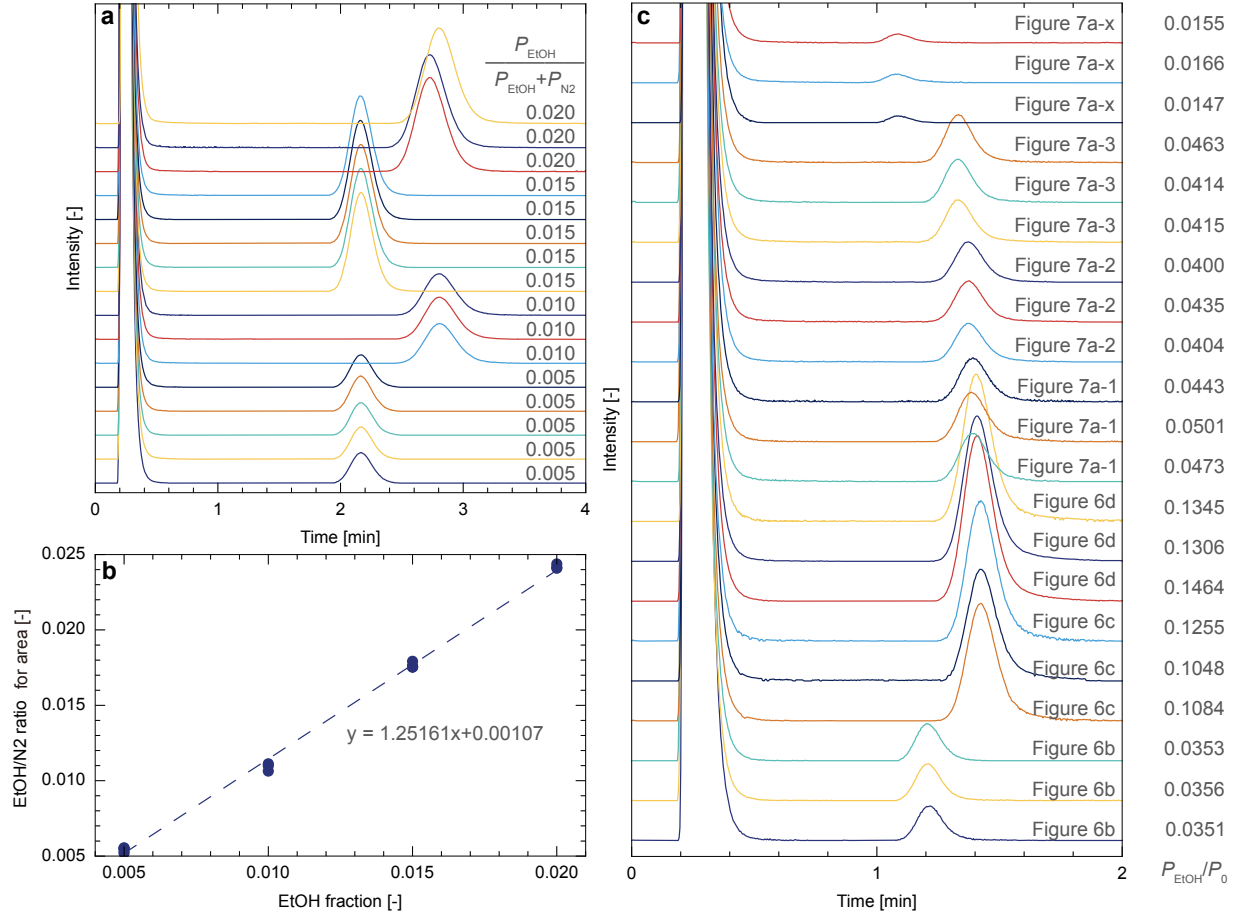


Figure S15: (a) Gas chromatograph results with fixed $P_{\text{EtOH}}/(P_{\text{EtOH}} + P_{\text{N}_2})$ values for (b) the calibration curve. (c) Calibrated results for gas chromatography three times for each AFM measurement.

S17. All measured force profiles for ELM-12

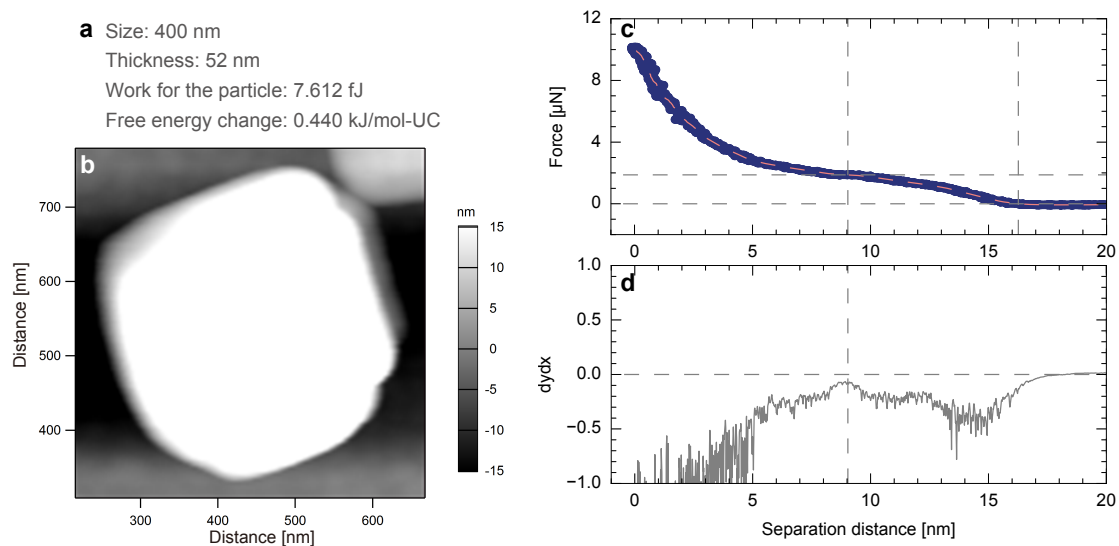


Figure S16: Under the $P_{\text{EtOH}}/P_0 = 0$ condition.

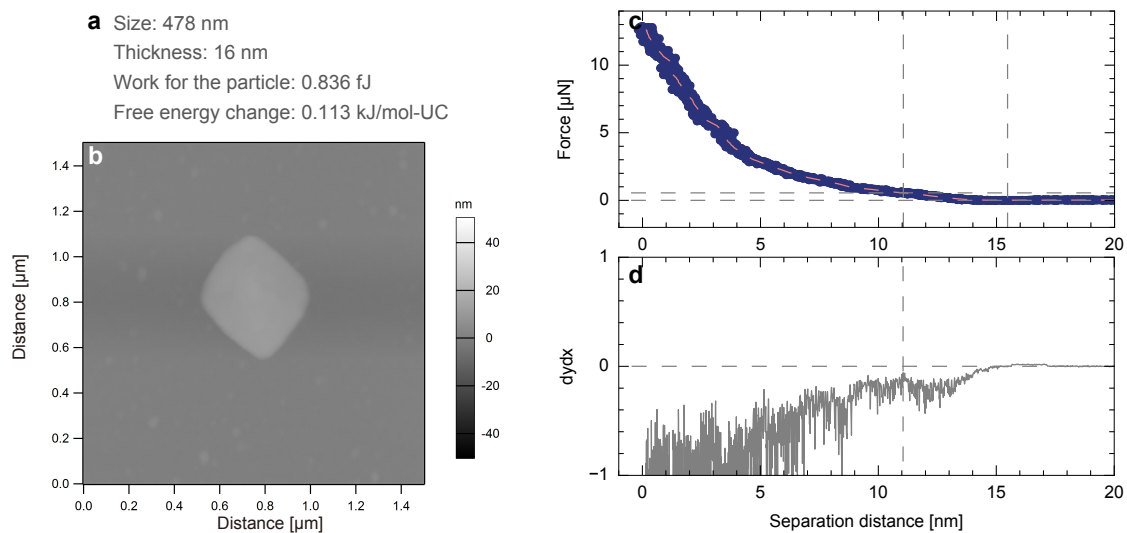


Figure S17: Under the $P_{\text{EtOH}}/P_0 = 0$ condition.

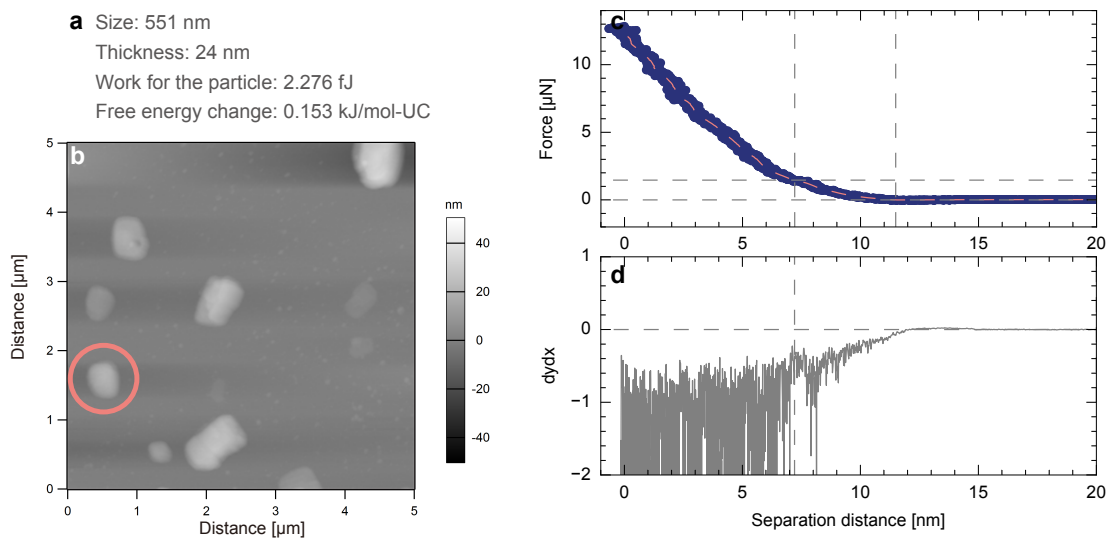


Figure S18: Under the $P_{\text{EtOH}}/P_0 = 0$ condition.

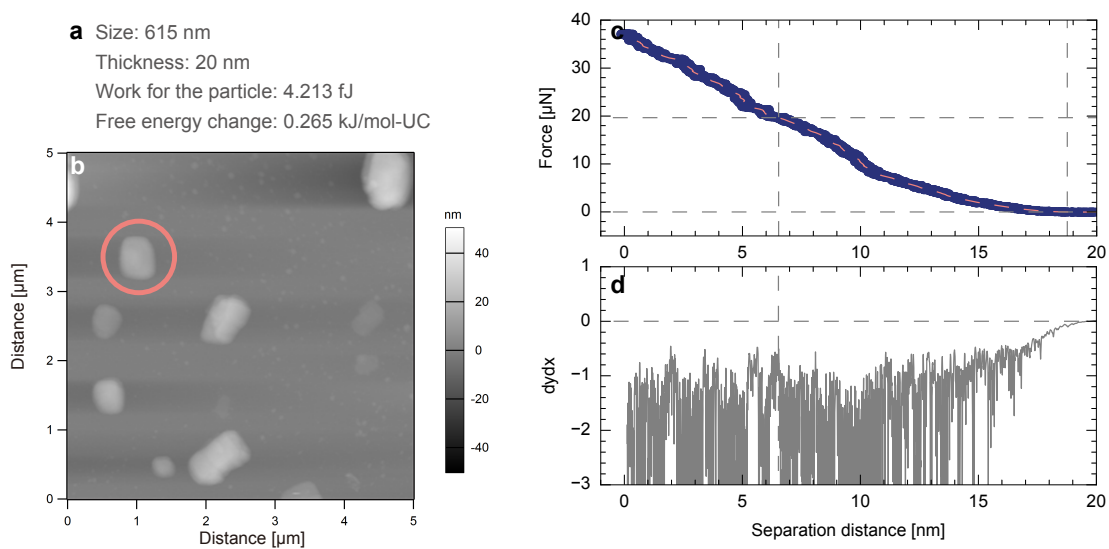


Figure S19: Under the $P_{\text{EtOH}}/P_0 = 0$ condition.

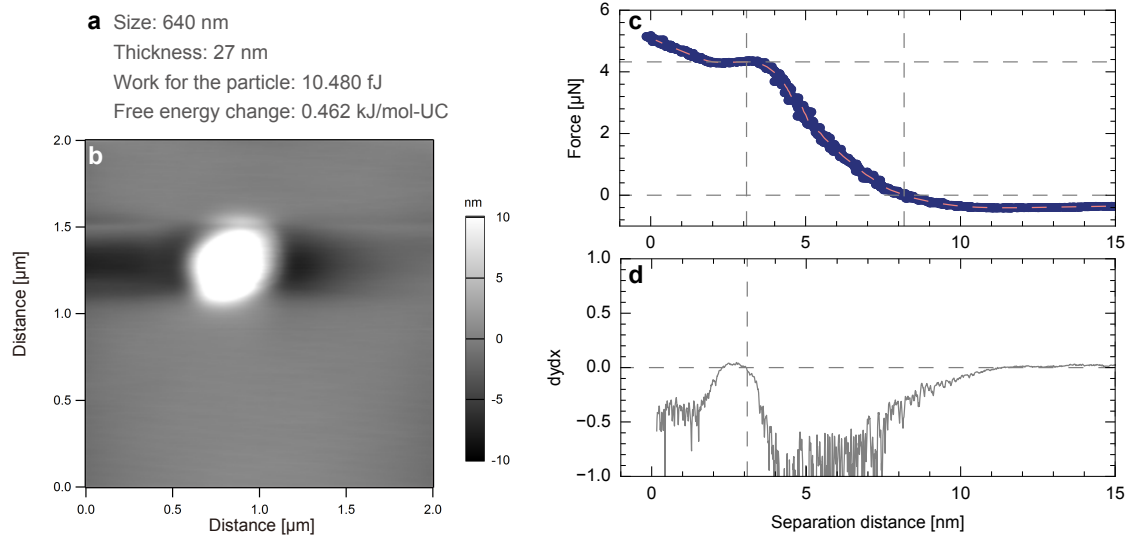


Figure S20: Under the $P_{\text{EtOH}}/P_0 = 0$ condition.

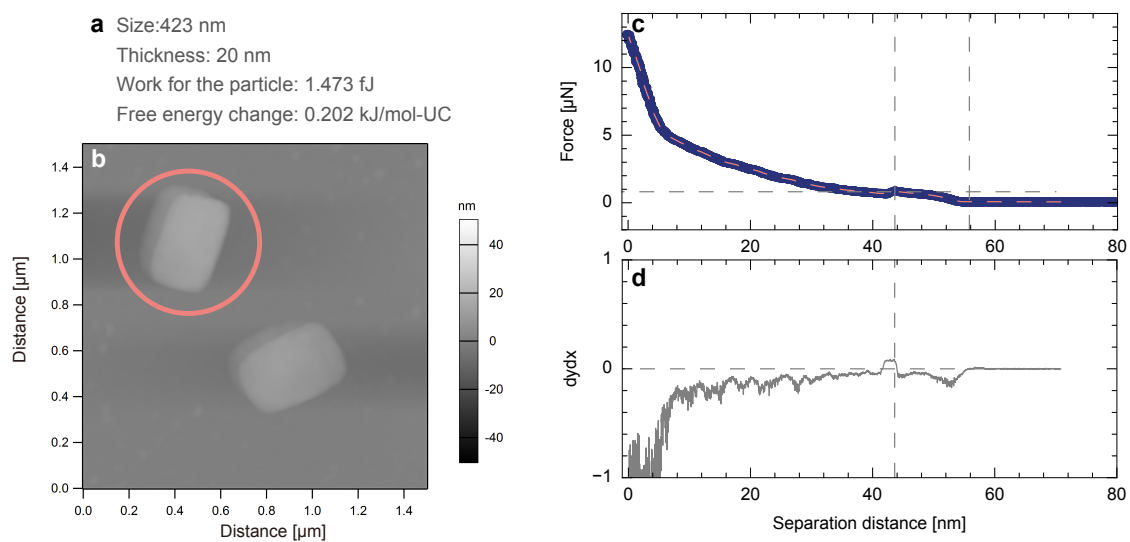


Figure S21: Under the $P_{\text{EtOH}}/P_0 = 0.016$ condition.

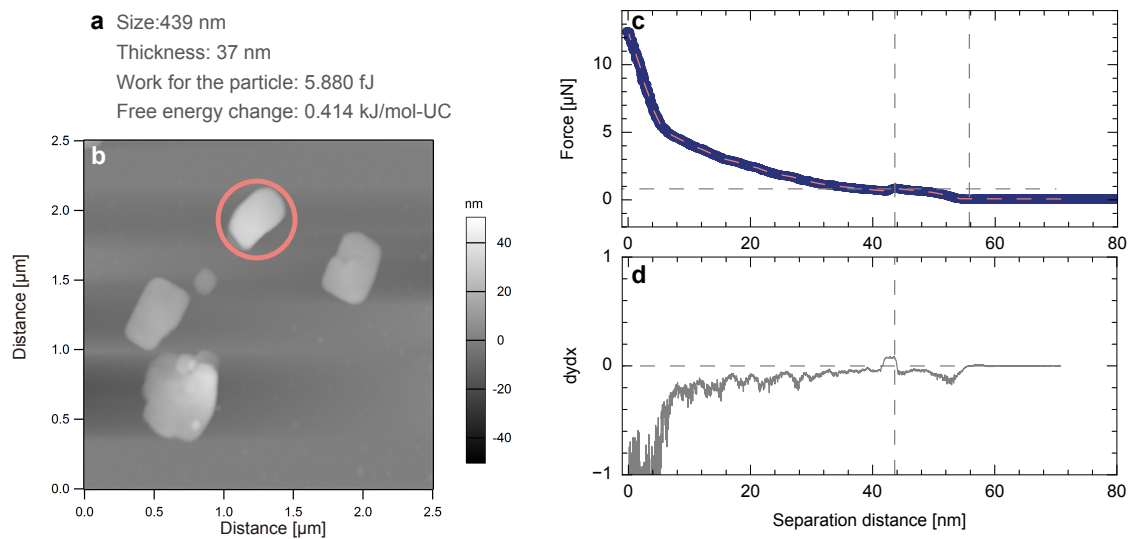


Figure S22: Under the $P_{\text{EtOH}}/P_0 = 0.016$ condition.

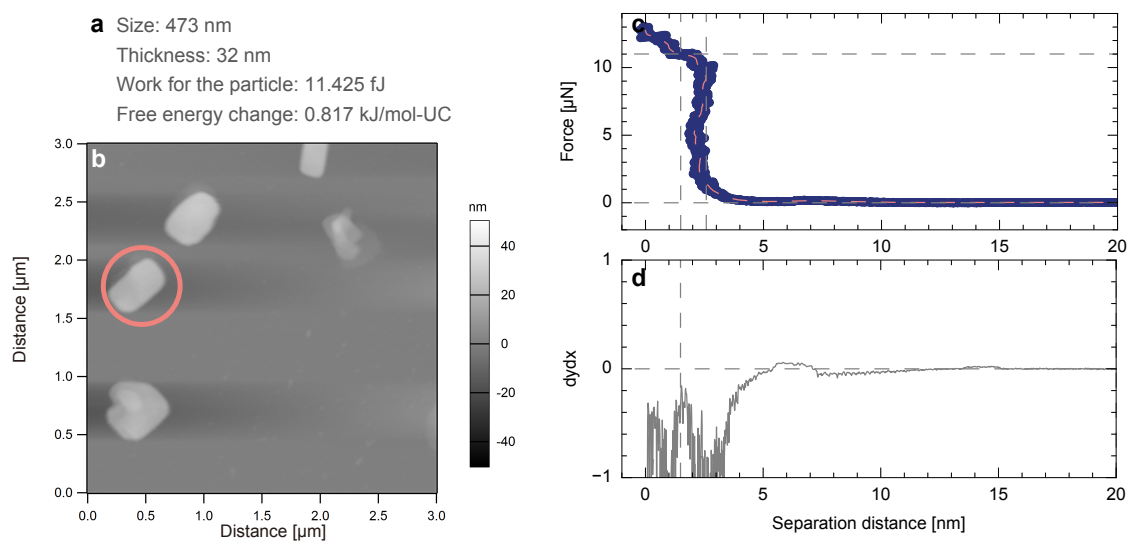


Figure S23: Under the $P_{\text{EtOH}}/P_0 = 0.016$ condition.

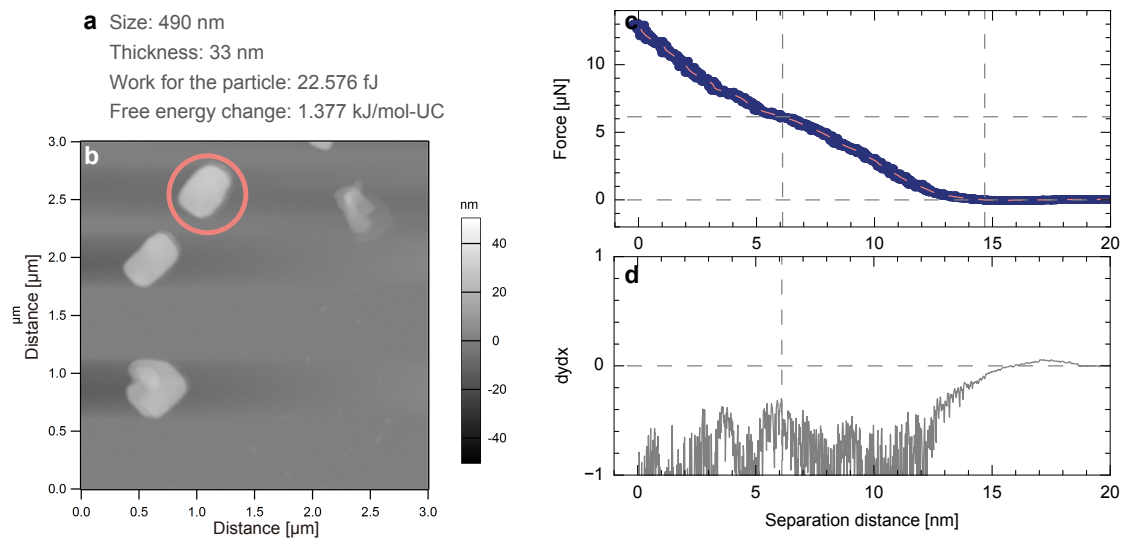


Figure S24: Under the $P_{\text{EtOH}}/P_0 = 0.016$ condition.

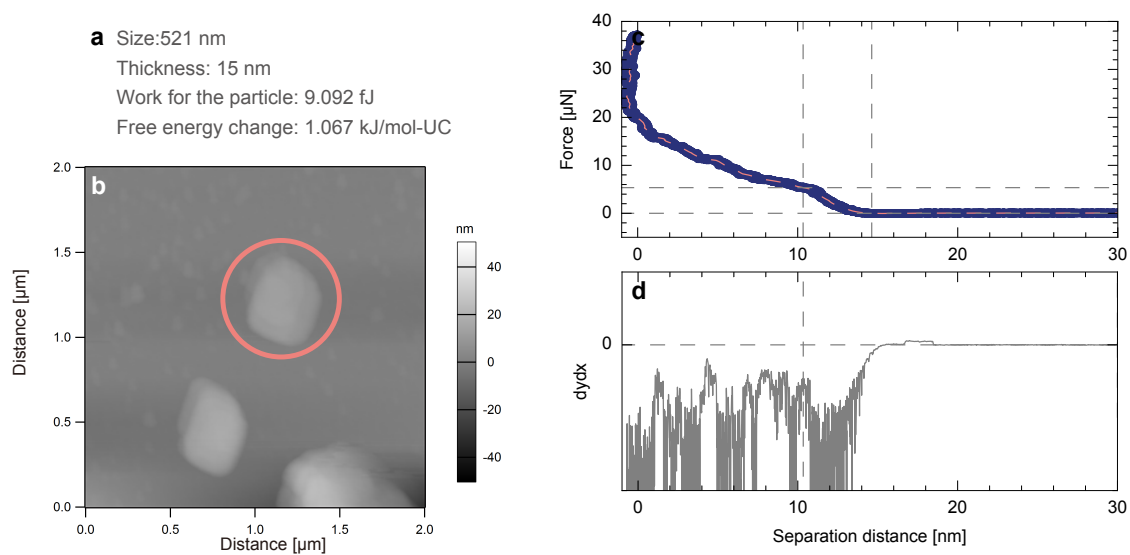


Figure S25: Under the $P_{\text{EtOH}}/P_0 = 0.016$ condition.

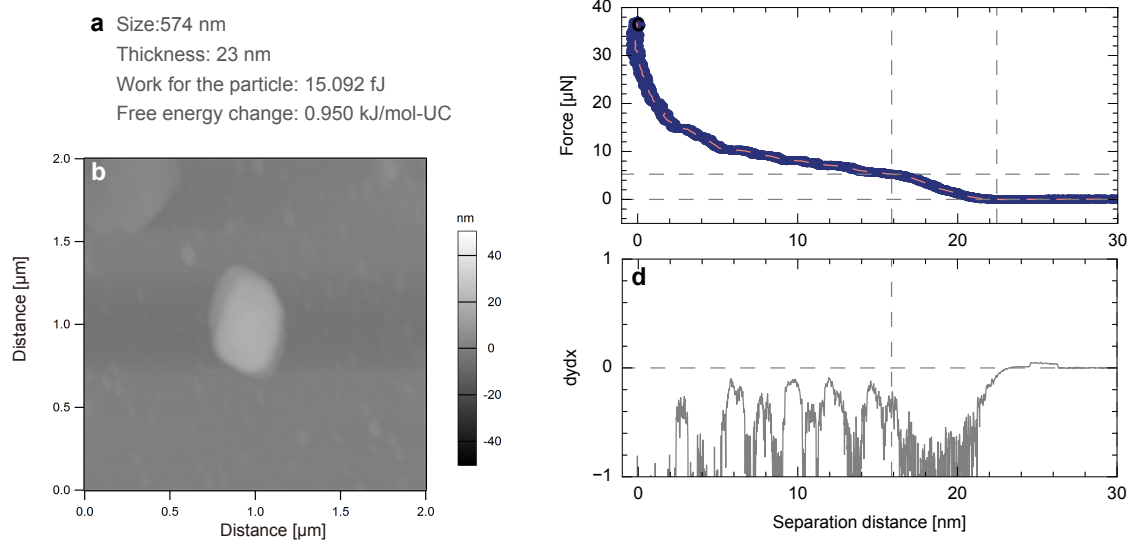


Figure S26: Under the $P_{\text{EtOH}}/P_0 = 0.016$ condition.

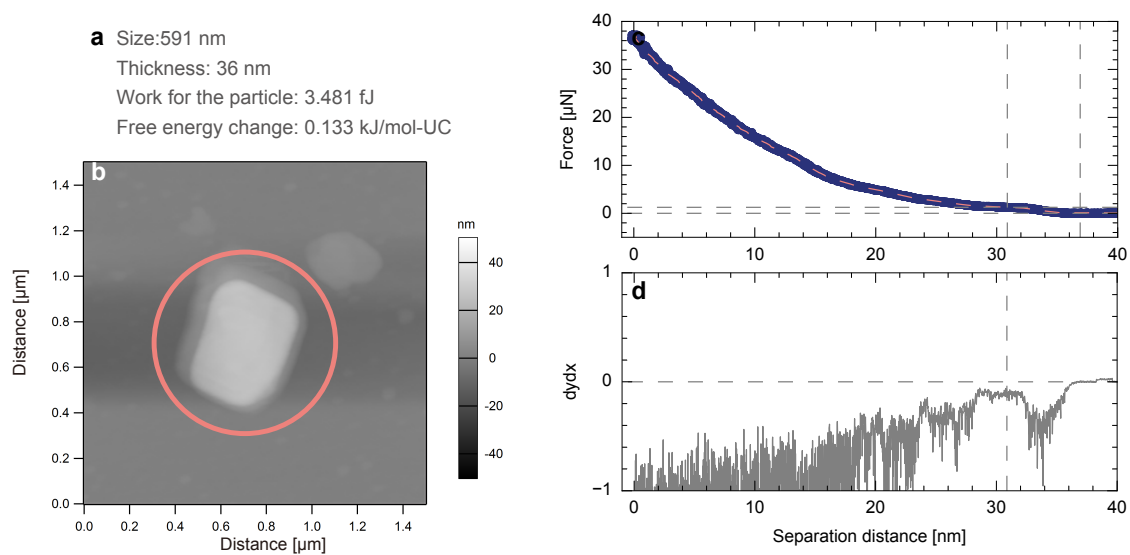


Figure S27: Under the $P_{\text{EtOH}}/P_0 = 0.016$ condition.

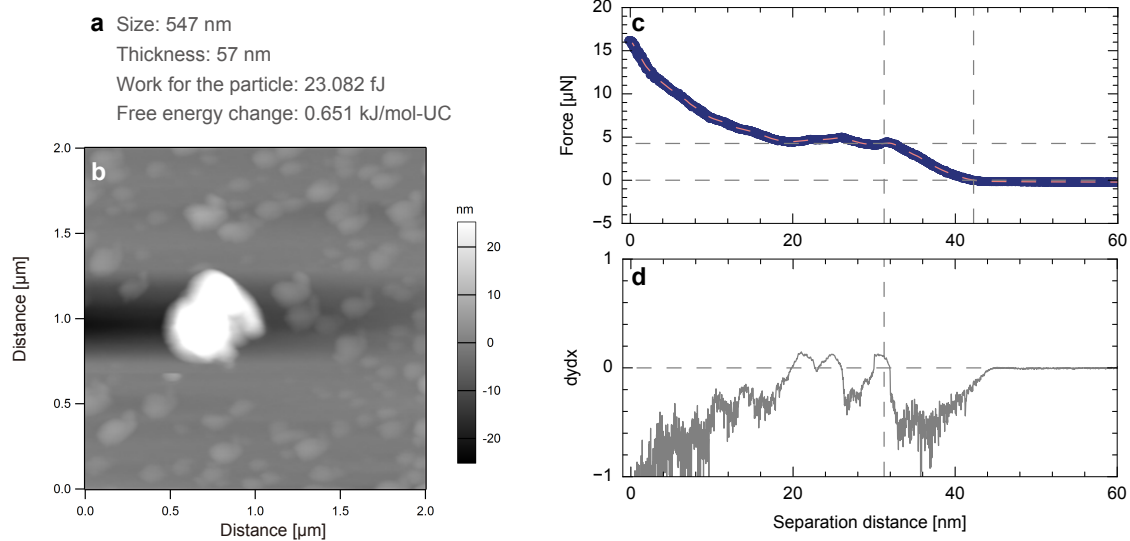


Figure S28: Under the $P_{\text{EtOH}}/P_0 = 0.035$ condition.

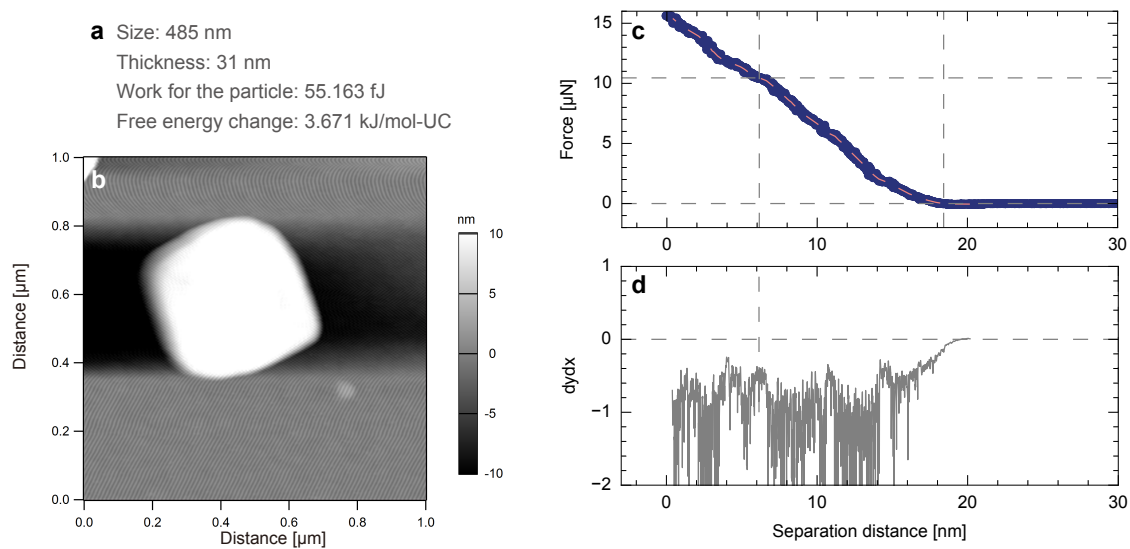


Figure S29: Under the $P_{\text{EtOH}}/P_0 = 0.041$ condition.

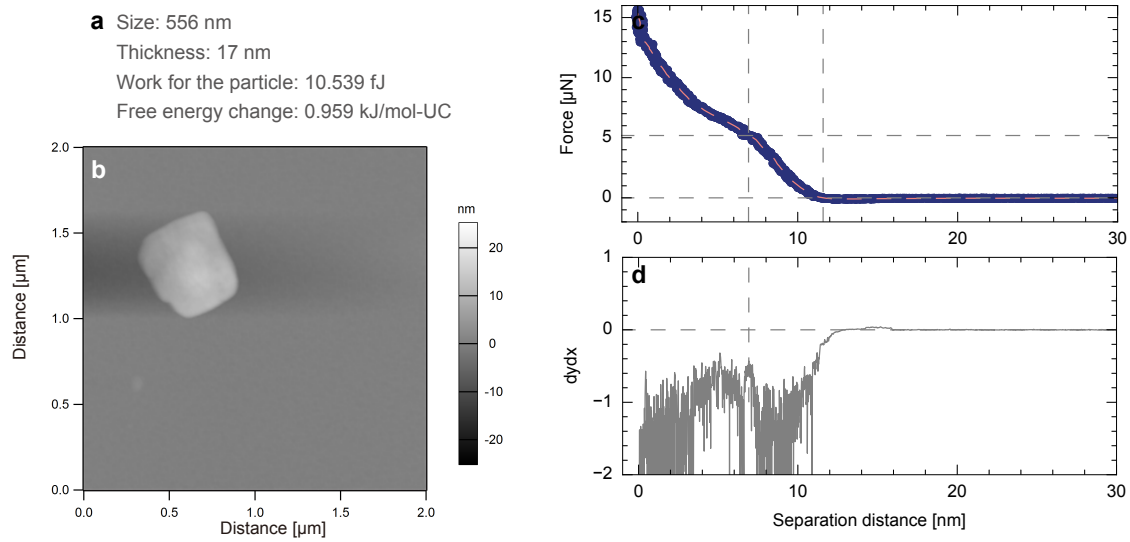


Figure S30: Under the $P_{\text{EtOH}}/P_0 = 0.041$ condition.

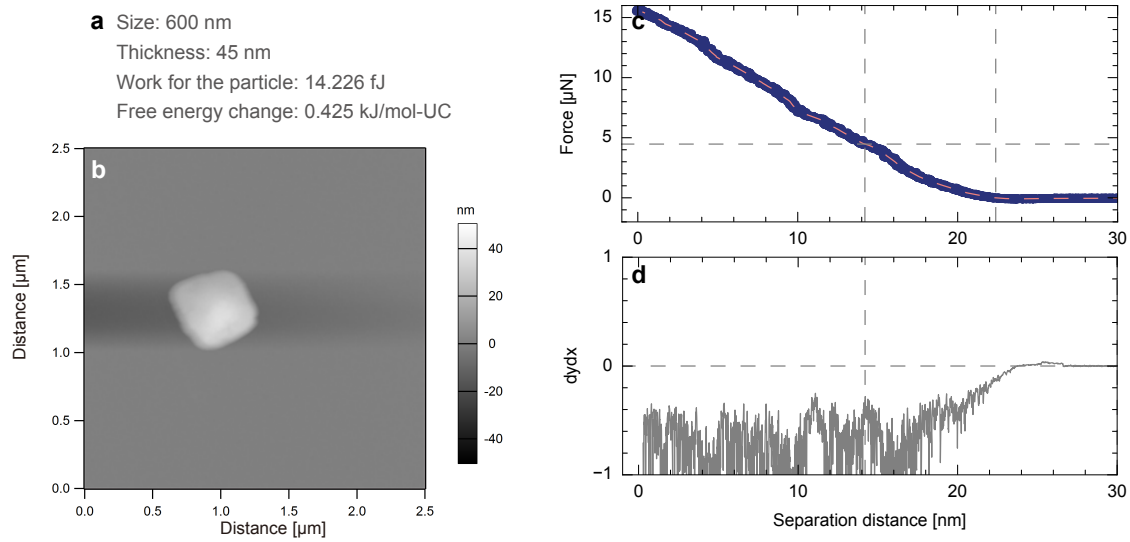


Figure S31: Under the $P_{\text{EtOH}}/P_0 = 0.041$ condition.

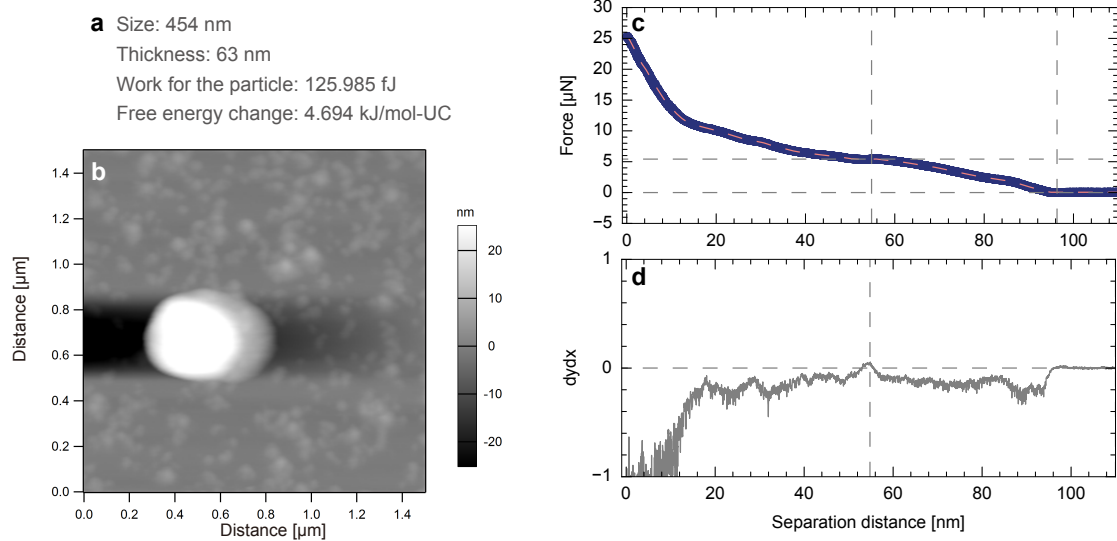


Figure S32: Under the $P_{\text{EtOH}}/P_0 = 0.047$ condition.

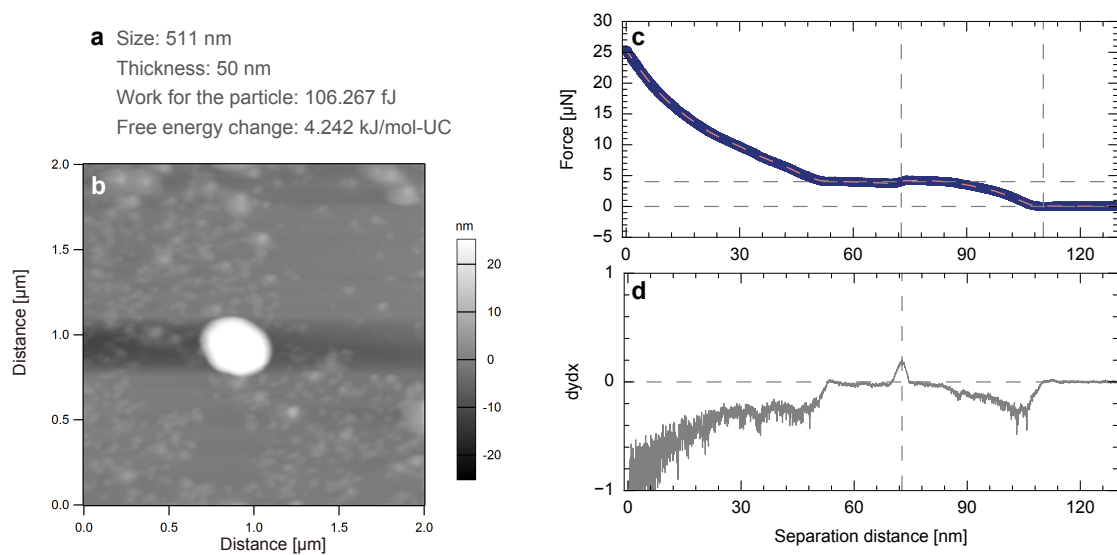


Figure S33: Under the $P_{\text{EtOH}}/P_0 = 0.047$ condition.

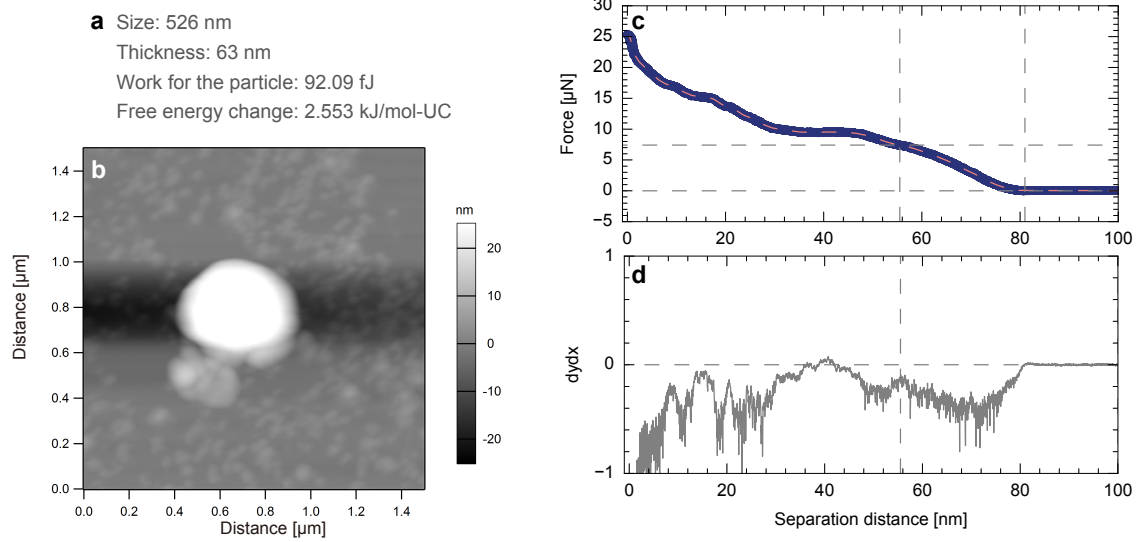


Figure S34: Under the $P_{\text{EtOH}}/P_0 = 0.047$ condition.

S18. Langmuir fitting result for the EtOH adsorption isotherm on ELM-12

Partially fitting adsorption and desorption isotherms with the Langmuir equation yielded the Langmuir parameters as $n_{\infty} = 1.11$ mol/mol and $K = 99.23$ kPa $^{-1}$. The fitting was performed for the amount adsorbed on the lp state after the corresponding plots were selected. As confirmed in Figure S35, the fitting did not go well. This is mainly because of the unsuitable model for fitting. Although the appropriate model must be applied, such as simulated isotherms, to reduce quantitative errors, it is challenging. Nevertheless, the qualitative trend introduced in the main paper remains the same.

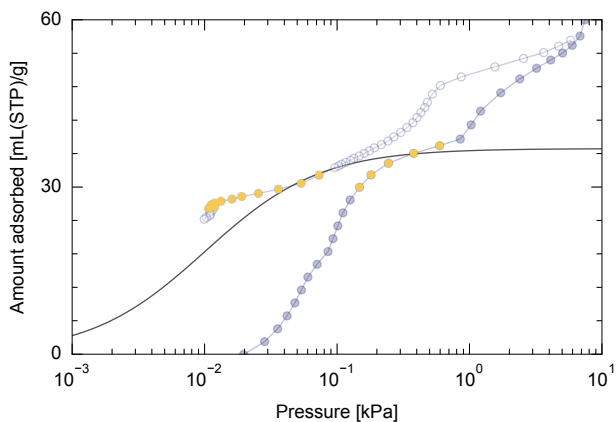


Figure S35: EtOH adsorption and desorption isotherms on the ELM-12 sample at 298 K, where the yellow markers were only used for the fitting. Closed and open symbols in the experimental results represent adsorption and desorption processes, respectively.

S19. Fitting adsorption isotherms on the np-state ELM-12

In this study, the amount adsorbed on the np state was assumed to be zero across the entire pressure range due to a lack of adsorption data necessary for fitting. This is the main reason why the individual gate desorption pressures estimated by analyzing force profiles significantly differ from that observed in the desorption isotherm. If the amount adsorbed on the np state was modeled with the Langmuir equation, characterized by n_{np} and K_{np} , equation 9 is rewritten as

$$\Delta\Omega_{os} = -n_{lp}k_B T \ln \frac{1 + K_{lp}P_{measured}}{1 + K_{lp}P_{gate}} + n_{np}k_B T \ln \frac{1 + K_{np}P_{measured}}{1 + K_{np}P_{gate}}$$

where the n_{lp} and K_{lp} were replaced by n_{∞} and K , respectively. Based on the equation, the P_{gate} value can also be calculated when the $\Delta\Omega_{os}$ and $P_{measured}$ were known, though the equation cannot be written down analytically. Figure S36 depicts fitting results with various parameters and numerical calculation results, indicating that the values of gate desorption pressures depend on the fitting parameters, though the quantitative trend remained. The reversal of the order in some values is attributed to differences in the measurement pressures, but it was not significantly changed. As the several values were comparable to that obtained in the desorption isotherm, the accurate modeling may enhance the estimation.

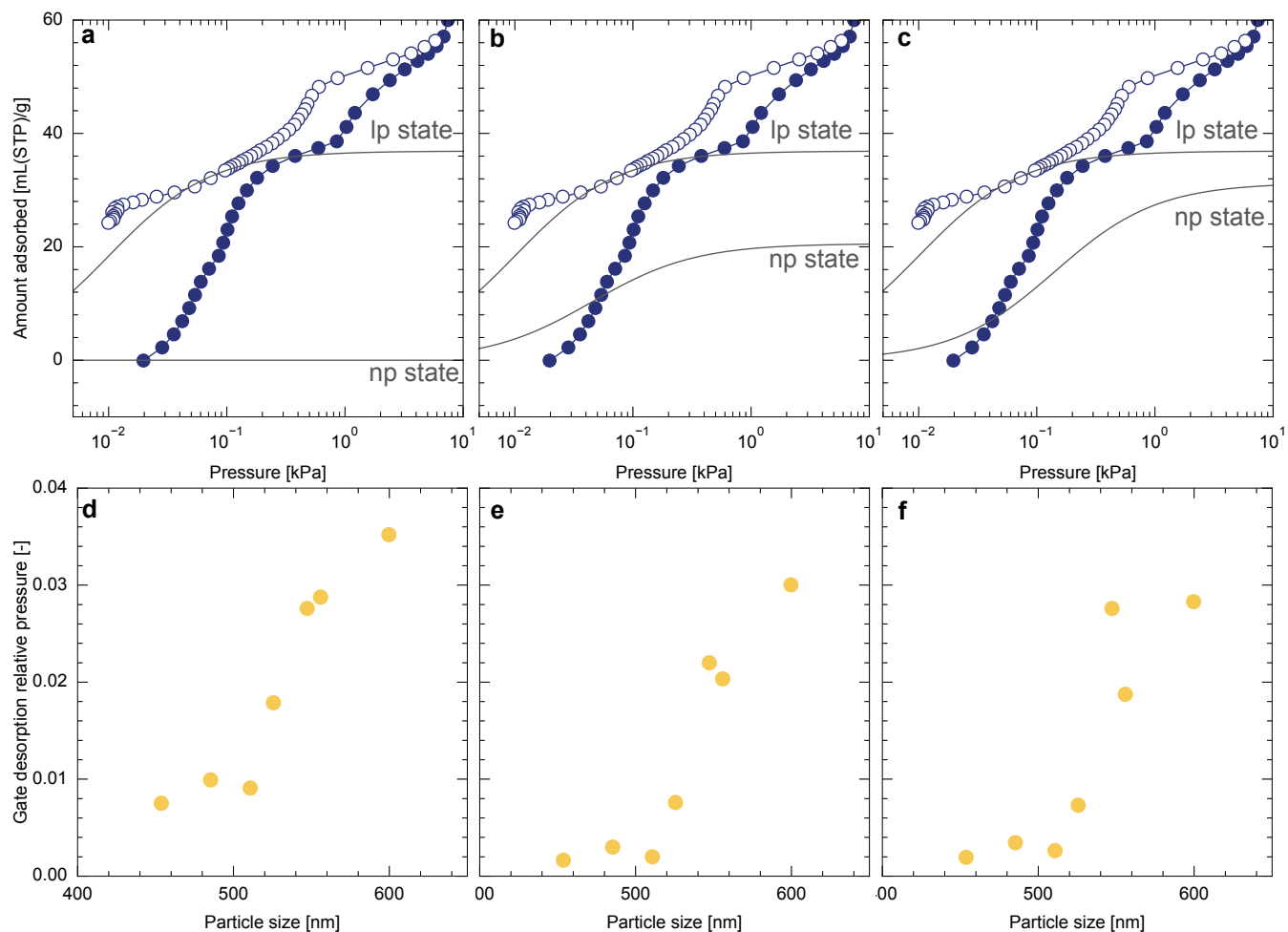


Figure S36: (a)–(c) Langmuir fitting for EtOH adsorption and desorption isotherms on the ELM-12 sample at 298 K with the parameters of $(n_{np}, K_{np}) = (0 \text{ mol/mol}, -)$, $(0.62 \text{ mol/mol}, 22.25 \text{ kPa}^{-1})$, $(0.94 \text{ mol/mol}, 7.04 \text{ kPa}^{-1})$, respectively. The fitting differentiated the calculation values of gate desorption pressures, (d)–(f), namely.

References

- (S1) 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.
- (S2) Kondo, A.; Kajiro, H.; Noguchi, H.; Carlucci, L.; Proserpio, D. M.; Ciani, G.; Kato, K.; Takata, M.; Seki, H.; Sakamoto, M.; Hattori, Y.; Okino, F.; Maeda, K.; Ohba, T.; Kaneko, K.; Kanoh, H. Super Flexibility of a 2D Cu-Based Porous Coordination Framework on Gas Adsorption in Comparison with a 3D Framework of Identical Composition: Framework Dimensionality-Dependent Gas Adsorptivities. *J. Am. Chem. Soc.* **2011**, *133*, 10512–10522.