

# Full Exclusion of Branched Hexanes from Their Linear Isomer by a Robust Aluminum Metal–Organic Framework with Tailored Pore Structure

Liang Yu,<sup>†</sup> Saif Ullah,<sup>†</sup> Jinze Yao, Danxia Lin, Jiajin Huang, Shi Tu, Haoyuan Luo, Qibin Xia,<sup>\*</sup> Timo Thonhauser, and Hao Wang<sup>\*</sup>



Cite This: *ACS Materials Lett.* 2023, 5, 1532–1536



Read Online

ACCESS |



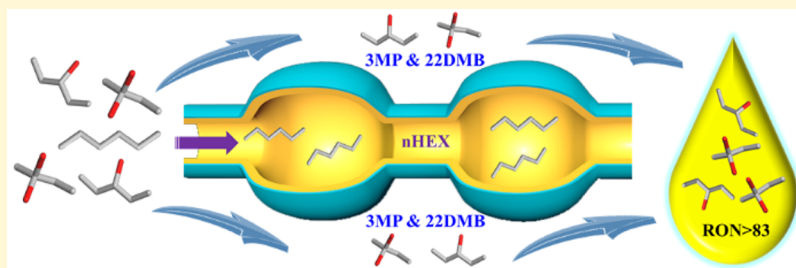
Metrics & More



Article Recommendations



Supporting Information



**ABSTRACT:** High-efficiency separation of hexane isomers through selective molecular exclusion represents an important yet challenging task in the petrochemical industry. It has stringent requirements on the adsorbents' pore shape and dimensions. Here we report the complete exclusion of branched hexanes from their linear isomer by an aluminum metal–organic framework, CAU-21-ODB (ODB = 4,4'-oxidibenzoate) with high stability. The unique gourd-shaped channels with suitable pore aperture lead to substantial uptake of nHEX (141 mg/g at 30 °C) but negligible adsorption of its branched isomers under identical conditions. The capability of CAU-21-ODB for the separation of hexane isomers has been verified by multicomponent breakthrough experiments. DFT calculations further confirm the size-exclusion-based separation mechanism.

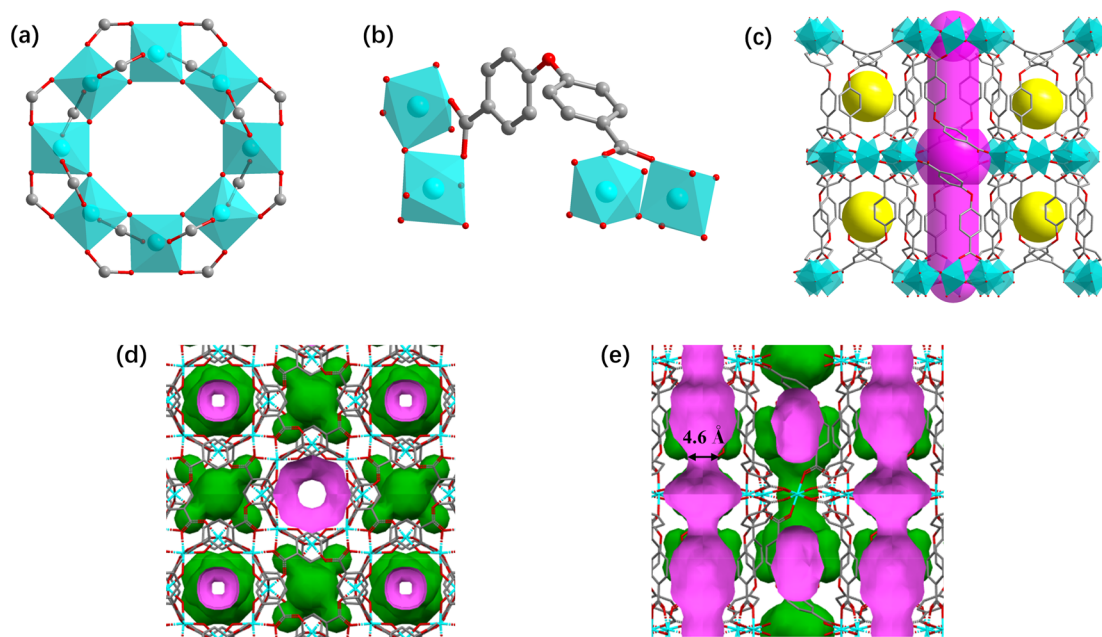
As an important petrochemical feedstock, each component of light hydrocarbons has a specific value in manufacturing different chemical products.<sup>1</sup> For example, hexanes have five isomers with varying degrees of branching. The linear component, *n*-hexane (nHEX), is premium feed for ethylene production, the most important process in the petrochemical industry. The presence of branched isomers in the process can lower ethylene yield. In contrast, the research octane number (RON) of hexane isomers increases with the number of branched chains. For example, the RONs for *n*-hexane (nHEX), 3-methylpentane (3MP), and 2,2-dimethylbutane (22DMB) are 30, 75, and 94, respectively.<sup>2</sup> Thus, the branched hexanes are superior gasoline blending components while the linear isomer with the lowest RON needs to be removed.<sup>2</sup> To fulfill the specific role and make the best of each hexane isomer, the linear and branched components of hexane isomers must be separated efficiently.<sup>3</sup> Traditional separation relies primarily on energy-intensive heat-driven distillations.<sup>4</sup> The energy consumption associated with the process could be

potentially reduced assuming alternative technology such as adsorptive separation could be implemented.<sup>5–7</sup>

The key to efficient adsorptive separation is to develop optimal adsorbents with high separation efficiency. In this context, metal–organic frameworks (MOFs) hold great promise to address this challenging separation in light of their structural diversity and tunable pore size, pore shape, and surface functionality. MOFs have been extensively studied in recent years for gas/vapor adsorption and separation, especially for the separation of light hydrocarbons.<sup>8–10</sup> As for the separation of hexane isomers, a proof-of-concept study with

Received: March 20, 2023

Accepted: April 19, 2023



**Figure 1.** Crystal structure of CAU-21-ODB. (a)  $\text{Al}_8$  building unit. (b) The coordination mode of the linker ODB. (c) Cavities and 1D channels of CAU-21-ODB. (d and e) Simulated channel shape and dimensions of CAU-21-ODB. Color scheme: Al, cyan; O, red; C, gray. The simulation of the channels and the pore surface was performed using the Mercury software with a probe radius of 1.2 Å.

$\text{Fe}_2(\text{bdp})_3$  demonstrated the discrimination of hexanes with different branching through a thermodynamically controlled mechanism.<sup>11</sup> A number of MOFs have been explored for this separation over the past few years; however, MOFs that can fully split hexane isomers through selective molecular exclusion remain scarce. Complete separation of the isomers by taking advantage of their different molecular dimensions has a stringent requirement on the pore shape and pore size of the adsorbent. In this work, we present the efficient discrimination of hexane isomers by a robust aluminum MOF, CAU-21-ODB (ODB = 4,4'-oxidibenzoate). It possesses 1D gourd-shaped channels with a pore window of 4.6 Å that falls right between the kinetic diameter of nHEX (4.3 Å) and those of its branched isomers (>5 Å). Single-component adsorption and multicomponent separation measurements demonstrated that CAU-21-ODB is capable of splitting nHEX from its branched isomers through selective molecular exclusion. The underlying separation mechanism was further confirmed through DFT calculations.

**Results and Discussion.** CAU-21-ODB was synthesized following the previous report with slight modifications<sup>12</sup> (see [Supporting Information](#) for synthesis details). Solvothermal reactions of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_2\text{ODB}$  in a mixed solvent of DMF/water at 120 °C for 2 days yielded the as-synthesized CAU-21-ODB. It crystallized in a tetragonal crystal system with a space group of  $I422$ . The structure of CAU-21-ODB was developed from the connection of eight-membered ring bricks  $\text{Al}_8$  (Figure 1a), and each V-shaped ODB ligand coordinated with two different  $\text{Al}_8$  clusters (Figure 1b). Each  $\text{Al}_8$  octamer unit consists of eight  $\text{AlO}_6$  polyhedra via edge-sharing (through  $\mu\text{-OH}$  groups) in cis-connection, and the octamers are further interconnected through ODB to form a 3D bcu-type network with 1D gourd-shaped channels (Figure 1c–e). The 1D channels contain independent cavities with an accessible pore aperture of 4.6 Å.

The phase purity of the as-synthesized CAU-21-ODB was confirmed via powder X-ray diffraction (PXRD) measure-

ments, where the pattern of the as-synthesized and methanol-exchanged sample matched well with the theoretical one (Figure S1). Thermogravimetric analysis (TGA) of the as-synthesized sample showed a continuous mass loss; however, the curve of the methanol-exchanged sample displayed a long plateau up to 400 °C following an initial weight loss before 60 °C, indicating successful exchange of the high-boiling-point solvents by methanol (Figure S2). The structure of CAU-21-ODB was well-retained after being immersed in water at 80 °C, or exposed to 90% humidity for 1 week, and or heated at 200 °C in open air for 1 week (Figure 2a). These results suggested the high stability of the compound. CAU-21-ODB adsorbed only a small amount of  $\text{N}_2$  at 77 K (Figure S3), and thus its permanent porosity was evaluated by the adsorption of  $\text{CO}_2$  at 195 K (Figure S4), which yielded a BET surface area of 275  $\text{m}^2/\text{g}$  (Figure S5). Its pore size distribution curve was centered at  $\sim 4.7$  Å, determined by the Horvath–Kawazoe (H–K) model (Figure S6), which was consistent with the value estimated from the crystal structure. The PXRD patterns of the activated sample and sample after adsorption tests revealed that the crystallinity was fully retained.

The robust framework and suitable pore dimensions of CAU-21-ODB prompted us to evaluate its adsorption and separation toward hexane isomers. Single-component adsorption experiments of nHEX, 3MP, and 22DMB were performed at 30 °C (Figure 2b). CAU-21-ODB showed negligible adsorption of 3MP and 22DMB; however, it demonstrated a typical Type-I profile for the adsorption of nHEX with a considerable capacity of 141 mg/g (173  $\text{mg}/\text{cm}^3$ ). This indicated that CAU-21-ODB represents a splitter for a complete separation of linear hexane from its branched isomers. The adsorption capacity of CAU-21-ODB is higher than most of the previously reported MOF adsorbents that can split linear and branched alkanes including Zr-btpc,<sup>13</sup> HIA-203,<sup>14</sup> Ni-Asp,<sup>15</sup> Zn-adtb,<sup>16</sup> and Ca-tcpb<sup>17</sup> (Table S2). In addition, the adsorption capacity of nHEX for CAU-21-ODB is slightly higher than that of zeolite 5A at 80 °C (Figure S8).

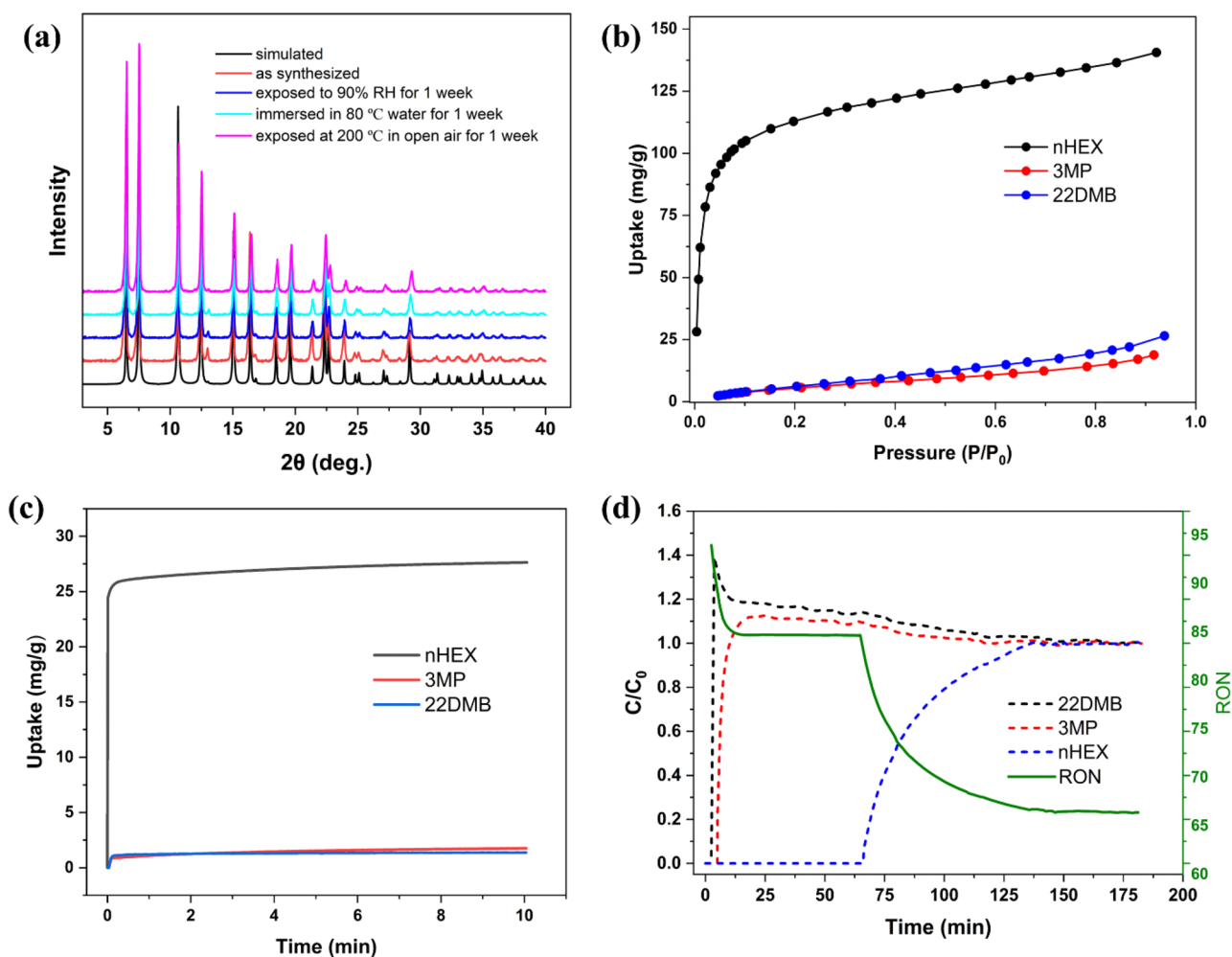


Figure 2. (a) PXRD patterns of CAU-21-ODB under various conditions. (b) Single-component adsorption isotherms of hexane isomers at 30 °C. (c) Adsorption kinetics of nHEX, 3MP, and 22DMB of the first data point from the corresponding adsorption isotherm at 30 °C. (d) Multicomponent breakthrough curves of a ternary mixture of hexane isomers on CAU-21-ODB at 30 °C.

The adsorption kinetics of the different isomers suggested that the adsorption of linear nHEX reached equilibrium in seconds, while 3MP and 22DMB showed essentially no adsorption with an increase in equilibrium time (Figure 2c). This confirmed that the separation of linear and branched hexane isomers is based on a selective molecular sieving process rather than a kinetically controlled mechanism due to insufficient equilibration. We believe the selective molecular exclusion by CAU-21-ODB can be attributed to its gourd-shaped channels with optimal pore aperture.

To further evaluate the separation capability of the CAU-21-ODB on hexane isomers, multicomponent column breakthrough experiments were carried out with equimolar binary mixtures (nHEX/3MP and nHEX/22DMB) and an equimolar ternary mixture (nHEX/3MP/22DMB) at 30 °C. The results of column breakthrough measurement with equimolar nHEX and 22DMB showed that 22DMB eluted at the beginning of the process while nHEX was retained in the column and did not break out until the 72nd minute (Figure S9). Before nHEX penetrated the column, a high-quality gasoline blending component of 22DMB with a RON of 94 was obtained. The column breakthrough measurement with equimolar nHEX and 3MP showed a similar result (Figure S10). 3MP broke out immediately, while nHEX was retained for 75 min. These

results indicated that both 3MP and 22DMB were fully excluded by CAU-21-ODB under dynamic adsorption conditions. The ability of CAU-21-ODB to efficiently separate hexane isomers with different branching was further examined by column breakthrough experiments (Figure 2d) with an equimolar ternary mixture of nHEX, 3MP, and 22DMB. As expected, branched hexanes including both 3MP and 22DMB eluted immediately from the column at the beginning of the measurement. In contrast, nHEX was retained in the column for 66 min. The real-time RON indicated that the value was higher than 84 before the breakthrough of nHEX, which well meets the requirement for industrially refined hexane blends.<sup>11</sup> This is consistent with the aforementioned single-component results. These results are not surprising, considering the kinetic diameters of 3MP (5.0 Å) and 22DMB (6.2 Å).

To model the interactions between nHEX and the framework, and understand the underlying separation mechanism of CAU-21-ODB, we performed *ab initio* calculations with projected augmented wave (PAW) pseudopotentials along with a van der Waals density functional (vdW-DF1)<sup>18–20</sup> as implemented in the VASP code.<sup>21,22</sup> All three hexane isomers were loaded at various positions to identify their optimum binding sites. A very strong interaction of nHEX with the framework is noted (Figure S11), leading to a



binding energy of 1.23 eV (one molecule per unit cell). By virtue of their larger sizes, the binding interaction becomes unfavorable for 3MP and 22DMB at various sites within the pore. Additionally, we also used the climbing image nudged elastic band method (a transition-state search algorithm) to calculate diffusion barriers for hexane isomers in the pores of CAU-21-ODB.<sup>23</sup> To that end, five transition-state geometries were considered between the initial and final states. The calculated barriers for nHEX and 3MP were 0.76 and 1.86 eV, respectively (Figure 3). The very high barrier for 3MP was due

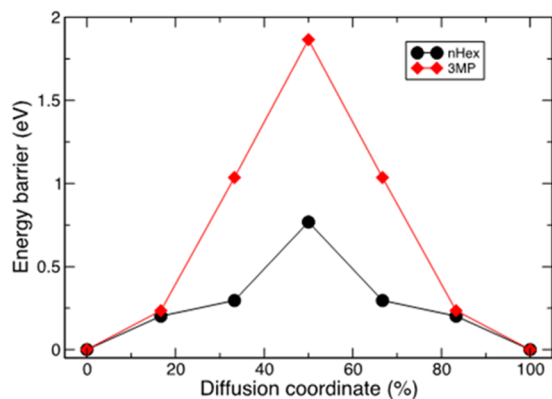


Figure 3. Diffusion energy barriers of nHEX and 3MP.

to its unfavorable binding energy at various sites within the pore. Also, the barrier of 22DMB was too high for it to diffuse into the channel. The induced charge density—i.e., the charge rearrangement upon bond formation—suggests that nHEX interacts with H and O from the framework (Figure S11). These results further confirmed the size-exclusion-based separation mechanism for hexane isomers by CAU-21-ODB.

**Conclusion.** In this study, we demonstrate the efficient splitting of linear and branched hexane isomers by an inexpensive and robust microporous aluminum MOF, CAU-21-ODB. The compound possesses gourd-shaped channels, and only nHEX with a relatively small kinetic diameter can pass through the narrow neck, while the larger 3MP and 22DMB were completely excluded. Multicomponent column breakthrough experiments showed that CAU-21-ODB can effectively separate hexane isomers through selective molecular exclusion. The separation mechanism of CAU-21-ODB for hexane isomers was further confirmed at the molecular level by *ab initio* calculations. Our findings provide useful information for the future design of MOFs for separating light hydrocarbons in the petrochemical industry.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.3c00282>.

Experimental details, PXRD data, TGA, adsorption isotherms, breakthrough curves, induced charge density of nHEX, kinetic diameter and RON of C6 alkane isomers, and comparison of the uptake of nHEX on different MOFs (DOCX)

## ■ AUTHOR INFORMATION

### Corresponding Authors

Qibin Xia — School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China; [orcid.org/0000-0002-8563-6715](https://orcid.org/0000-0002-8563-6715); Email: [qbxia@scut.edu.cn](mailto:qbxia@scut.edu.cn)

Hao Wang — Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, Shenzhen, Guangdong 518055, P.R. China; [orcid.org/0000-0001-7732-778X](https://orcid.org/0000-0001-7732-778X); Email: [wanghao@szpt.edu.cn](mailto:wanghao@szpt.edu.cn)

### Authors

Liang Yu — School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China; Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, Shenzhen, Guangdong 518055, P.R. China

Saif Ullah — Department of Physics and Center for Functional Materials, Wake Forest University, Winston-Salem, North Carolina 27109, United States; [orcid.org/0000-0001-8836-9862](https://orcid.org/0000-0001-8836-9862)

Jinze Yao — School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

Danxia Lin — School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

Jiajin Huang — School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

Shi Tu — School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

Haoyuan Luo — School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

Timo Thonhauser — Department of Physics and Center for Functional Materials, Wake Forest University, Winston-Salem, North Carolina 27109, United States; [orcid.org/0000-0003-4771-7511](https://orcid.org/0000-0003-4771-7511)

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsmaterialslett.3c00282>

### Author Contributions

<sup>†</sup>L.Y. and S.U. contributed equally. The manuscript was written through contributions of all authors. CRediT: Liang Yu investigation, methodology.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (22178119), Shenzhen Science and Technology Program (No. RCYX20200714114539243, KCXFZ20211020163818026). Work in the U.S. was supported by the U.S. Department of Energy, Basic Energy Sciences, Division of Materials Sciences and Engineering (Grant No. DE-SC0019902). Computations were performed using the Wake Forest University High Performance Computing Facility, a centrally managed computational resource with support provided in part by the university.

## REFERENCES

- (1) Wang, H.; Li, J. Microporous Metal-Organic Frameworks for Adsorptive Separation of C5-C6 Alkane Isomers. *Acc. Chem. Res.* **2019**, *52*, 1968–1978.
- (2) Yu, L.; Ullah, S.; Wang, H.; Xia, Q.; Thonhauser, T.; Li, J. High-Capacity Splitting of Mono- and Dibranch Hexane Isomers by a Robust Zinc-Based Metal-Organic Framework. *Angew. Chem., Int. Ed.* **2022**, *61*, e202211359.
- (3) Su, Y.; Chen, R.; Zhang, P.; He, X.; Liu, X.; Liu, Y.; Xiong, H.; Zhao, Z.; Luo, J.; Chen, J.; Chen, S.; Zeng, Z.; Bao, Z.; Deng, S.; Wang, J. Dual pore-size sieving in a novel oxygenate-pillared microporous adsorbent for C6 alkane isomers separation. *AIChE J.* **2022**, *69*, e17937.
- (4) Liang, B.; Zhang, X.; Xie, Y.; Lin, R. B.; Krishna, R.; Cui, H.; Li, Z.; Shi, Y.; Wu, H.; Zhou, W.; Chen, B. An Ultramicroporous Metal-Organic Framework for High Sieving Separation of Propylene from Propane. *J. Am. Chem. Soc.* **2020**, *142*, 17795–17801.
- (5) Wang, H.; Dong, X.; Ding, J.; Wang, K.; Yu, L.; Zhang, S.; Han, Y.; Gong, Q.; Ma, A.; Li, J. Upgrading Octane Number of Naphtha by a Robust and Easily Attainable Metal-Organic Framework through Selective Molecular Sieving of Alkane Isomers. *Chemistry* **2021**, *27*, 11795–11798.
- (6) Wang, H.; Luo, D.; Velasco, E.; Yu, L.; Li, J. Separation of alkane and alkene mixtures by metal-organic frameworks. *J. Mater. Chem. A* **2021**, *9*, 20874–20896.
- (7) Xie, F.; Yu, L.; Wang, H.; Li, J. Metal-Organic Frameworks for C6 Alkane Separation. *Angew. Chem., Int. Ed.* **2023**, *62*, e202300722.
- (8) Li, J. R.; Kuppler, R. J.; Zhou, H. C. Selective gas adsorption and separation in metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504.
- (9) Wu, H.; Gong, Q.; Olson, D. H.; Li, J. Commensurate Adsorption of Hydrocarbons and Alcohols in Microporous Metal Organic Frameworks. *Chem. Rev.* **2012**, *112* (2), 836–868.
- (10) Herm, Z. R.; Bloch, E. D.; Long, J. R. Hydrocarbon Separations in Metal-Organic Frameworks. *Chem. Mater.* **2014**, *26*, 323–338.
- (11) Herm, Z. R.; Wiers, B. M.; Mason, J. A.; van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. Separation of hexane isomers in a metal-organic framework with triangular channels. *Science* **2013**, *340*, 960–964.
- (12) Kruger, M.; Inge, A. K.; Reinsch, H.; Li, Y. H.; Wahiduzzaman, M.; Lin, C. H.; Wang, S. L.; Maurin, G.; Stock, N. Polymorphous Al-MOFs Based on V-Shaped Linker Molecules: Synthesis, Properties, and in Situ Investigation of Their Crystallization. *Inorg. Chem.* **2017**, *56*, 5851–5862.
- (13) Wang, H.; Dong, X.; Lin, J.; Teat, S. J.; Jensen, S.; Cure, J.; Alexandrov, E. V.; Xia, Q.; Tan, K.; Wang, Q.; Olson, D. H.; Proserpio, D. M.; Chabal, Y. J.; Thonhauser, T.; Sun, J.; Han, Y.; Li, J. Topologically guided tuning of Zr-MOF pore structures for highly selective separation of C6 alkane isomers. *Nat. Commun.* **2018**, *9*, 1745.
- (14) Lin, Y.; Yu, L.; Ullah, S.; Li, X.; Wang, H.; Xia, Q.; Thonhauser, T.; Li, J. Temperature-Programmed Separation of Hexane Isomers by a Porous Calcium Chloranilate Metal-Organic Framework. *Angew. Chem., Int. Ed.* **2022**, *61*, e202214060.
- (15) Chen, R.; Zhou, F.; Sheng, B.; Zhang, Z.; Yang, Q.; Yang, Y.; Ren, Q.; Bao, Z. Robust Nickel Aspartate Framework for Shape Recognition of Hexane Isomers. *ACS Sustainable Chem. Eng.* **2022**, *10*, 11330–11337.
- (16) Velasco, E.; Xian, S.; Wang, H.; Teat, S. J.; Olson, D. H.; Tan, K.; Ullah, S.; Osborn Popp, T. M.; Bernstein, A. D.; Oyekan, K. A.; Nieuwkoop, A. J.; Thonhauser, T.; Li, J. Flexible Zn-MOF with Rare Underlying scu Topology for Effective Separation of C6 Alkane Isomers. *ACS Appl. Mater. Interfaces* **2021**, *13*, 51997–52005.
- (17) Wang, H.; Dong, X.; Velasco, E.; Olson, D. H.; Han, Y.; Li, J. One-of-a-kind: a microporous metal-organic framework capable of adsorptive separation of linear, mono- and di-branched alkane isomers via temperature- and adsorbate-dependent molecular sieving. *Energy Environ. Sci.* **2018**, *11*, 1226–1231.
- (18) Berland, K.; Cooper, V. R.; Lee, K.; Schroder, E.; Thonhauser, T.; Hyldgaard, P.; Lundqvist, B. I. van der Waals forces in density functional theory: a review of the vdW-DF method. *Rep. Prog. Phys.* **2015**, *78*, 066501.
- (19) Langreth, D. C.; Lundqvist, B. I.; Chakarova-Kack, S. D.; Cooper, V. R.; Dion, M.; Hyldgaard, P.; Kelkkanen, A.; Kleis, J.; Kong, L.; Li, S. A density functional for sparse matter. *J. Phys.: Condens. Matter* **2009**, *21*, 084203.
- (20) Thonhauser, T.; Zuluaga, S.; Arter, C. A.; Berland, K.; Schroder, E.; Hyldgaard, P. Spin signature of nonlocal-correlation binding in metal organic frameworks arXiv. *Phys. Rev. Lett.* **2015**, *115*, 136402.
- (21) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B Condens. Matter.* **1996**, *54*, 11169–11186.
- (22) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (23) Henkelman, G.; Uberuaga, B. P.; Jonsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys. B* **2000**, *113*, 9901–9904.