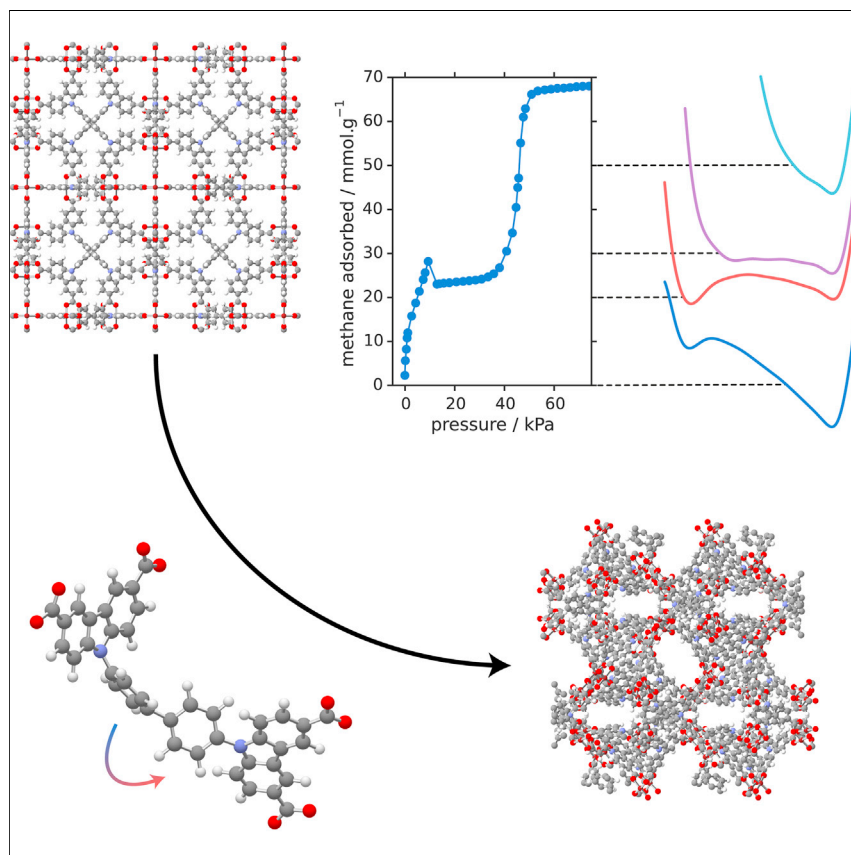


Article

Origins of Negative Gas Adsorption



Highly flexible metal-organic framework DUT-49 shows an unexpected phenomenon whereby, as the material fills with gas, it contracts suddenly and releases a significant fraction of the adsorbed methane. This negative gas adsorption process is extremely rare and has not been observed in porous materials previously. Coudert and colleagues reveal the microscopic mechanism behind this non-conventional behavior, highlighting its roots in mechanics and thermodynamics by using multiscale computer simulations.

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HIGHLIGHTS

Negative gas adsorption is a decrease in adsorption upon increase of pressure

Molecular simulations reveal its microscopic mechanism

It is enabled by the buckling of the DUT-49 linker under stress

Thermodynamics reveals the driving force of the transition



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Article

Origins of Negative Gas Adsorption

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SUMMARY

Negative gas adsorption by a porous crystalline solid, DUT-49, observed by spontaneous desorption of gas during a pressure increase raises fundamental questions on the physical origin of this puzzling behavior. Importantly, a framework that can transform a large amount of strain into pressure has many possible technological applications. To address this question, we studied the mechanics and thermodynamics of DUT-49 at both the molecular unit and framework scales by applying quantum density functional theory and extensive classical molecular-dynamics simulations. We demonstrate that negative gas adsorption originates from molecular buckling of the organic structural unit and thus allows a colossal framework transformation. Methane adsorption is subsequently shown to activate this transition, in full agreement with experimental observations. The molecular insight presented here unveils the mechanics and thermodynamics responsible for negative gas adsorption and provides unparalleled understanding to aid the discovery of new examples of similarly responsive porous metamaterials.

INTRODUCTION

Metal-organic frameworks (MOFs) differ from conventional inorganic porous materials in that many demonstrate large-scale flexibility of their structure, which results in appealing physical and chemical properties.¹ Notably, there are increasing reports of soft porous crystals² whose flexibility manifests as large-scale transformations induced by modest physico-chemical stimulation, such as changes in temperature, mechanical constraints, and guest adsorption.³ Among the large variety of behaviors exhibited by stimuli-responsive materials, we can cite the widely studied phenomena of gated adsorption and breathing,⁴ which have applications in gas separation,⁵ storage⁶ and sensing.⁷

A particularly intriguing phenomenon resulting from this soft nature of MOFs is that of negative gas adsorption (NGA) in DUT-49, which was recently reported by Krause et al.⁸ DUT-49 is an MOF constructed from dinuclear paddlewheel copper(II) metal centers and 9,9'-(1,1'-biphenyl)-4,4'-diylbis(9*H*-carbazole-3,6-dicarboxylate) (BBCDC) linkers, forming a cubic mesoporous framework (Figure 1A).⁹ For conventional, rigid materials, the laws of thermodynamics mandate that, at equilibrium and at constant temperature, the absolute amount of substance in the adsorbed phase increases with increasing pressure of the adsorbate, which results in the positive slopes observed for single-component adsorption isotherms.¹⁰ However, upon adsorption of gases such as methane or *n*-butane, DUT-49 displays an NGA step (Figure 1B), causing an unexpected pressure amplification triggered by a sudden structural transition of the nanoporous framework.⁸ It is the first material known to exhibit this property, which was attributed to the filling of the micropores by guests and the occurrence of a metastable state of the loaded framework. However, so far, there has been no direct account of the microscopic nature of the transition itself, and the detailed balance of thermodynamic driving forces is unknown.

The Bigger Picture

Conventional nanoporous materials have a wide range of technological applications as desiccants, ion exchangers, and catalysts. However, it is increasingly evident that emerging flexible metal-organic framework materials are particularly advantageous in separation processes and responsive applications. In particular, the flexible material DUT-49 shows an unexpected phenomenon where, as the material fills with gas, it contracts suddenly and releases a significant portion of methane. This negative gas adsorption process is extremely rare and has not been observed in porous materials previously. Here, we demonstrate the mechanics and thermodynamics responsible for this non-conventional behavior by using multiscale computer simulations. This fundamental understanding is crucial for the future application of negative gas adsorption materials, which include advanced micro-pneumatic components and stimuli-responsive separation processes.

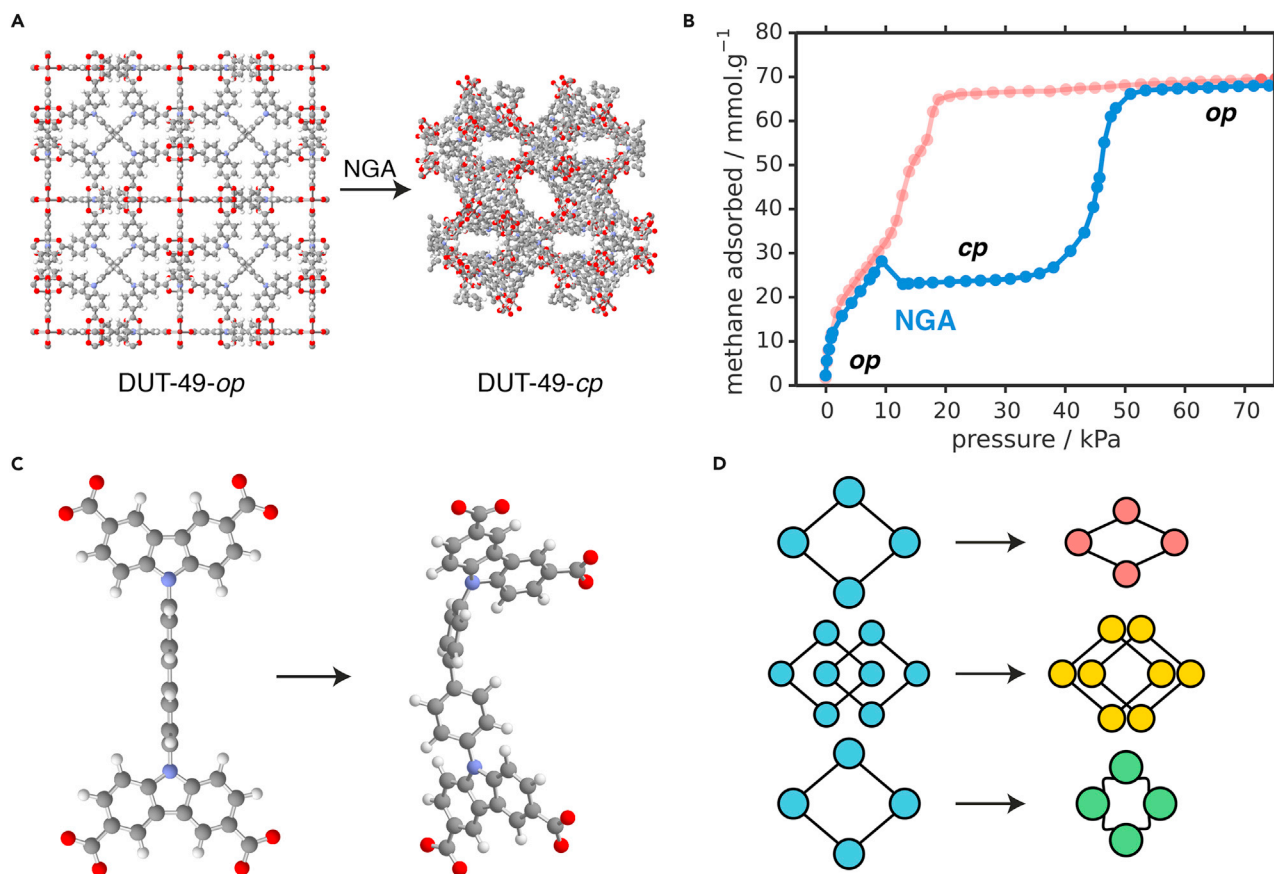


Figure 1. Negative Gas Adsorption in DUT-49

(A) A summary of the crystal structure of DUT-49-op (open pore) and DUT-49-cp (contracted pore), including the transitions present during negative gas adsorption (NGA) and subsequent pore saturation.

(B) An example of the experimental isotherm observed for DUT-49 during methane adsorption at 111 K and the type 1 isotherm, calculated by simulation, for the static DUT-49-op structure (blue and red, respectively).⁸

(C) Buckling-like deformation of the BBCDC ligand demonstrated during the NGA process.

(D) Stylistic representation of structural transformations in MOFs: hinging mechanism (red), sub-lattice displacement (yellow), and the mechanism observed in DUT-49 (green).

In situ X-ray diffraction was used to elucidate the open-pore (op) and contracted-pore (cp) structures of DUT-49, as depicted in Figure 1A.⁸ The structural transformation observed in this material—linked to the NGA—is localized to a deformation of the BBCDC ligand (Figure 1C). This is in stark contrast with previously known examples of large structural transitions in MOFs, where organic linkers are seen as rigid struts. Commonly, flexible MOFs rely upon either a hinging mechanism, where the deformation occurs in the coordination of the metal node,^{11–13} or sub-lattice displacement,¹⁴ as illustrated stylistically in Figure 1D. Moreover, the periodic array of geometrically and elastically coupled buckling units in DUT-49 is analogous to the folding and unfolding of maps, wings, petals, and the artificially constructed Miura-ori pattern.^{15,16} We thus hypothesize that the deformation observed for the ligand, and the collective behavior coupling these deformations throughout the crystal, is crucial to the NGA phenomenon to allowing for an accessible, rapid, and large structural transformation.

Herein, we detail multiscale molecular simulations of DUT-49 to provide insight into the mechanics and thermodynamics of the NGA transition, linking this

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astonishing macroscopic behavior to a mechanism at the atomistic scale. We combine quantum chemistry calculations at the density functional theory (DFT) level with classical molecular-dynamics simulations to provide a complete picture of this phenomenon.

RESULTS AND DISCUSSION

To understand the NGA transition at the microscopic level, we combined a variety of methods including DFT calculations of the vital components of the DUT-49 framework and classical simulation of the crystal and adsorbates.

Ligand Mechanics

Initial investigation of the experimental crystal structures of DUT-49, *op* and *cp*, showed that the copper paddlewheel environment is almost undeformed in the *cp* structure, whereas the BBCDC ligand is significantly bent, with the deformation localized on the biphenyl unit.⁸ In the world of macroscopic mechanics, this behavior of the ligand is akin to the buckling of a column upon application of a critical load.¹⁷ The phenomenon of buckling is characterized by a sudden sideways failure of a structure subjected to significant axial compressive stress, where the compressive stress at the point of failure is less than the ultimate compressive stress that the material is capable of withstanding. To test the relevance of this analogy, we performed DFT optimizations of a single isolated ligand with a series of fixed decreasing N-atom-to-N-atom (N-N) distances. All other internal coordinates were freely optimized. The choice of constraint here is somewhat arbitrary, provided that it involves two atoms near the extremities of the molecule. We chose to constrain the N-N distance because it corresponds to the symmetry of the BBCDC molecule and minimizes out-of-plane forces. By deriving the resulting energy-strain curve, we obtained the stress-strain profile depicted in Figure 2. The constrained structures clearly reflect the dihedral-like rotation of carbazole moieties when the linker is compressed and bends, as observed in the experimental *cp* structure. We quantified the bending of the linker by a “deflection” parameter, which we took as the N-centroid-N angle.

Figure 2 reveals two distinct regimes upon the application of strain to the ligand. First, small deformations result in no deflection as the ligand retains a linear structure. This elastic regime merely corresponds to the compression of interatomic bonds with, as expected, a linear response to deformation. For deformations greater than 3 Å, a buckling transition occurs, with a sudden large deflection of the ligand and a non-linear mechanical response. Previously, if only the static structures of DUT-49-*op* and DUT-49-*cp* were considered, the energy cost of 91 kJ·mol⁻¹ per ligand would appear to present a significant penalty to the transformation.⁸ However, the analysis provided here shows that the critical event requires significantly less energy at 10 kJ·mol⁻¹. Subsequently, upon the onset of buckling, the ligand continues to collapse at constant stress.

All features of the buckling of the ligand are similar to those observed for macroscopic materials (Figure 2B, inset). This elastic response of the ligand, which has not been previously observed in MOFs, produces a bending-dominated framework, which is observed commonly with foam lattice-structured materials.¹⁸ A consequence of the buckling feature in these materials is that their stiffness is significantly reduced to that expected for stretch-dominated structures. For example, a typical foam with buckling behavior is less stiff by a factor of 10 than a stretch-dominated framework of the same density.¹⁸ This mechanical perspective demonstrates how,

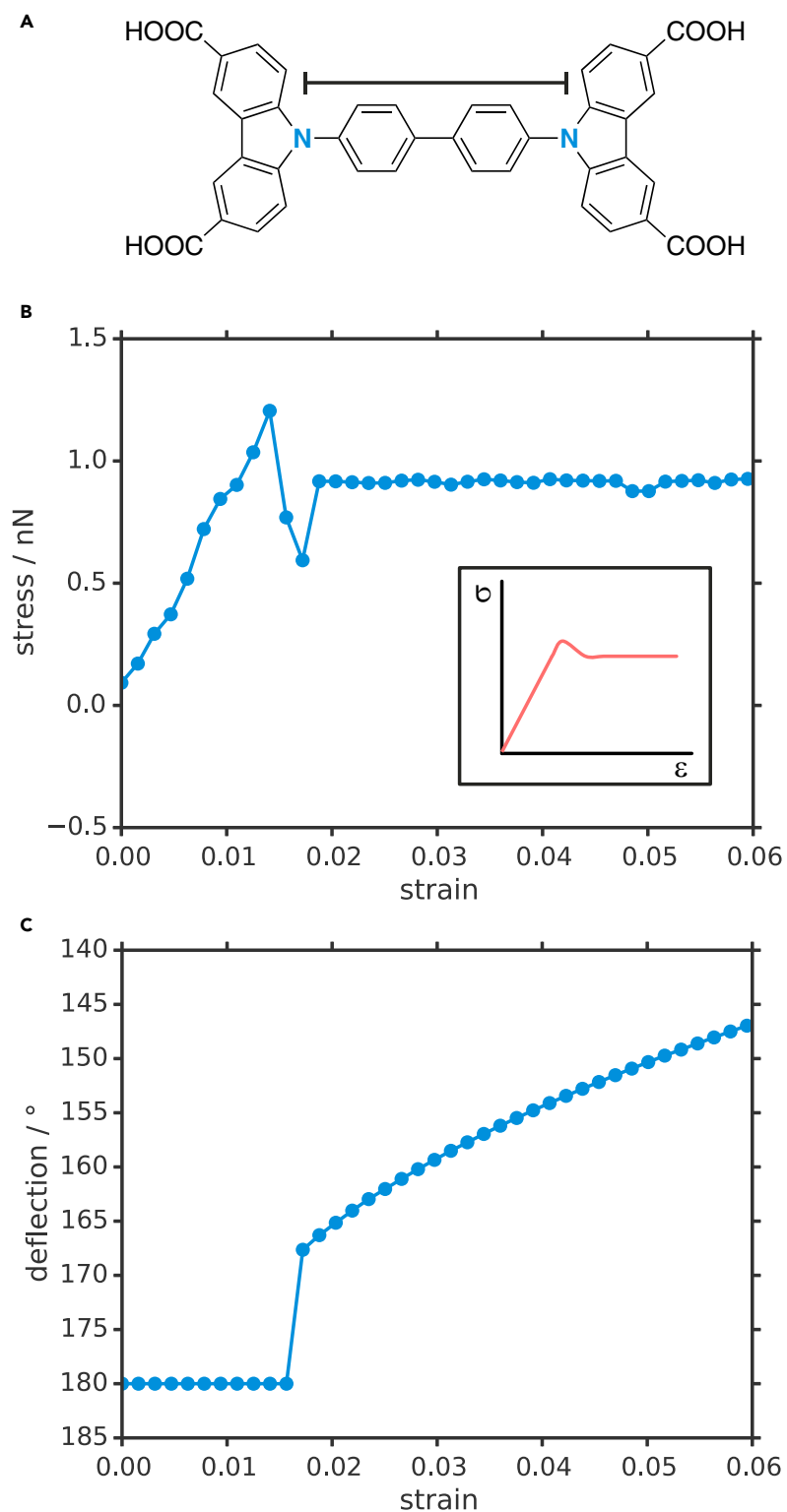


Figure 2. Buckling of the DUT-49 Ligand

(A) BBCDC ligand with the N–N distance highlighted.

(B) Stress-strain curve of the BBCDC ligand in relation to axial compression. Inset: a typical stress-strain curve found for macroscopic materials with buckling.¹⁷

(C) Deflection angle of the ligand, measured as the N-centroid–N angle.

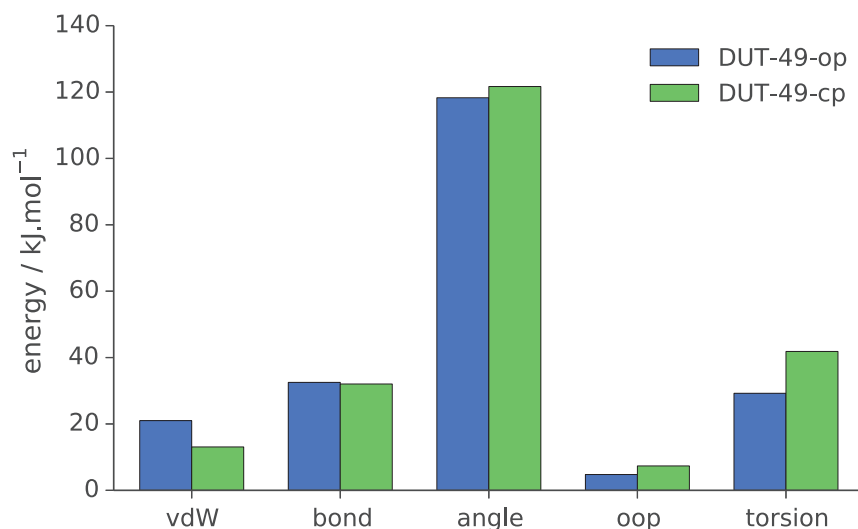


Figure 3. Energy Breakdown in DUT-49

Average energy contributions per ligand for van der Waals interactions (vdW), bond stretching, angle bending, out-of-plane forces (oop), and torsion terms during (*N*, *P*, *T*) simulations of guest-free DUT-49-*op* and DUT-49-*cp* under ambient conditions.

with modest stress, the BBCDC ligand buckles and thus produces an accessible pathway to a colossal change in the volume of the DUT-49 structure.

Structural Description and Energetics

Although DFT calculations show how the mechanical behavior of the organic ligand allows for the structural transition to take place, simulations are required on a larger scale to unveil the precise thermodynamics of NGA. Because of the large size of the DUT-49 unit cell, with 1,836 atoms, simulations at the DFT level have proved computationally prohibitive. We thus used classical molecular-dynamics simulation to capture the structure, energetics, and dynamics of the transition. The force field was based on the high-accuracy MOF-FF force field,¹⁹ which is known to perform extremely well for MOFs and frameworks based on copper paddlewheels in particular. This was extended with MM3 for the organic parts (such as the biphenyl unit) not available in MOF-FF.^{20,21}

To ensure the accuracy of the classical simulation methodology used here, we first generated trajectories of DUT-49-*op* and DUT-49-*cp* by using initial configurations from DFT-optimized structures. The 5 ns (*N*, *P*, *T*) simulations at 300 K and 1 atm demonstrated that the chosen potential parameters accurately describe the geometry and framework characteristics of both the *op* and *cp* forms of the structure. We found that MOF-FF reproduces the unit-cell parameters within $\approx 3\%$ of the experimental values for both the *op* and *cp* structures. Importantly, this demonstrates that DUT-49 is intrinsically bistable. Additional details of the comparisons can be found in Table S1. Notably, these differences are quite small, considering that the force field was not adjusted on experimental data for DUT-49, and illustrate that the force field is applicable to both the *op* and *cp* forms without scaling or further adjustment.

Furthermore, we computed a breakdown of the energy balance between the *op* and *cp* phases of DUT-49 in terms of various contributions to the average total energy, plotted in Figure 3: van der Waals (dispersion and repulsion)

interactions, bond stretching, bending, torsion, and out-of-plane energies. This analysis, which can be performed because of the analytical nature of the interactions described by the force field, clearly illustrates the balance of intramolecular strain (dominated by torsion energy and favoring the *op* structure) and intermolecular dispersive interactions (favoring the *cp* structure), which results in a significantly smaller energy penalty to the distorted DUT-49-*cp* structure. Overall, we found that the *op* phase was energetically more stable than the *cp* phase (by $270 \text{ kJ}\cdot\text{mol}^{-1}$ per unit cell) in the absence of adsorbate, which is in line with previous DFT results.⁸

Transition Dynamics

We next turn to the description by molecular simulations of the actual transition between the two metastable *op* and *cp* structures of DUT-49. Experimentally, Krause et al.⁸ have shown that these structural transitions can be caused by adsorption and desorption of guest molecules. Because the stable form of the evacuated material at ambient conditions is that with the largest volume (*op*), it is expected from thermodynamics that the *op* $\rightarrow$ *cp* transition can also be triggered by application of external pressure, as is the case for the “breathing” transition in MIL-53 and MIL-47 materials.^{12,22}

To check this hypothesis and observe the transition dynamics in the simplest possible case, without adsorbate, we performed constant-pressure simulations where the pressure applied was varied over time. The simulation trajectories, all conducted at 300 K, started from the *op* phase. They consisted of 0.5 ns of initial equilibration at atmospheric pressure, a compression period with constant isotropic pressure $+P$ for 0.5 ns, additional equilibration at atmospheric pressure for 1 ns, a decompression (or tension) period with negative pressure $-P$ for 0.5 ns, and a final equilibration at atmospheric pressure for 1 ns.

At modest pressure, we tested only the elastic behavior of the *op* structure upon compression and tension, with small variations in unit-cell volume, as can be seen in Figure 4A for $P = 50 \text{ MPa}$ (light blue curve). However, with pressure increments equal to or larger than $P = 60 \text{ MPa}$, we observed the NGA transition. The *op* $\rightarrow$ *cp* transition was observed upon compression, confirming the possibility of triggering the NGA transition with a mechanical constraint. Upon release of the pressure, we found that the *cp* structure was retained, confirming its metastability, in line with experimental findings. And finally, upon the application of equal opposite stress (negative pressure), the DUT-49-*op* structure was recovered.

To confirm that the transformation was the result of the buckling of the BBCDC ligand, as described previously, we can look at the molecular motions during the transition for the full unit cell (Movie S1) or focus on a single linker (Movie S2). We also charted the evolution of critical bond parameters, displayed in Figures S1–S3. We observed no significant changes in mean or standard deviation in bond lengths of Cu–Cu, Cu–O, and C–N. However, we found significant and abrupt changes in N–N distances, biphenyl dihedrals, and carbazole dihedrals during the trajectory, which are depicted in Figure 4B. These structural features are caused by buckling of the ligand, but the other features remain invariable. Additionally, as found for the initial simulations under ambient conditions, the accounting of the energy contributions during the trajectory (Figure S4) explicitly illustrates the balance of energy between unfavorable torsional strain and favorable dispersion interactions.

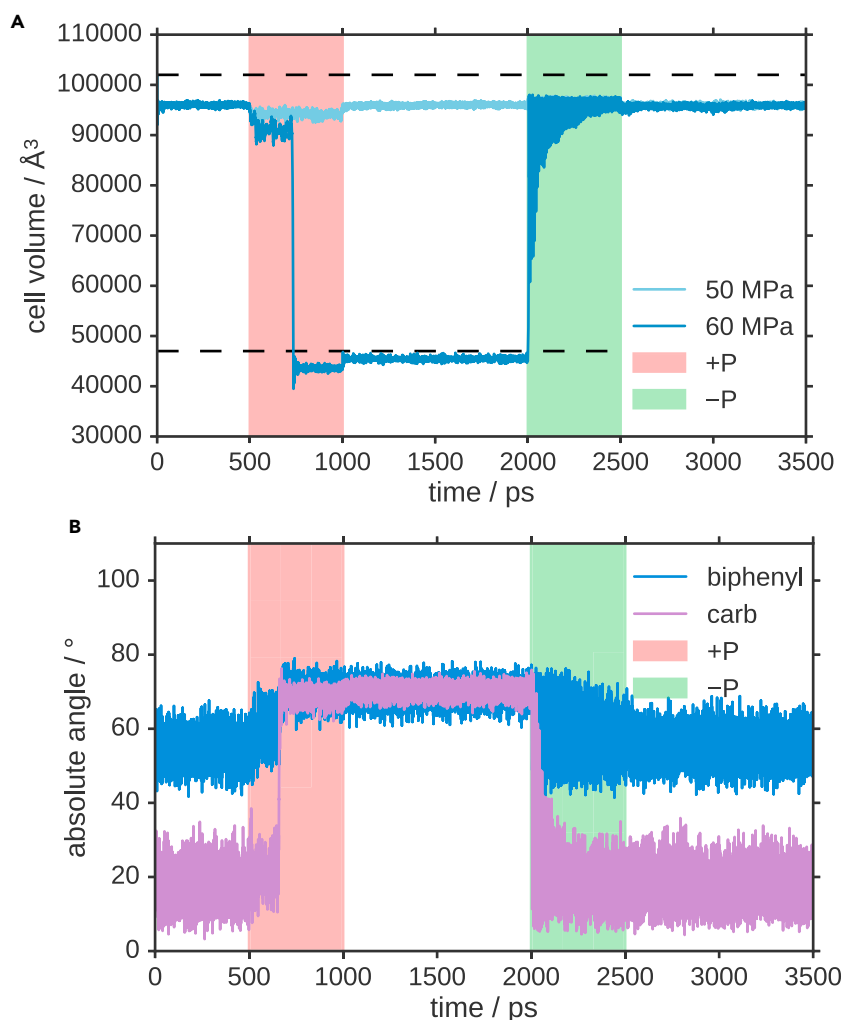


Figure 4. Behavior of DUT-49 under Compression and Tension

(A) Evolution of the unit-cell volume during (N , P , T) simulations of DUT-49, including duration of applied pressure for pressures of ± 50 and ± 60 MPa (see main text for details). The volumes of the *op* and *cp* phases under ambient conditions are indicated by dotted lines.

(B) Averaged absolute dihedral angles of the biphenyl and carbazole (carb) moieties of the BBCDC ligand during these simulations.

Thermodynamics of NGA

In previous work from our group, we demonstrated the understanding provided by explicitly calculating osmotic potential profiles.²³ However, this is a computationally intensive endeavor that has yet to be applied to a system the size of DUT-49 and uses non-Boltzmannian free-energy methods to improve the efficiency of phase-space sampling.²⁴ As a result, we decided to investigate the NGA transition in DUT-49 by obtaining free energy as a function of volume at constant loading, $F(V)$, which yields crucial insight into the relative stability and metastability of the respective phases. For example, this was recently applied to the case of adsorption in the “breathing” MOFs: MIL-53(Al) and MIL-47(V).^{25,26} In practice, the $F(V)$ curve can be calculated by thermodynamic integration of the internal pressure of the system as a function of volume. We performed several constant-volume (N , V , T) molecular-dynamics simulations to obtain the internal pressure at each point, $P_i(V)$, in the range of volumes studied. Thus, the free-energy profile is

$$F(V) - F(V_{\text{ref}}) = - \int_{V_{\text{ref}}}^V \langle P_i(V') \rangle dV', \quad (\text{Equation 1})$$

where we chose V_{ref} , the *op* structure, as the reference volume. The resulting profiles of internal pressure and free-energy landscapes are plotted in Figure 5. In addition, the internal energy, U , was also calculated at each point.

The pressure profile of DUT-49 (Figure 5A) reveals the stable and metastable structures found at a given external pressure. Crystal structures of the two distinct phases of DUT-49 were measured at atmospheric pressure, and according to the profile, three structures correspond to this pressure: the *op* form, the *cp* form, and a transition state situated between these. However, the positive derivative ($\partial P/\partial V$) observed at the transition state makes it mechanically unstable. Further analysis of this pressure landscape also predicts how the DUT-49 structure evolves when the external pressure is decreased or increased because, at mechanical equilibrium, the internal pressure is equivalent to the external pressure. For pressures above ≈ 60 MPa, we found that only one stable state exists where the system remains in the *cp* state. In contrast, DUT-49 exists as the large-pore structure for pressures below ≈ -60 MPa. In between, the two phases are metastable, in line with both experimental data and the results of direct molecular dynamics under pressure.

The free-energy profile generated for DUT-49 (Figure 5B) shows two distinct minima corresponding to the *op* and *cp* structures. Additionally, there exists an energetic barrier of $\Delta F^\ddagger = 130 \text{ kJ}\cdot\text{mol}^{-1}$ to the *cp*-to-*op* transition, which prohibits the *cp* structure from spontaneously opening to the large-pore structure without external stimuli. This mirrors experimental observations in which stress by gas adsorption at saturation is required to regenerate the *op* structure.⁸ A free-energy difference between the two phases of $\Delta F = 1,010 \text{ kJ}\cdot\text{mol}^{-1}$ is predicted (per unit cell). The magnitude of this difference is in good agreement with the $2,184 \text{ kJ}\cdot\text{mol}^{-1}$ energy difference reported previously via DFT methods, despite the two totally different approaches and levels of theory.

Finally, the entropy of the DUT-49 structural transition can be established by comparison of the free-energy and internal-energy profiles obtained from the classical molecular simulation, demonstrated in Figure 5B, as $F = U - TS$. Remarkably, we found that the role of entropy was small in the transition, which was mainly driven by energetic contributions. The entropy difference between the *op* and *cp* phases was calculated to be $\Delta S = 0.0433 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and entropy played a larger role in the free-energy barrier to the transition ($\Delta S^\ddagger = 0.184 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). This is in stark contrast with the structural transitions previously observed in “breathing” MOFs, where the flexibility is based on a hinging mechanism and deformation of coordination at the metal center. In those materials, which have been extensively studied from the thermodynamic point of view, the transition is known to be linked to a balance between energetic and entropic criteria.^{27,28} Thus, one outcome is that temperature has little effect on the relative free energies of the phases of DUT-49, and the transition cannot be triggered by changes in temperature, unlike in MIL-53 materials.

Transition upon Gas Adsorption

After demonstrating that the structural transition in DUT-49 can be triggered by mechanical pressure in a guest-free framework, and given insight into its thermodynamics, we now turn to understanding the thermodynamics of adsorption for the novel phenomenon of NGA. By combining free-energy simulations, as described previously, with an increasing amount of methane present in the simulation cell,

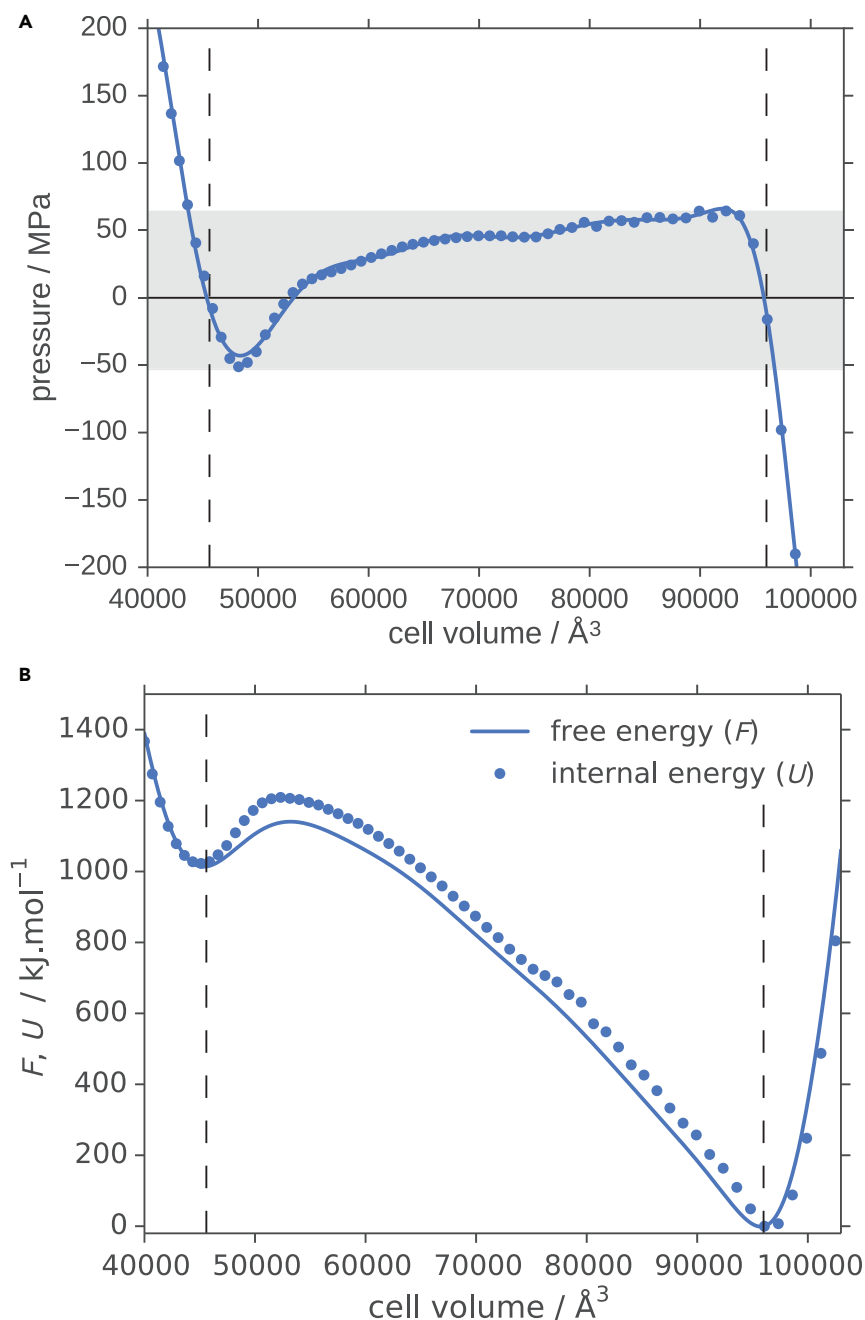


Figure 5. Thermodynamics of Guest-Free DUT-49

Profiles of internal pressure (A) and free and internal energy (B) were obtained from (N , V , T) simulations as a function of unit-cell volume at 300 K. The pressure from simulation is displayed as points with the polynomial fit as a line. Furthermore, the pressure range for which the structure can exist as two different metastable states is highlighted in gray. Internal energy is displayed in (B) as points compared with free energy, calculated by thermodynamic integration, depicted as a line. Additionally, the volumes of the *op* and *cp* phases are shown as dashed lines.

we were able to chart the stability of the two phases at various points over the entire isotherm. In this case, (N , V , T) simulations were performed at 120 K, comparable with the conditions observed for NGA, with methane loadings of 200, 400, 600, 800, and 1,000 molecules per unit cell. Subsequently, these simulations

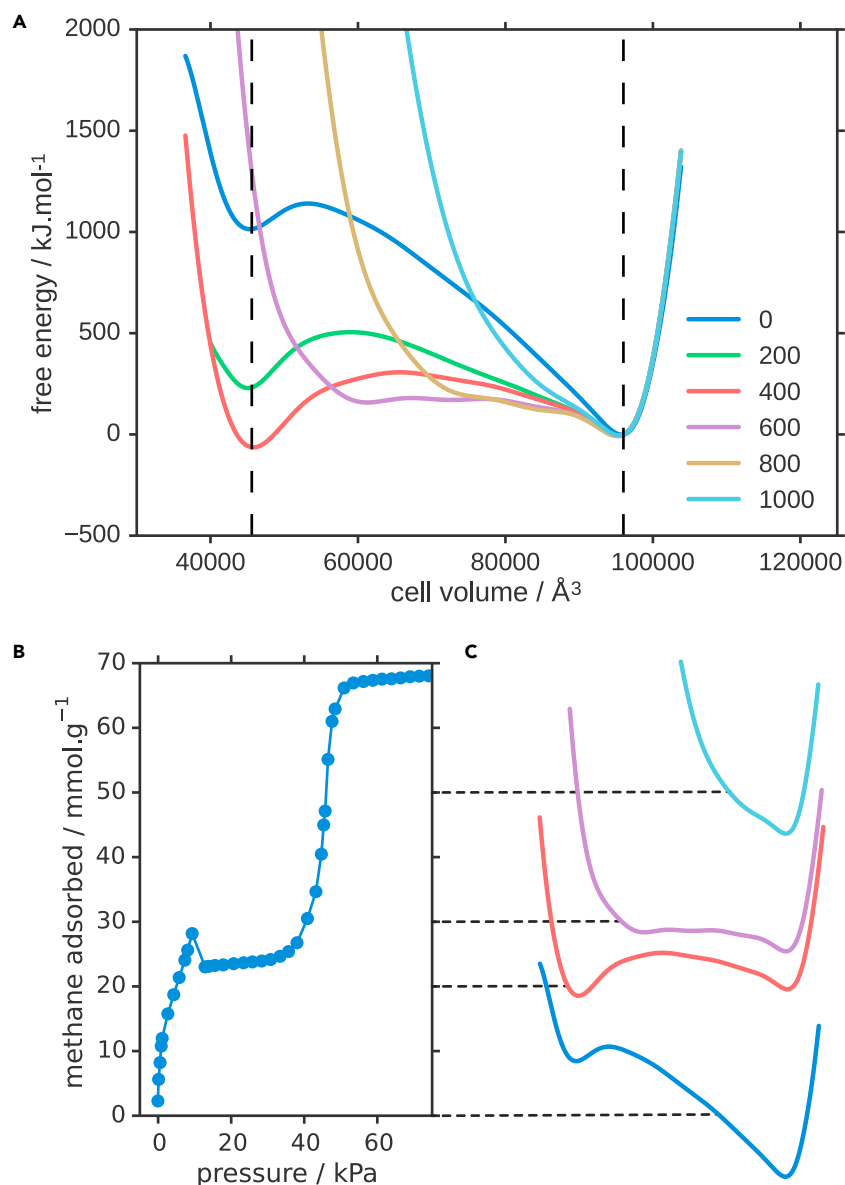


Figure 6. Thermodynamics of Methane Adsorption in DUT-49

(A) Free-energy profiles were obtained from (N, V, T) simulations as a function of unit-cell volume at 120 K with increasing amounts of methane molecules (molecules per unit cell). Volumes corresponding to the *op* and *cp* phases are displayed as dashed lines.

(B and C) The methane isotherm for DUT-49 at 111 K (B) is shown with the corresponding free-energy profile for a given methane loading (C).

resulted in valuable thermodynamic information, including variation of the internal-pressure profiles (Figure S5), the total energy (Figure S6), and free-energy profiles (Figure 6).

Upon methane adsorption, DUT-49 begins in the *op* phase because this corresponds to the most energetically favorable phase. However, as the methane loading increases up to 400 molecules per unit cell (20.2 mmol.g⁻¹), the *cp* phase is stabilized and becomes the most thermodynamically favorable phase. This is because the host-guest interactions are more favorable in the contracted structure as a result

Table 1. Differences in Total Energy, Free Energy, and Entropy for the Transition DUT-49-*op* → DUT-49-*cp*

CH ₄ Adsorbed	Difference in Total Energy, ΔU (kJ·mol ⁻¹)	Difference in Free Energy, ΔF (kJ·mol ⁻¹)	Difference in Entropy, ΔS (kJ·mol ⁻¹ ·K ⁻¹)
0	1,020	1,010	0.0833
200	68.6	234	-1.38
400	-979	-57.1	-7.68
600	-155	1,380	-12.8
800	2,390	8,360	-49.8
1,000	17,100	26,000	-74.2

Differences were calculated from (N, V, T) simulations at 120 K with increasing amounts of methane molecules (molecules per unit cell).

of smaller wall-wall distances and the low entropic cost corresponding to this loading of methane (Table 1). Despite this shift in global minima, there remains a significant barrier, of the order of 300 kJ·mol⁻¹, associated with the *op* → *cp* transition. Upon further methane adsorption to 600 molecules per unit cell (30.4 mmol·g⁻¹), the barrier to transition decreases to ≈ 180 kJ·mol⁻¹, allowing the structure to explore phases of higher density. Importantly, we found that the free-energy landscape for this loading does not include a minimum at the *cp* phase because there is significant entropic expense to condensing the quantity of methane in a low-capacity pore structure. We thus conclude that by undergoing NGA, which releases methane from the structure, the structure can transform from a metastable state at 600 molecules per unit cell to a stable *cp* phase at 400 molecules per unit cell.

Finally, as the amount of methane increases to saturation, the low-capacity *cp* state is unfavorable as a result of guest-guest and guest-wall short-range repulsion; the stable structure at these loadings is then the highly porous *op* phase, if we account for the “reopening” *cp* → *op* transition. The thermodynamic analysis presented here allows us to provide a precise understanding of the structural transformations during gas adsorption. In addition, we demonstrate an interplay between the driving forces of the framework and the adsorption process, which gives rise to NGA.

Conclusions

We used a multiscale computational approach to shed light on the energetics, dynamics, and thermodynamics of the NGA phenomenon in the highly flexible MOF, DUT-49. By using DFT simulations, we found that the complex yet compliant structure of the DUT-49 ligand allows for buckling upon modest stress. The elastic coupling of these buckling units allows for the large-scale structural transformation of the entire framework, which is thus significantly softer than would be expected for rigid building units. This microscopic mechanism for flexibility is entirely new and presents a great contrast with previously known flexible MOFs, which rely either on sub-lattice displacement or on hinging around metal nodes with rigid linkers.

Furthermore, we investigated the NGA transition by using molecular-dynamics simulations. We have demonstrated that NGA requires a bistable porous material in which the empty *op* phase is thermodynamically more stable but the *cp* phase is metastable under ambient conditions. In addition to these generic criteria, which many “breathing” MOFs can exhibit, NGA requires the relative stability of *cp* and *op* phases to change with gas adsorption. Specifically, we expect the decreased transition barrier, observed for DUT-49 at 600 molecules per cell of

methane, accompanying the absence of a minimum of the *cp* volume to be a crucial feature of this process. We have also shown that the structural transition in DUT-49 can be triggered by purely mechanical constraints in the absence of guest molecules.

This investigation has elucidated the mechanics and thermodynamics that govern the phenomenon of NGA and will undoubtedly aid in the discovery of other systems with this desirable property.

EXPERIMENTAL PROCEDURES

The behavior and mechanical properties of the BBCDC ligand were investigated for the corresponding acid via DFT optimizations within the CRYSTAL14 software²⁹ with localized TZVP basis sets³⁰ and the hybrid exchange-correlation functional PBE0.³¹ Long-range dispersion corrections were included via the Grimme "D2" approach.³² The ligand structure was strained by a decrease in the N–N length from the local minimum at 9.827 Å to 9.227 Å in 40 steps. At each step, the structures were optimized with the N–N length fixed. Consequently, a stress-strain curve relative to this axial deformation of the ligand was generated; stress is defined by the gradient of the energy, and strain is the relative decrease in N–N length.

Initial periodic structures of DUT-49-*op* and DUT-49-*cp*, which correspond to the *op* and *cp* structures, respectively, were obtained from DFT-optimized models reported by Krause et al.⁸ Classical simulations used the MOF-FF force field to describe the unsaturated Cu paddlewheels present in the structure.¹⁹ Parameters missing from MOF-FF for the description of the ligand and methane were taken from the MM3 force field for organic molecules, which is itself the basis of MOF-FF.^{20,21} Importantly, we treated the dihedral parameters of the ligand to allow unrestricted rotation of the phenyl groups that make up the biphenyl section. Classical molecular-dynamics simulations were undertaken with the pydlpoly software, a Python-wrapped version of DL_POLY Classic,³³ by Bureekaew and Schmid.³⁴ To first ensure the accuracy of the force field and potential parameters chosen, we completed (*N*, *P*, *T*) simulations for DUT-49-*op* and DUT-49-*cp*. We then studied the NGA transition by performing a series of (*N*, *V*, *T*) simulations at varying guest loadings *N* and volumes *V*. We used constant-volume simulations, with an initial 100 ps for equilibration and a final 500 ps for obtaining a converged value of internal pressure, to compute the average internal pressure for a given volume.³⁵ From a series of constant-volume simulations, we could thus integrate the internal pressure to find free-energy profiles as a function of volume.²⁵ This was repeated with the addition of an increasing number of methane molecules to the simulation cells, which were grown during initial equilibration. All classical molecular-dynamics simulations used a time step of 1 fs and the Nosé-Hoover thermostat and barostat^{36,37} for the (*N*, *P*, *T*) simulations, with a thermostat relaxation time of 1 ps and barostat relaxation time of 2 ps.

SUPPLEMENTAL INFORMATION

Supplemental Information includes six figures, one table, two movies, and two data files and can be found with this article online at <http://dx.doi.org/10.1016/j.chempr.2016.11.004>.

AUTHOR CONTRIBUTIONS

All authors designed and performed the research and wrote and revised the manuscript.

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