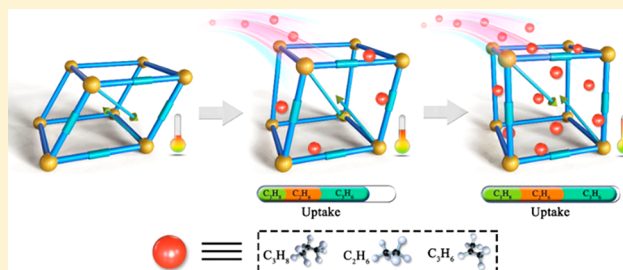


Enhanced Gas Uptake in a Microporous Metal–Organic Framework via a Sorbate Induced-Fit Mechanism

Mei-Hui Yu,[†] Brian Space,[§] Douglas Franz,[§] Wei Zhou,^{||} Chaohui He,[⊥] Libo Li,[⊥] Rajamani Krishna,[#] Ze Chang,[†] Wei Li,[†] Tong-Liang Hu,^{*,†} and Xian-He Bu^{*,†,‡}[†]School of Materials Science and Engineering, National Institute for Advanced Materials, Nankai University, Tianjin 300350, China[‡]State Key Laboratory of Elemento-Organic Chemistry, and Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, China[§]Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, Tampa, Florida 33620, United States^{||}NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, United States[⊥]Shanxi Key Laboratory of Gas Energy Efficient and Clean Utilization, College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan, 030024 Shanxi, China[#]Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, Amsterdam 1098, XH, The Netherlands

Supporting Information

ABSTRACT: Physical adsorption of gas molecules in microporous materials is an exothermic process, with desorption entropy driving a decrease in uptake with temperature. Enhanced gas sorption with increasing temperature is rare in porous materials and is indicative of sorbate initiated structural change. Here, sorption of C₂H₆, C₃H₆, and C₃H₈ in a flexible microporous metal–organic framework (MOF) {Cu-(FPBDC)]·DMF}_n (NKU-FlexMOF-1) (H₂FPBDC = 5-(5-fluoropyridin-3-yl)-1,3-benzenedicarboxylic acid) that increases with rising temperature over a practically useful temperature and pressure range is reported along with other small molecule and hydrocarbon sorption isotherms. Single X-ray diffraction studies, temperature-dependent gas sorption isotherms, *in situ* and variable temperature powder X-ray diffraction experiments, and electronic structure calculations were performed to characterize the conformation-dependent sorption behavior in NKU-FlexMOF-1. In total, the data supports that the atypical sorption behavior is a result of loading-dependent structural changes in the flexible framework of NKU-FlexMOF-1 induced by sorbate-specific guest–framework interactions. The sorbates cause subtle adaptations of the framework distinct to each sorbate providing an induced-fit separation mechanism to resolve chemically similar hydrocarbons through highly specific sorbate–sorbent interactions. The relevant intermolecular contacts are shown to be predominantly repulsion and dispersion interactions. NKU-FlexMOF-1 is also found to be stable in aqueous solutions including toleration of pH changes. These experiments demonstrate the potential of this flexible microporous MOF for cost and energy efficient industrial hydrocarbon separation and purification processes. The efficacy for the separation of C₃H₆/C₃H₈ mixtures is explicitly demonstrated using NKU-FlexMOF-1a (i.e., activated NKU-FlexMOF-1) for a particular useful temperature range.



INTRODUCTION

Among various porous materials, metal–organic frameworks (MOFs), also known as porous coordination polymers, are a promising class of crystalline materials with voids or internal surface areas that have become a focus in both chemistry and materials science.^{1–9} MOFs are inherently inorganic–organic hybrids with structural bond strengths that permit sorbate induced flexibility, distinguishing them from other porous solids.^{10–12} Considering extant MOFs, about 100 of some 20 000 reported MOFs exhibit breathing or flexibility, making them exciting candidates for storage, selectivity, separations, and sensing.^{13–22} The flexibility of MOFs can be attributed to many mechanisms, such as the rotation of the organic ligands,

multiple accessible configurations of metal nodes and clusters, the sliding of interpenetrated subnetworks, and the inherent collective vibrational relaxation of a particular topology.^{13,23} Reversible motions result from external stimuli including changes in temperature or pressure, the presence or removal of guest molecules, photoactive moieties, or electrical and magnetic interactions that trigger structural flexibility.^{24,25} Understanding tailoring and exploitation of the dynamic phenomena occurring in flexible frameworks and their pores suggests tunable or desired properties that help realize the

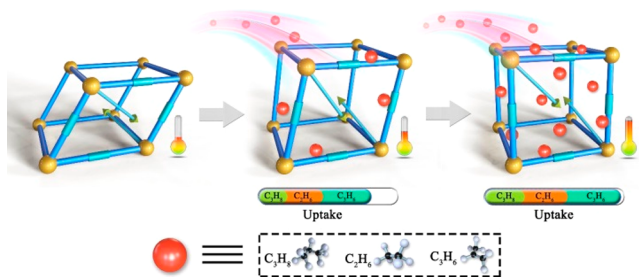
Received: July 22, 2019

Published: October 11, 2019

promise of smart materials.²⁵ Therefore, focused efforts are underway to construct flexible MOFs and understand their structure–property relationships while tailoring them to specific aims.^{10,11,25,26} For example, NH₂-MIL-53(Al) is a flexible MOF that when mixed with PSF Udel P-3500 forms a nanocomposite membrane that produces increased CO₂/CH₄ selectivity up to 77 with increased pressure. The mixed matrix membrane's (MMM) ability to achieve high selectivity was attributed to the dynamic behavior of NH₂-MIL-53(Al) particles.^{27,28} In addition, the MOF [Cu(aip)(H₂O)](solvent)_n (aip = 5-azidoisophthalate) selectively sorbs CO with adaptable pores; unprecedented high selectivity was achieved by CO molecules coordinating with copper(II) ions, resulting in a global transformation of the framework.²⁹ Flexible MOFs for light hydrocarbons applications, exhibiting selective sorption behavior, are desirable due to the importance of hydrocarbons as energy resources and commodity chemicals in the petrochemical industry.^{4,30–36}

Here, a flexible microporous MOF {Cu(FPBDC)}·DMF_n (NKU-FlexMOF-1) (H₂FPBDC = 5-(5-fluoropyridin-3-yl)-1,3-benzenedicarboxylic acid) was synthesized using [Cu₂(COO)₄N₂] paddle-wheel SBUs and FPBDC^{2−} ligands. The MOF, [Cu(FPBDC)] (NKU-FlexMOF-1a), exhibits a guest-specific structural deformation of the flexible framework when activated. The material subtly adapts to each sorbent *via* an induced-fit mechanism where electronic repulsion and intermediate range dispersion interactions balance in a manner sufficiently distinct for each sorbate that the energetics allows for chemical resolution of similar species. To this point, as a result of the MOF's framework responding to the presence of sorbates, NKU-FlexMOF-1a exhibits inversely temperature enhanced sorption behavior for C₂H₆, C₃H₆, and C₃H₈ over a measured temperature range. Distinct from conventional gas adsorption behaviors inherent in rigid porous materials, the maximum saturated uptake amounts gradually increase with temperature in a practically useful temperature and pressure range, as suggested in Scheme 1 and demonstrated in Figure 2.

Scheme 1. On the Basis of the Strongly Guest-Triggered Structure Deformation of the Flexible Framework, the Framework Exhibits Inversely Enhanced Adsorption Behaviors for C₂H₆, C₃H₆, and C₃H₈



The unusual sorption behavior associated with the flexibility results from the framework adapting aptly with increased temperature to produce species-specific induced fits; NKU-FlexMOF-1a captures relatively larger amounts of C₃H₈ at a higher temperature and can efficiently separate C₃H₆/C₃H₈ at the lower temperatures studied while maintaining a recognizably similar sorbate–sorbent structure and associated physical interactions. It was found that the repulsion and dispersion interactions are determined by small structural changes and the

electrostatic environment remains very similar for the related chemical sorbates (e.g., C₂H₆/C₃H₆/C₃H₈).

RESULTS AND DISCUSSION

Synthesis, Crystal Structure, and Stability of NKU-FlexMOF-1. The reaction of H₂FPBDC and CuCl₂·2H₂O under solvothermal conditions produced a porous framework NKU-FlexMOF-1. Single-crystal X-ray diffraction analysis of NKU-FlexMOF-1 (Table S1) showed that each Cu(II) ion is coordinated by four carboxylic oxygen atoms and one pyridine nitrogen atom from five FPBDC^{2−} ligands and that the two adjacent Cu(II) ions constitute a [Cu₂(COO)₄N₂] paddle-wheel SBU (Figure 1a). Each FPBDC^{2−} ligand coordinates to

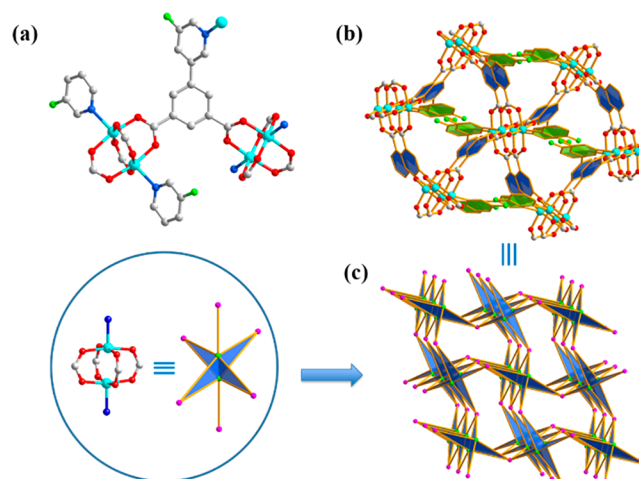


Figure 1. (a) Coordination environment of ligand FPBDC^{2−} and Cu(II). Key: Cu in turquoise, C in light gray, N in blue, O in red, and F in green. All H atoms were omitted for clarity. (b) 3D structure showing the narrow open triangular 1D channels. (c) Simplified 3D structure that suggests its continuous deformability *via* the “hinges”.

three paddle-wheel SBUs, giving a three-dimensional (3D) coordination framework with narrow open triangular 1D channels along the *a*-axis (Figure 1b), similar to a previously reported MOF compound NJU-Bai7.³⁷ As shown in Figure 1b, two open triangular channels sharing the same open angle constitute a homologous rhombic channel along the *a*-axis (Figure 1c). The known flexibility of frameworks with rhombic channels led to investigating potential framework distortions in response to sorption.^{38,39} Because there is a DMF molecule in its asymmetric unit, the occupied channels are sterically expanded. When the DMF molecules are removed, there is structural relaxation, consistent with the induced-fit properties of the material.

The solvent and thermal stabilities of NKU-FlexMOF-1 were first demonstrated by PXRD and thermogravimetric (TG) analyses (Figures S1–S3). The TG curve and VT-PXRD patterns show that the thermal stability of NKU-FlexMOF-1 extends to about 340 °C. As shown in the PXRD pattern (Figure S3), NKU-FlexMOF-1 exhibits good stability to a wide pH range (3–11). After immersing in aqueous solutions with different pH values, the samples were analyzed by optical microscopy and scanning electron microscopy (SEM), demonstrating their crystalline state and stable morphology (Figures S4 and S5). The aqueous solutions were measured to assess the content of Cu²⁺ by ICP, which results in Table S4 show that there are only small pH-independent concentrations

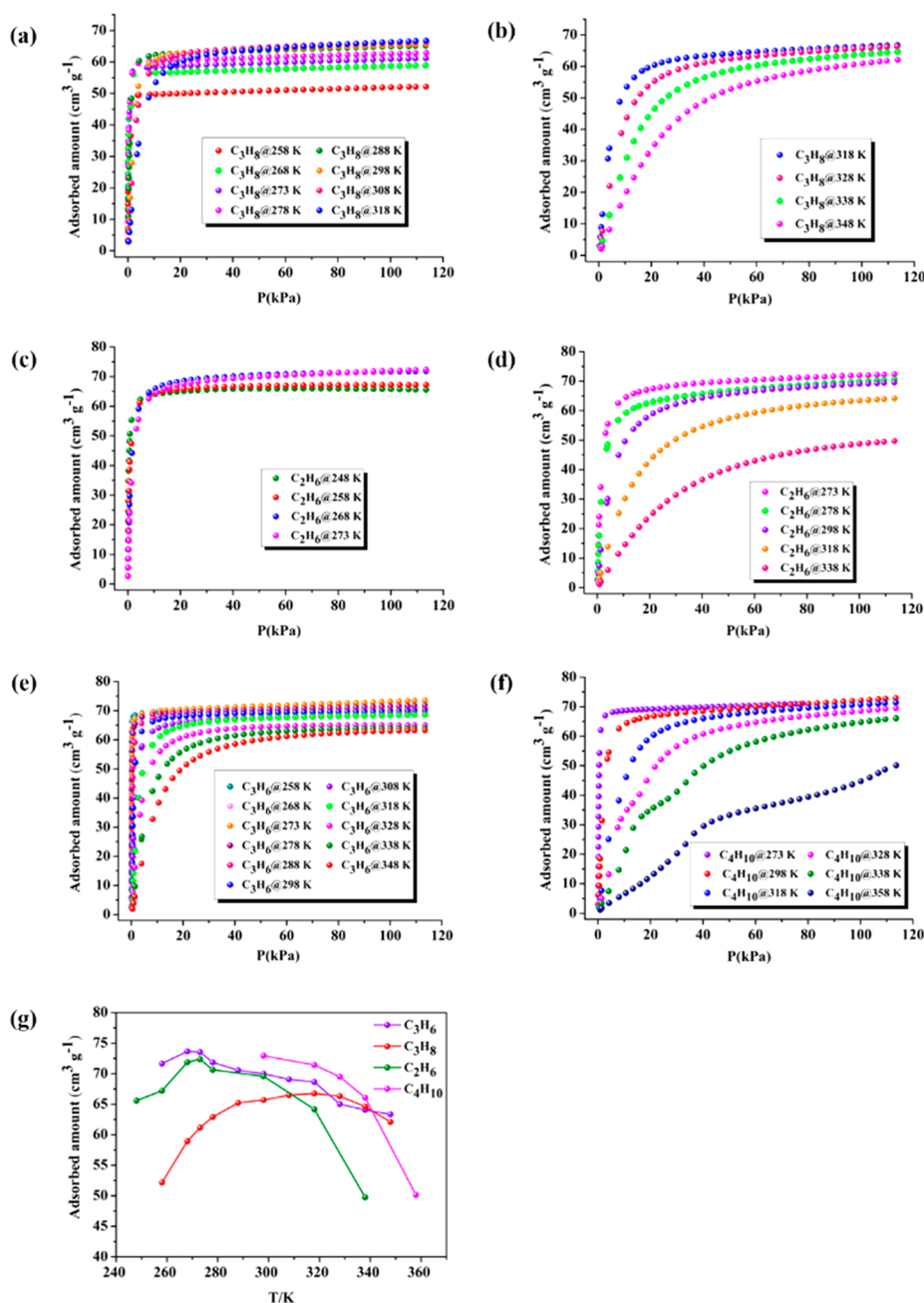


Figure 2. (a) C₃H₈ adsorption isotherms from 258 to 318 K. (b) C₃H₈ adsorption isotherms from 318 to 348 K. (c) C₂H₆ adsorption isotherms from 248 to 273 K. (d) C₂H₆ adsorption isotherms from 273 to 338 K. (e) C₃H₆ adsorption isotherms from 258 to 348 K. (f) C₄H₁₀ adsorption isotherms from 273 to 358 K. (g) Temperature-dependent uptake amounts for C₂H₆, C₃H₆, C₃H₈, and C₄H₁₀ demonstrating the enhanced uptake phenomenon.

of Cu²⁺, confirming that NKU-FlexMOF-1 has good stability in pH range 3–11. These robust properties, especially water stability, which is uncommon and highly desired for MOFs, make NKU-FlexMOF-1 practically useful.

Gas Adsorption Properties of NKU-FlexMOF-1a. Prior to gas adsorption measurements, NKU-FlexMOF-1 was activated by heating the material to 140 °C under a dynamic vacuum to obtain the desolvated NKU-FlexMOF-1a. At 77 K, N₂ adsorption measurements were then used to assess the porosity and structural flexibility. The evacuated Brunauer–Emmett–Teller and Langmuir surface areas of NKU-FlexMOF-1a were calculated to be 952 and 993 m² g⁻¹, respectively (Figure S7). The N₂ adsorption isotherm exhibits

a series of discrete steps apparent on a log plot at low pressure (Figure S6), indicating that NKU-FlexMOF-1a shrinks when solvent molecules are fully evacuated and responsively transforms to a series of expanded structures under increasing guest gas pressure, assuming a new conformation for each sorbed molecule. Thus, the transitions are gradual rather than an abrupt gated phenomena. At 1.0 bar, NKU-FlexMOF-1a reaches an expanded phase with a captured N₂ density of 270.9 cm³ g⁻¹ (3.9 mol mol⁻¹).

Next, single-component adsorption isotherms of guest-free NKU-FlexMOF-1a for N₂, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, and C₄H₁₀ were measured at 273 and 298 K and other temperatures for selected species. As shown in Figures S8–

S14, with the increase of sorbate size, correlating with stronger dispersion interactions, the adsorption isotherms become steeper for very low pressures. Consider the empirical kinetic diameters are 3.3 Å (CO_2), 3.758 Å (CH_4), 4.163 Å (C_2H_4), 4.443 Å (C_2H_6), 4.678 Å (C_3H_6), 4.3–5.118 Å (C_3H_8), and 4.687 Å (*n*-butane).⁴⁰ Note that the larger gas sorbates with electron rich double bonds have stronger host–guest interactions between these molecules and the NKU-FlexMOF-1a framework relative to those with single bonds; compared to molecules of similar size, the molecule with a double bond typically has a stronger binding with the framework *via* electrostatic and related interactions.

In addition, the isosteric heats of gas sorption (Q_{st} , Figure S26a), calculated *via* the common Clausius–Clapeyron approach using isotherm fits to a virial type equation, are consistent with this interpretation. The isosteric heats were also estimated using an integrated version of the Clausius–Clapeyron equation shown in Figure S26b,c.⁴¹ The integrated form of the equation is equivalent to the differential form when employed over a small, effectively infinitesimal, temperature range. For the multitemperature measurements common in gas sorption, the integrated form has the advantage that multiple collinear points demonstrate that the inherent approximations are reasonable. This is especially important in the case of continuously flexible frameworks where a large change in structure or chemical environment makes Clausius–Clapeyron heats a reasonable estimate of the thermodynamics, but not a precise quantitative measure. The resulting temperature-dependent isosteric heats are reported and support the same conclusions. Note there is not a perfect way to extract sorption heats from isotherms in a continuously flexible material where Q_{st} will be everywhere loading and T dependent without performing calorimetry explicitly. This is also true for rigid frameworks if the sorption mechanism changes between isotherm temperatures. Nonetheless, the Clausius–Clapeyron Q_{st} values remain a valuable guide here. It is clear that specific sorbate–sorbent interactions are discernible from the neat isotherms, and this suggests their involvement in inducing sorbent conformational changes.

As shown in Figure S26a, the estimated initial Q_{st}^0 values of NKU-FlexMOF-1a are 32.2 kJ mol^{−1} for CO_2 , 24.4 kJ mol^{−1} for CH_4 , 33.5 kJ mol^{−1} for C_2H_6 , 34.5 kJ mol^{−1} for C_2H_4 , 52.5 kJ mol^{−1} for C_3H_8 , 61.6 kJ mol^{−1} for C_3H_6 , and 57.4 kJ mol^{−1} for C_4H_{10} . While the adsorption isotherms of N_2 , CO_2 , CH_4 , C_2H_6 , C_2H_4 , C_3H_6 , and C_4H_{10} are typical at 273 and 298 K, for C_3H_8 the behavior is anomalous. When the temperature is raised from 273 to 298 K, the overall C_3H_8 uptake increases as well; this phenomenon is rare in an exothermic physisorption process. Because entropic free energy contributions are favored at higher temperatures, sorption enthalpies must substantially increase with temperature. This too implies that collective structural changes take place in the porous material to account for the resulting stronger interactions.

Specifically, it is found that while the electrostatic environment remains remarkably similar for even different hydrocarbons (Table S8), the induced-fit nature of the compound provides repulsion and dispersion, aka van der Waals interactions, that lead to the observed distinct energetics. The structural changes are demonstrated to be small even in the fully loaded structures (Figure S45). However, the calculated energetics are still quite different, as shown in Table S7. The calculated energy differences are substantial and give rise to the observed separations and temperature

enhanced sorption. The energetic differences necessarily arise largely from the repulsion and dispersion portions of the intermolecular potential energy. The repulsions are well thought of as exponentially distant dependent, and the dispersion attractions are a large inverse power of the distance. Thus, a subtle interplay between these functions gives rise to unique energetics for each sorbate and temperature. This situation is analogous to what is typically found in enzyme–substrate interactions with similar useful structure or function relationships.

To further explore this unusual behavior, the adsorption isotherms for C_3H_8 at different temperatures (258, 268, 273, 278, 288, 298, 308, 318, 328, 338, and 348 K) were measured. As shown in Figure 2a, in the range 258–318 K, the maximum saturated uptake amounts at 113 kPa gradually increase with increasing temperature. The sorbed amount reaches a maximum at about 318 K. At temperatures above 318 K, NKU-FlexMOF-1a exhibits typical adsorption behavior, where the sorption decreases as the temperatures increase (Figure 2b). From 258 to 318 K, the C_3H_8 uptake capacity in NKU-FlexMOF-1a increases considerably from 52.2 cm³ g^{−1} (258 K) to 66.8 cm³ g^{−1} (318 K), a change of 14.6 cm³ g^{−1}.

Considering the atypical sorption behavior of NKU-FlexMOF-1a for C_3H_8 , the adsorption isotherms for C_2H_6 , C_3H_6 , and C_4H_{10} at different temperatures were also measured (Figure 2c–f). Interestingly, the sorption behaviors of C_2H_6 and C_3H_6 are similar to that of C_3H_8 . Maximum saturated uptake amounts appear at 273 K for C_2H_6 and at 268 K for C_3H_6 ; subsequently, the uptake amounts gradually decrease with increasing temperature (Figure 2c–e). The magnitude of increasing sorption with temperature is different for C_2H_6 , C_3H_6 , and C_3H_8 . For C_2H_6 , when the temperature is increased from 248 to 273 K, the maximum saturated uptake increased by 6.8 cm³ g^{−1}, from 65.6 cm³ g^{−1} (248 K) to 72.4 cm³ g^{−1} (273 K). Considering C_3H_6 , the maximum saturated uptake amount increased by 2.0 cm³ g^{−1}, from 71.7 to 73.7 cm³ g^{−1} over a temperature range of 258–268 K. The resulting rates of change are 0.27, 0.20, 0.24 cm³·g^{−1}·K^{−1} for C_2H_6 , C_3H_6 , and C_3H_8 , respectively.

Conversely, the adsorption isotherms for C_4H_{10} are typical with respect to uptake with temperature, but with an inflection clearly visible in the lower temperature isotherms (Figure 2f), reflecting the flexibility of the framework. The more typical uptake pattern indicates the sorbate–sorbent interactions are not strongly increasing with temperature; the larger size sorbate likely inhibits the ability to interact as effectively with the framework. Interestingly, the estimated isosteric heat still increases with loading on the basis of the differential, virial form analysis of the isotherms. Figure 2g shows the variation of saturated uptakes for C_2H_6 , C_3H_6 , C_3H_8 , and C_4H_{10} at different temperatures highlighting the temperature enhanced sorption for C_2H_6 , C_3H_6 , and C_3H_8 within a particular temperature and pressure range.

Analysis of Framework Flexibility. The adsorption isotherms of NKU-FlexMOF-1a for N_2 and CO_2 at 77 and 195 K, respectively (Figures S6 and S16), exhibit a series of distinct steps at very low pressures from the framework flexibility. The structural changes resulting from guest loading conditions are challenging to characterize but can lead to an understanding of host–guest interactions and the corresponding framework flexibility.⁴² Although some techniques, such as IR/Raman spectroscopy, NMR, and powder X-ray diffraction, have been used to probe the nature of sorbates in MOF

Table 1. Crystal Data Parameters for NKU-FlexMOF-1 at Different Conditions

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (deg)	β (deg)	γ (deg)	<i>V</i> (Å ³)	<i>T</i> (K)
NKU-FlexMOF-1 ^a	10.551	11.001	14.830	90	108.79	90	1629.7	298
NKU-FlexMOF-1a ^b	10.486	10.537	15.045	90	106.84	90	1591.2	298
NKU-FlexMOF-1a-N ₂ -a ^c	10.488	10.412	15.057	90	107.25	90	1571.3	100
NKU-FlexMOF-1a-N ₂ -b ^d	10.563	11.333	14.625	90	108.25	90	1662.7	100
NKU-FlexMOF-1a-CO ₂	10.557	11.404	14.324	90	108.73	90	1633.1	195
NKU-FlexMOF-1a-C ₂ H ₆	10.489	10.449	15.108	90	106.79	90	1585.2	298
NKU-FlexMOF-1a-C ₃ H ₈	10.574	10.656	15.227	90	108.49	90	1627.2	298

^aThe compound contained solvent molecules DMF. ^bThe compound removed solvent molecules DMF. ^cThe compound contained one N₂ molecule in its asymmetric unit. ^dThe compound contained three N₂ molecules in its asymmetric unit.

structures, the use of *in situ* single-crystal X-ray diffraction (SCXRD) is useful because it provides unequivocal structural information relating to different sorbent conformational states. Thus, single-crystal X-ray diffraction and *in situ* powder X-ray diffraction experiments were performed to characterize the flexibility of the framework NKU-FlexMOF-1a in the presence of sorbates.

Analyzing crystal data parameters (Table 1), the *b*-axis and *c*-axis of NKU-FlexMOF-1a change by -0.464 Å and $+0.215$ Å, respectively, compared with solvated NKU-FlexMOF-1, which demonstrates that the framework has shrunk after removing guest solvent DMF molecules. In addition, the crystal structures containing N₂ molecules at low or high pressures were obtained, respectively (the pressure of NKU-FlexMOF-1a-N₂-a < the pressure of NKU-FlexMOF-1a-N₂-b). With increasing N₂ pressure, the number of N₂ molecules in the channels increases and induces a swelling of the framework. This is evidenced by distinct changes of the *b*-axis and *c*-axis ($+0.921$ Å for *b*-axis and -0.432 Å for *c*-axis); the size and angles of the channel are also modified (Figure 3a). The sizes of the triangular channel changed from $8.24 \times 9.54 \times 8.74$ Å³ to $8.28 \times 9.64 \times 9.74$ Å³, and the angles of triangular channel changed from $96.6^\circ \times 89.0^\circ \times 92.2^\circ$ to $92.6^\circ \times 89.5^\circ \times 91.3^\circ$. These changes are facilitated by the flexibility of the FPBDC²⁻ ligand.

To better understand this behavior, the potential energy profile of H₂FPBDC at different conformations was calculated using density functional theory. With changing torsion angles between the pyridyl and phenyl rings, an energy barrier was located at the coplanar conformation. Its magnitude was found to be 1.7 kJ mol⁻¹ between the two stable conformations (Figure S43). NJU-Bai7, using a similar ligand (5-(pyridin-3-yl) isophthalic acid) without an F-group, resulted in a structure analogous to that of NKU-FlexMOF-1a, but it is a N₂ adsorption isotherm that does not exhibit adsorption steps.³⁷ This suggests that the H₂FPBDC moiety, a short and flexible ligand, can be twisted to produce a framework change by overcoming a relatively low thermally accessible barrier *via* external stimuli.⁴³ The F-group on the ligand adds lability to the torsion, resulting in the stepwise N₂ adsorption behavior at 77 K. Thus, the functional group on the organic linker plays a significant role for the flexibility of the final MOF framework.⁴⁴ As a result, as shown in Figure S34, the dihedral angle between pyridyl and phenyl rings was enlarged by 3.489° , changed from 45.094 to 48.583° , when the number of N₂ molecules in the asymmetric unit increased. Further, the twist of the FPBDC²⁻ ligand results in the angle between paddle-wheel SBUs and phenyl rings changing by -5.207 from 46.929 to 41.722° , and -0.996 from 21.482 to 20.486° .

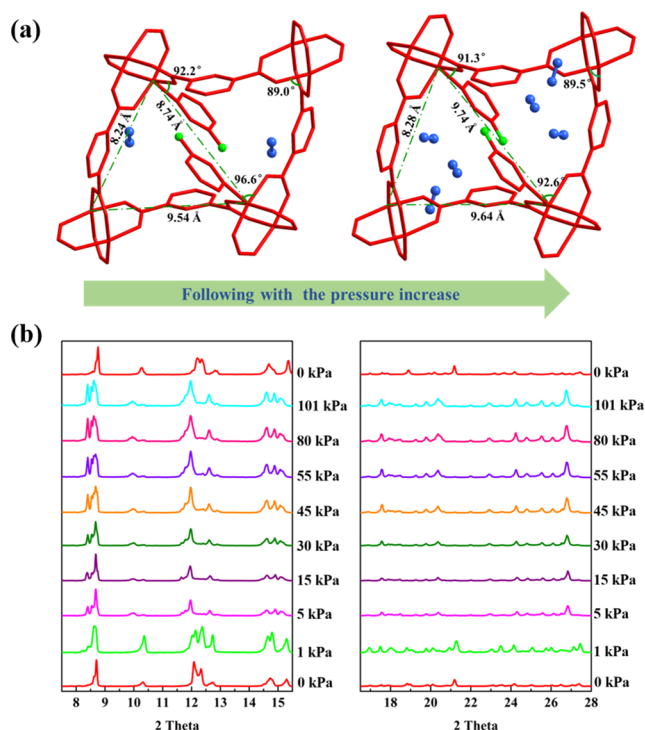


Figure 3. (a) With increasing N₂ pressure, the sizes and angles of triangular channels for NKU-FlexMOF-1a-N₂-a and NKU-FlexMOF-1a-N₂-b are shown from SCXRD. (b) *In situ* powder X-ray diffraction patterns are shown for NKU-FlexMOF-1a at 83 K and variable N₂ pressures (as indicated) and are consistent with the structures seen in SCXRD.

Next, in order to understand the structural transformation in depth, *in situ* powder X-ray diffraction experiments were performed under various pressures of N₂ at 83 K. As shown in Figure 3b, from 0 to 5 kPa, there are substantial changes of the positions of the diffraction peaks, but between 5 and 101 kPa, there are only very small changes in position and minor changes to the intensities of some diffraction peaks. In the vacuum state, the PXRD pattern is the same as that of the sample at 0 kPa, which indicates that the expanded phase is reversibly converted back to the collapsed phase.

Further, the refinement of the *in situ* PXRD patterns of NKU-FlexMOF-1a at different N₂ pressures was performed. The results, as shown in Table S5, revealed that unit cell volume increases slowly followed by the increase of pressure, which shows the framework has the property of guest-induced flexibility. However, as shown in Figure S35, at 273 K the PXRD pattern does not exhibit obvious changes with an increase in N₂ pressure. Thus, the guest N₂ gas molecules at

low temperatures are sorbed with stronger framework interactions that trigger the ligand torsion leading to the structural changes reflected in the isotherms and a PXRD consistent with the low thermal barrier noted above with an energy corresponding to a temperature of about 200 K, as shown in Figure S43.

Guest-Induced Flexibility. In order to further explore the effect of CO₂ and hydrocarbon guest molecules on the flexible behavior of framework, the *in situ* powder X-ray diffraction patterns were measured at 298 K under different gas atmospheres ($P = 100$ kPa) corresponding to the asymptotic region of the gas isotherms where structural changes are complete for the sorbates considered. As shown in Figure 4

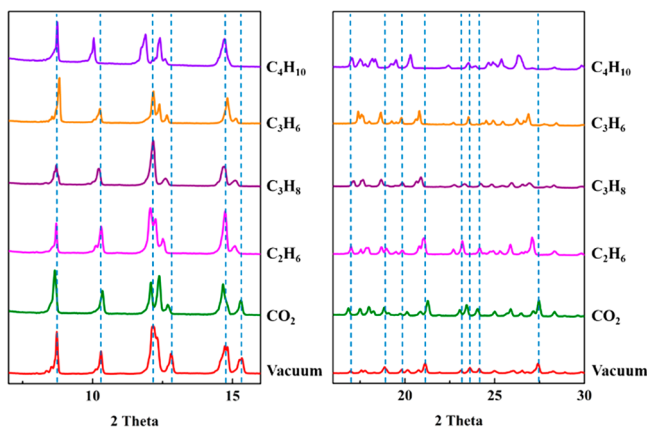


Figure 4. *In situ* powder X-ray diffraction patterns for NKU-FlexMOF-1a at room temperature and variable gas atmosphere (as indicated).

compared with NKU-FlexMOF-1a under a vacuum condition, the structural transformations induced by the guest molecules are evident. The changes are characteristic of the sorbate as reflected in the changes to the positions of the diffraction peaks in Figure 4 and correspond to distinct fits to each sorbate adapting to their mutual steric and attractive interactions. The diffraction peaks moving toward low angles indicate pore size increase, and the degrees of movement increase with the size of the guest molecules. Furthermore, considering a sample loaded with propane, the positions of the diffraction peaks exhibit mild shifts with varied temperature (Figure S40). This reflects that the framework loaded with propane changing with temperature.

In addition to *in situ* powder X-ray diffraction measurements, the crystal structures containing C₂H₆, C₃H₈, or CO₂ molecules were measured. When the crystal data of NKU-FlexMOF-1a-C₂H₆, NKU-FlexMOF-1a-C₃H₈, and NKU-FlexMOF-1a-CO₂ are compared with the crystal data of NKU-FlexMOF-1a (Table 1), the unit parameters of NKU-FlexMOF-1a-C₂H₆ are similar to the parameters of NKU-FlexMOF-1a, which coincides with *in situ* PXRD result that exhibits relatively small changes compared with those of other gas molecules. For NKU-FlexMOF-1a-C₃H₈ and NKU-FlexMOF-1a-CO₂, their unit cell parameters show obvious changes. In the NKU-FlexMOF-1a-C₃H₈ unit cell, all axes increase mildly and the β angle increases by 1.65°. When CO₂ molecules are entered into the channel of NKU-FlexMOF-1a, the unit cell parameter of the *b*-axis increases 0.9 Å and the *c*-axis decreases 0.7 Å. On the basis of above results, it can be confirmed that the different guest molecules lead to distinct

conformational accommodations. At the room temperature, the sample was kept in equilibrium for long times in a C₃H₈ atmosphere, and the phase was assessed by using *in situ* powder X-ray diffraction; the sample was activated under a dynamic vacuum and the recovered phase was characterized. The experiments were recorded over four cycles, which exhibited good reversibility (Figure S41). Furthermore, the morphologies of NKU-FlexMOF-1, NKU-FlexMOF-1a, and the crystals after multiple cycles were compared by optical microscopy and scanning electron microscopy (SEM). As shown in Figure S42, the morphologies of the crystals after multiple cycles are retained.

These transformations reflect different intermolecular interactions between the guest molecules and the framework; a structure that responds distinctly, i.e., adapts subtly but meaningfully, to an array of chemically related species is a promising candidate for applications where physical sorbate–sorbent interactions seek to resolve similar molecules. This makes NKU-FlexMOF-1 a desirable platform for hydrocarbon capture and separation, as the flexible framework response to sorption acts to distinguish between the chemical entities by more extensive interactions, e.g., through shape, charge, dispersion, or polarization, that are not possible in rigid sorbate–sorbent systems. In rigid platforms, only a small subset of physical and chemical interactions are sampled, as the sorbate is in contact with the sorbent for a restricted set of orientations and distances that cannot be mutually optimized, interacting with a rigid substrate. This limits the potential chemical resolution achievable through the rigid interactions, while a flexible material can capture the differences in structures through enhanced sampling of the interactions *via* the adaptable solid state structure as seen in NKU-FlexMOF-1a.

First-Principles Calculations on Framework Flexibility. In order to further explore the flexible nature of NKU-FlexMOF-1a, we compare the SCXRD structure of the as-synthesized NKU-FlexMOF-1 with that of the activated sample NKU-FlexMOF-1a. Upon desolvation, the lattice unit cell shrinks slightly, mainly within the *b*–*c* plane. The overall unit cell volume decrease is quite small (only ~2.4%); however, the decrease in PLATON pore volume resulting from the structural change is significant at ~17% (0.291 vs 0.242 cc g^{−1}). This demonstrates how small structural accommodations can meaningfully adapt to sorbates.

To elucidate the mechanism of the structural flexibility, a detailed computational first-principles investigation was performed on the basis of dispersion-corrected density functional theory (DFT-D). The as-synthesized structure NKU-FlexMOF-1, using the coordinates with the solvent removed *in silico*, and the activated structure NKU-FlexMOF-1a were first fully geometry optimized. Then nudged elastic band calculations were performed to find a minimum energy path for the structural change between the two phases. An animation consisting of snapshots of the transformation clearly shows how the pore shrinks smoothly and continuously along the structural change coordinate (see Animation of transformations-1 Supporting Information).

In the NKU-FlexMOF-1 structure, the [Cu₂(COO)₄N₂] paddle-wheel, the linker phenyl ring, and the linker pyridine ring are relatively rigid, while the joints connecting these three types of rigid units are flexible, particularly in terms of the relative orientation of the linked units. These flexible

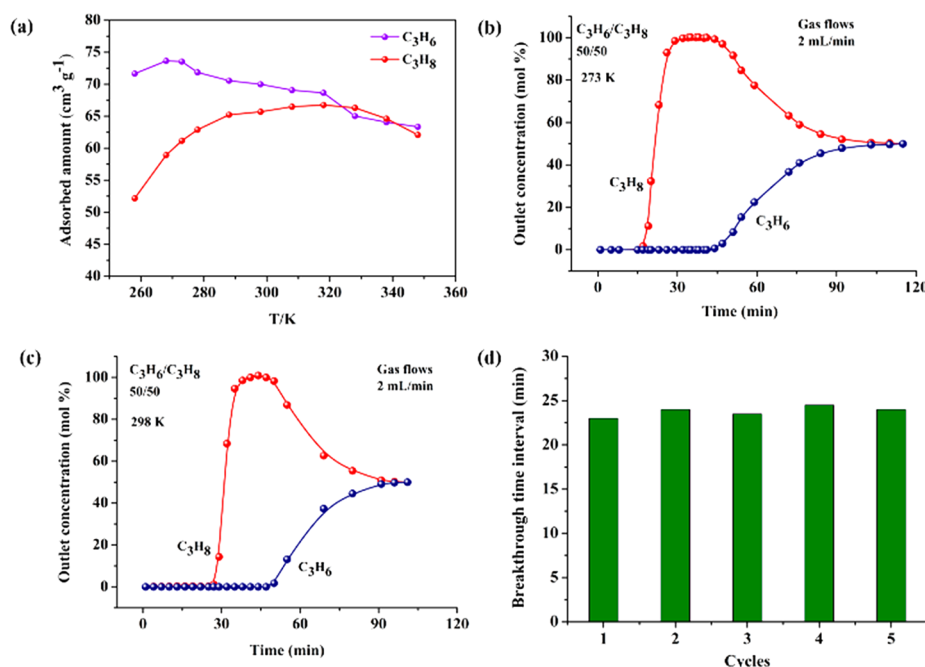


Figure 5. (a) Variation tendencies of saturated uptake amounts for C₃H₆ and C₃H₈ at different temperature (from 258 to 348 K at 1.1 bar). Experimental breakthrough curves for the C₃H₆/C₃H₈ (50/50, v/v) mixture through a bed of NKU-FlexMOF-1a material at (b) 273 and (c) 298 K. (d) Cyclic C₃H₆/C₃H₈ (50%/50%) separation on NKU-FlexMOF-1a material at 298 K and 1 bar.

coordination bonds are largely responsible for the flexibility of the NKU-FlexMOF-1 framework.

Our lattice dynamics calculation on the activated structure NKU-FlexMOF-1a further shows that there are several low energy “soft” phonons, i.e., collective structural relaxation coordinates, resulting from these flexible coordination bonds (see Figure S44). Shown as an example in Supporting Information as Animation of transformations-2 is a phonon with ~4 meV energy (32 cm⁻¹), involving the rotation of the pyridyl rings. Upon guest inclusion, internal structural distortion takes place, mediated by the low frequency collective coordinates and may further couple with lattice distortions. Subtle conformational changes then mutually “optimize” the structure to interact effectively with different sorbates.

Breakthrough Experiments for Binary C₃H₆/C₃H₈ Mixtures. Remarkably, due to the unique adsorption behaviors for C₃H₆ and C₃H₈, as shown in Figure 5a, at a lower temperature range (258–273 K), the uptake amount of C₃H₆ is distinctly larger than that of C₃H₈, indicative of the C₃H₆/C₃H₈ selectivity in this range. This is confirmed *via* a breakthrough experiment for a C₃H₆/C₃H₈ (50/50, v/v) mixture on NKU-FlexMOF-1a material at 273 and 298 K (Figure S46), to check its actual separation ability for the gas mixture. As shown in Figure 5b,c C₃H₈ first broke through the adsorption bed and yielded a high purity gas (>99.99%), whereas after a certain time C₃H₆ slowly eluted. The long breakthrough time interval between C₃H₆ and C₃H₈ suggests that NKU-FlexMOF-1a material is effective for practical C₃H₆/C₃H₈ separation as was suggested by the thermodynamic and structural results above. According to the breakthrough experiment, as shown in Table S6 and Figure S23, the calculated adsorption capacity of C₃H₆ is 1.96 mmol g⁻¹ and the selectivity is 2.31 at 1 bar at 298 K, and the adsorption capacity and selectivity are 2.13 mmol g⁻¹ and 2.66 at 1 bar at 273 K, respectively. The calculated adsorption capacity of C₃H₈ at 298 K is higher than that at 273 K, which is

in line with the adsorption results. In addition, after the breakthrough experiment, the purity of desorbed propylene is 85.2%, as shown in Figure S24, which was consistent with the calculated selectivity. Afterward, cycling breakthrough experiments on NKU-FlexMOF-1a material were carried out under the same conditions. The breakthrough time intervals for C₃H₆/C₃H₈ mixtures in five cycles (Figure 5d) are close (~24 min), showing that this material has a good regenerability. Note the difference of adsorption capacity is the largest at 258 K, but our current laboratory setup is unable to perform the analogous colder experiments. Then we carried out breakthrough simulations for a C₃H₆/C₃H₈ (50/50, v/v) mixture, in a fixed bed to demonstrate the feasibility of separation of propylene and propane in a pressure swing adsorption operation at 258 K (Figure S25). The simulations also demonstrate the NKU-FlexMOF-1a is of potential use for this challenging separation of C₃H₆/C₃H₈ mixtures.

Analysis of Gas Adsorption and Separation Behavior.

Flexible MOFs have transformable frameworks that are able to reversibly respond to external stimuli such as temperature, pressure, light, electric/magnetic fields, or the presence of particular species. Understanding how these materials change when perturbed will have applications in the development of smart materials and superior separations. Ideally, identification of extant and design of aspirational materials with adaptive properties is possible given a detailed understanding of relevant intermolecular interactions.

Here, a flexible microporous MOF showing inversely enhanced adsorption behavior for C₂H₆, C₃H₆, and C₃H₈ in a defined temperature and pressure range is presented. The increase in sorption with temperature is attributed to the dynamic behavior of NKU-FlexMOF-1a where guest molecules subtly interacting with an adaptive framework lead to an induced-fit specific to each sorbate. Notably, the material geometry and chemical environment is little changed between sorbates and the energetic differences are attributable to the

detailed changes in the van der Waals, aka repulsion and dispersion, interactions similar to enzyme–substrate interaction mechanisms. Further, to confirm that equilibrium phenomena is not the determining factor, the C_3H_8 isotherm at 258 and 298 K was obtained with long equilibration intervals between two points (at least 124 min). As shown in Figure S15, the adsorption amount at 298 K is consistently larger than that at 258 K, which is consistent with the trend reported in the pristine measurement. These results indicate that the inversely increased gas uptake at higher temperature should be due to the structure change of the **NKU-FlexMOF-1a** at different temperatures instead of the different diffusion resistances.

To understand why it is requisite that the framework is adaptive in response to sorbate contact, examine the thermodynamics of sorption. Because the magnitude of thermodynamic sorption at constant pressure (P) and temperature (T) is governed by the Gibbs free energy $G = H - TS$, an increase in temperature will necessarily lead to decreased sorption if the material can be considered a rigid framework. Consider the entropy of the sorbate is decreased with substantial interaction with a rigid or flexible framework as the conformational space it can explore is restricted; for example, the rotations are hindered, and the relatively large translational entropy contribution is greatly diminished. Thus, the entropy change upon “binding” is negative. Because the intermolecular interactions are temperature independent (i.e., the potential energy function is not T dependent), the only way for the free energy to decrease is for the enthalpy to sharply decrease with increasing temperature.

Given the enthalpy, $H = E + PV$, there is no significant differential contribution from the PV term upon contact, and thus the interaction energy must substantially decrease as T increases. This can only happen as a result of the material changing its conformation to produce more stable interactions with sorbates, implying closer contacts with more favorable molecular interactions than were present in the lower T structure. To this point, consider that a single structure will have larger amplitude thermal motions with increasing temperature that would tend to decrease the sorbate–sorbsent system enthalpy, and only a mutually beneficial structural change can explain the observed increase in sorption that is referred to herein as an induced-fit mechanism. This is what is observed in the case of **NKU-FlexMOF-1a**, a flexible MOF that has adaptive conformational transformations in response to contact with the different sorbate molecules tested. Many of them show atypical increases in sorption with temperature, all of which have isotherms characteristic of material structural changes in response to sorption and similar structures for comparable loadings.

The nature of the conformational changes observed is guest specific and related to the detailed sorbate–sorbsent interactions in the adaptive micropores of **NKU-FlexMOF-1a**. The maximum saturated uptake amounts of C_2H_6 , C_3H_6 , and C_3H_8 gradually increase, which is an atypical behavior compared with conventional physical adsorption. CO_2 , N_2 , and C_4H_{10} also induce structural changes but show typical diminished sorption as temperature is increased. Understanding the detailed nature of the different behaviors requires further investigation and careful molecular modeling. Nonetheless, the distinct temperature dependence of the sorbsent enthalpies and the material stability make **NKU-FlexMOF-1a**

an exciting candidate for hydrocarbon and potentially other small molecule separations *via* the induced-fit mechanism.

Further, on the basis of the observed adsorption behavior at the different temperatures considered, there is a useful difference in adsorption capacity between C_3H_6 and C_3H_8 that can be employed for selective separation of C_3H_6/C_3H_8 . Along this line, the breakthrough experiment and simulation both demonstrate **NKU-FlexMOF-1a** is of potential use for this challenging separation of C_3H_6/C_3H_8 mixtures.

To better understand the separation mechanism, the saturated crystal structures, reported here, of C_3H_8 and C_2H_6 were taken and optimized using dispersion-corrected periodic DFT calculations in the program CP2K.⁴⁵ C_2H_6 calculations serve as a point of calibration and reference in interpreting the results. Next, the C_3H_8 molecules were mutated to C_3H_6 *in silico* and optimizations were performed with a resulting 0.204 Å RMSD between the resulting framework coordinates. The resulting structures are shown superimposed (Figure S45) and have analogous structures that imply separation mechanisms that are similarly mediated by different detailed energetics *via* van der Waals repulsions and attractions, consistent with the induced-fit mechanism.

The nature of the sorption is similar; the separation chemistry and surface areas will be comparable for the separations considered. This was further confirmed by examining derived partial charges for saturated structures that demonstrate the commensurate chemistry evidenced by the highly similar electrostatic environment (Table S8). The energy per sorbate was also calculated in the loaded, effectively zero temperature configuration, and calculations consistently show the sorption energy averaged over fully loaded configurations with $E(C_3H_8) \approx E(C_3H_6) \gg E(C_2H_6)$; values are presented in Table S7. While the double bonded C_3H_6 will clearly have enhanced electrostatic interactions, the conformational adaptation leads to enough increase in van der Waals energies that both propane and propene are substantially higher in binding energy than ethane that are similarly bound.

CONCLUSION

In summary, we report a flexible microporous MOF (**NKU-FlexMOF-1**), which exhibits sorbate induced-fit dynamic behavior. On the basis of the behavior, sorption of C_2H_6 , C_3H_6 , and C_3H_8 in **NKU-FlexMOF-1a** increases with rising temperature over a practically useful temperature and pressure range. Then the difference in adsorption capacity between C_3H_6 and C_3H_8 can induce the selective separation of C_3H_6/C_3H_8 . Therefore, this work provides not only a new flexible MOF with distinct and useful adsorption behaviors for C_2H_6 , C_3H_6 , and C_3H_8 but also a design strategy of seeking and constructing flexible, induced-fit MOFs with flexible ligand motions; the material responds distinctly to sorbates of interest for gas capture and separation, exploiting the extreme sensitivity of repulsion and dispersion interactions to small changes in distance. Materials with adaptive structural characteristics and tunable host–guest interactions as a function of both sorbate and temperature have a much wider range of utility than rigid materials. The induced-fit mechanism revealed in this study provides new directions for the design of flexible MOFs for the development of adsorption-based separation and capture technologies.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b07807.

NKU-FlexMOF-1 checkCIF/PLATON reports and CIF files (ZIP)

Materials and measurements, details of syntheses, gas sorption data, calculations on framework flexibility, and gas adsorption, tables of crystal data and structure refinement parameters, Cu²⁺ in aqueous solutions, unit cell parameters, PXRD patterns, binding energies, and average partial charges, figures of TG curves, VT-PXRD patterns, images of crystals, adsorption isotherms, adsorption points, calculated selectivity, components of desorbed mixtures, breakthrough simulations, isosteric heats, details of virial equations, structure analysis, X-ray diffraction patterns, torsional landscape, DFT-D calculated phonon density of states, and schematic diagram of device of breakthrough experiments (PDF)

Animation of transformations-1 (GIF)

Animation of transformations-2 (GIF)

■ AUTHOR INFORMATION

Corresponding Authors

*tlhu@nankai.edu.cn

*buxh@nankai.edu.cn

ORCID

Wei Zhou: 0000-0002-5461-3617

Rajamani Krishna: 0000-0002-4784-8530

Ze Chang: 0000-0002-3865-2165

Wei Li: 0000-0002-5277-6850

Tong-Liang Hu: 0000-0001-9619-9867

Xian-He Bu: 0000-0002-2646-7974

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the NSFC (21673120, 21606163, 21531005, and 91856124). We thank the staffs from the BL17B beamline of the National Facility for Protein Science in Shanghai (NFPS) at the Shanghai Synchrotron Radiation Facility for assistance during data collection. B.S. and D.F. acknowledge the National Science Foundation (Award No. DMR 1607989), including support from the Major Research Instrumentation Program (Award No. CHE 1531590). B.S. and D.F. acknowledge computational resources made available by a XSEDE Grant (No. TG DMR090028) and by Research Computing at the University of South Florida. The authors thank Prof. Banglin Chen (University of Texas at San Antonio, Texas) for discussions and help.

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