Accepted Article

Title: Temperature-Programmed Separation of Hexane Isomers by Porous Calcium Chloranilate Metal-Organic Framework

Authors: Yuhan Lin, Liang Yu, Saif Ullah, Xingyu Li, Hao Wang, Qibin Xia, Timo Thonhauser, and Jing Li

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

WILEY-VCH

RESEARCH ARTICLE

WILEY-VCH

Temperature-Programmed Separation of Hexane Isomers by Porous Calcium Chloranilate Metal-Organic Framework

Yuhan Lin,[a]# Liang Yu,[a][b]# Saif Ullah,[c] Xingyu Li,[a] Hao Wang,*[a] Qibin Xia,[b] Timo Thonhauser,[c] and Jing Li*[d][a]

[a]   Y. Lin, L. Yu, X. Li, Prof. H. Wang, Prof. J. Li
       Hoffmann Institute of Advanced Materials
       Shenzhen Polytechnic
       7098 Liuxian Boulevard, Shenzhen, Guangdong 518055, P. R. China
       E-mail: wanghao@szpt.edu.cn, jingli@rutgers.edu
       #These authors contributed equally to this work
[b]   L. Yu, Prof. Q. Xia
       School of Chemistry and Chemical Engineering
       South China University of Technology
       Guangzhou 510640, PR China
[c]   Dr. S. Ullah, Prof. T. Thonhauser
       Department of Physics and Center for Functional Materials
       Wake Forest University
       Winston-Salem, NC 27109, United States
[d]   Prof. J. Li
       Department of Chemistry and Chemical Biology
       Rutgers University
       123 Bevier Road, Piscataway, NJ08854, United States

       Supporting information for this article is given via a link at the end of the document.

Abstract: The full separation of alkane isomers as a function of different degrees of branching remains a daunting challenge due to its stringent requirement with respect to pore dimensions of the adsorbents. In this work, we report a novel microporous coordination network built on calcium (II) and chloranilate. The compound has a flexible framework and exhibits temperature-dependent adsorption behavior toward hexane isomers. At 30 °C, it accommodates substantial amounts of linear and monobranched hexanes but fully excludes their dibranched isomer, and at elevated temperatures such as 150 °C, it acts as a splitter for linear and branched alkanes. Its capability of efficient discrimination of hexane isomers as a function of branching is verified by experimental breakthrough measurements. *Ab initio* calculations have uncovered the underlying selective size-exclusion separation mechanism.

Introduction

Metal-organic frameworks (MOFs) or porous coordination networks (PCNs) represent a fascinating class of multifunctional, crystalline materials in light of their potential for various applications as well as their intriguing fundamental chemistry concerning their crystal structures and host-guest interactions.[1] Compared to traditional inorganic and organic porous solids, MOFs feature high porosity, adjustable functionality, and easily tunable pore structures, and thus hold great promise for molecular separation,[2, 3, 4] carbon dioxide capture,[5, 6] and water harvesting,[7, 8] to name a few. On the other hand, MOFs have fascinating structure diversity and framework flexibility that are rarely observed in traditional porous materials, which have endowed them with enriched chemistry.[9, 10]

Among various applications explored for MOFs, hydrocarbon separation represents a particularly fruitful field. Important progresses have been made in the separation of olefin/paraffin,[3, 11] alkyne/alkene,[4, 12, 13] alkane isomers,[14, 15] xylene isomers,[2] etc. Alkane isomers (mostly C_{5-7}) separation is a crucial process in the petrochemical industry to upgrade research octane number (RON) of gasoline and to optimize ethylene feedstock.[16] Linear and monobranched alkanes are of low RON values but they are valuable feed for ethylene production through steam/catalytic cracking. In contrast, dibranched or multibranched alkanes generally have high RON, which are premium gasoline components.[17] However, they suffer from low yield when used as ethylene feed. Thus the removal of linear or ideally linear/monobranched isomers from the alkane mixtures is a vital step to achieve high RON and high purity feed for ethylene. Current refineries rely heavily on heat-driven distillations for this separation process. Adsorptive separation by porous solids represents a promising alternative technique that may lower the energy input and suppress carbon dioxide emission.

Zeolite 5A is a benchmark adsorbent for the separation of alkane isomers and has been implemented in industrial process.[17] However, it adsorbs linear alkanes only and fully excludes all branched isomers, and thus it is incapable of discriminating between monobranched and dibranched alkanes. Another zeolite material, ZSM-5, is able to separate mono- and di-branched alkanes through a kinetically driven mechanism, but with relatively low adsorption capacity.[16] Highly efficient separation of alkane isomers as a function of different degrees of branching is challenging as it has stringent requirement on the pore shape/size of the adsorbent. In this context, structure diversity and tunable pore dimensions make MOFs particularly promising for this challenging separation. A number of MOF materials have been explored for the separation of alkane isomers through either thermodynamic or kinetic mechanism

over the past years.[15, 18, 19, 20, 21] MOFs that can fully split monobranched and dibranched alkanes through selective size exclusion are much needed as they offer high efficiency for naphtha separation. However, they were not reported until recently.[15] To this end, it remains challenging but imperative task to develop novel MOFs with optimal pore structures for efficient splitting of monobranched and dibranched alkane isomers.

In this work, we report the synthesis and characterization of a novel 3D microporous MOF structure built on Ca(II) and an easily attainable organic linker, chloranilate. The compound is prepared in an environmentally benign organic solvent, ethanol.

It possesses optimal 1D channels that can split monobranched and dibranched alkanes at room temperature through selective molecular exclusion, as validated by single-component adsorption and multicomponent column breakthrough experiments. More importantly, at elevated temperature, the adsorbent also excludes monobranched alkanes, and thus acts as a splitter for linear and branched isomers at such temperatures. The temperature-dependent adsorption behavior can be attributed to its flexible framework, and the selective molecular exclusion behavior has also been verified by *ab initio* calculations.
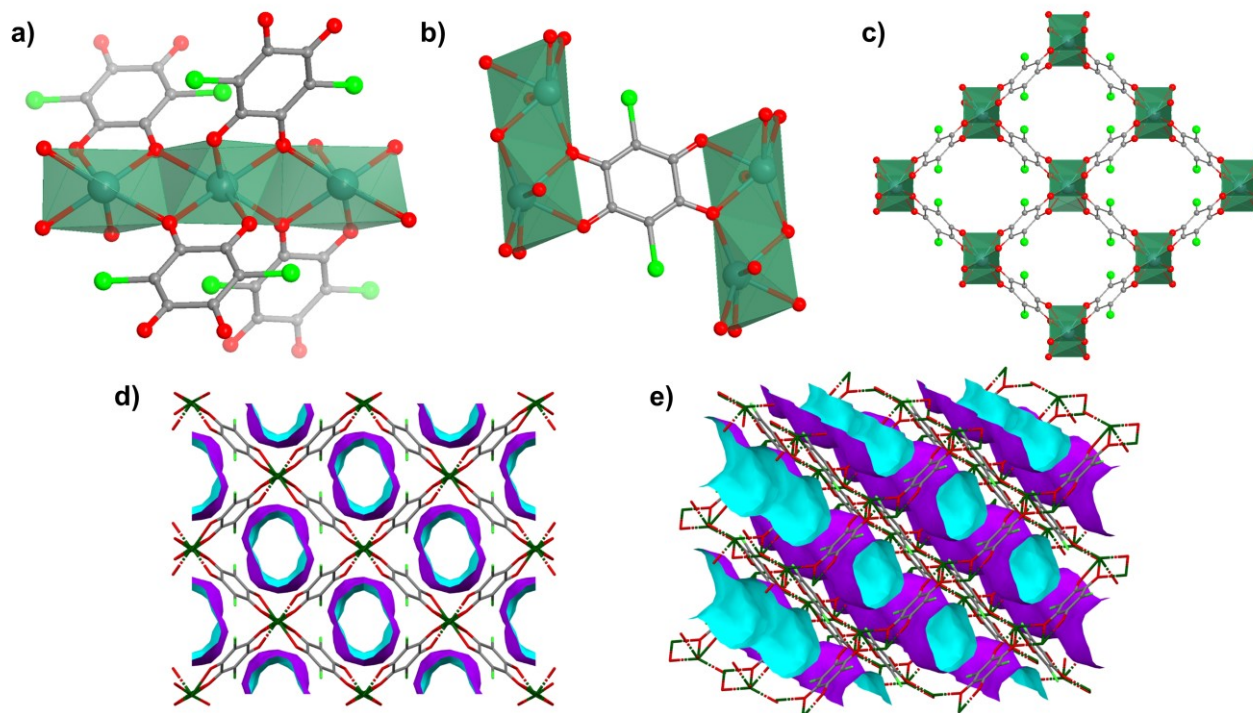

Figure 1. Crystal structure of HIAM-203. (a) Coordination environment of Ca(II), (b) coordination mode of the linker, (c) overall crystal structure of the compound showing one-dimensional channels, (d) and (e) Views of the shape of the channels. Color scheme: Ca: teal, C: grey, O: red, Cl: green. Terminal ethanol molecules are omitted for clarity. The pore shape was simulated by Mercury with a probe radius of 1.2 Å.

Results and Discussion

The title compound was synthesized through solvothermal reactions of $CaCl_2$ and chloranilic acid in ethanol at 150 °C for 2 days with high yield (see Supporting Information for synthesis details). Single-crystal X-ray diffraction analysis of the obtained strip-shaped purple crystals revealed that the compound crystallizes in the monoclinic crystal system with a space group of *C2/c* (Table S1, CCDC No. 219177**1**). The overall formula of the compound is $Ca(C_6O_4Cl_2)(C_2H_6O)$ (denoted as HIAM-203, HIAM = Hoffmann Institute of Advanced Materials). Each Ca(II) cation is seven-coordinated to six oxygen atoms from four different chloranilates and the remaining coordination site is occupied by a terminal ethanol molecule (Figure 1a). Each chloranilate linker is coordinated to four different Ca(II) centers with two oxygen atoms in bidentate fashion and the other two in monodentate mode (Figure 1b). The 1D Ca-O chains are further interconnected by chloranilate linkers to form the resulting 3D

network containing 1D rhombic channels with a diameter of 4.82 Å (C-C, excluding van der Waals radius, Figure 1c). The channels are roughly straight with a slight zig-zag pattern (Figure 1d-e). The overall framework features a **pts** topology as standard representation. However, it can also be regarded as a unique rod-MOF made of $Ca(\mu_3-O)_2(\mu_2-O)_2$. It can thus be described in two ways as 3,4-**dmd** PE&M or 4-**cds** STR (Figure S1).
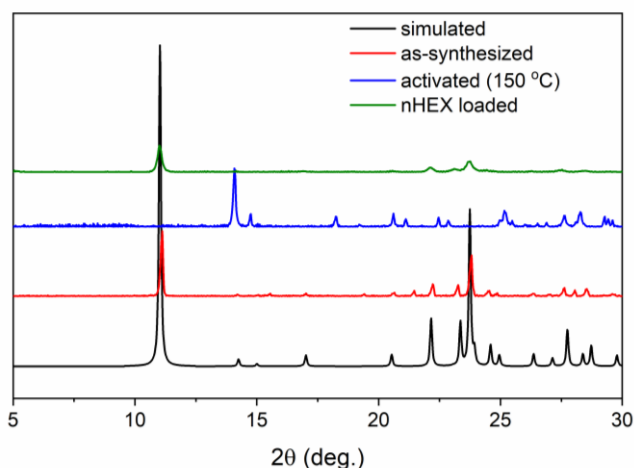
2

Accepted Manuscript

Figure 2. PXRD patterns of HIAM-203 under various conditions.

weight loss of 16.0% before 150 °C, corresponding to the removal of the coordinated ethanol molecules (calculated: 15.7%, Figure S2). The initial weight loss is followed by a plateau between 150 to 350 °C until the second weight loss relating to the decomposition of the framework. The coordinated ethanol solvents can be fully removed by thermally activating the compound at 150 °C under vacuum. Interestingly, a notable change in the PXRD pattern was observed for the activated phase, indicating a structural transformation of HIAM-203 upon removal of the initially coordinated ethanol solvents. It should be noted that the desolvated structure readily transformed back to its original state when the sample was immersed in ethanol. This suggests that the structural change is reversible, rather than irreversible framework degradation. Tremendous efforts have been made to the structure refinement of the activated phase through X-ray diffraction analysis or through computational modeling but have not succeeded yet. However, we can here anticipate that the flexibility of the structure should be found mainly along the a and b axis (shortening of b, and elongation of the a axis). This is determined by the rhombic shape of the pores and by the fact that the c axis is determined by the bridges that build the rod (Figure S1).
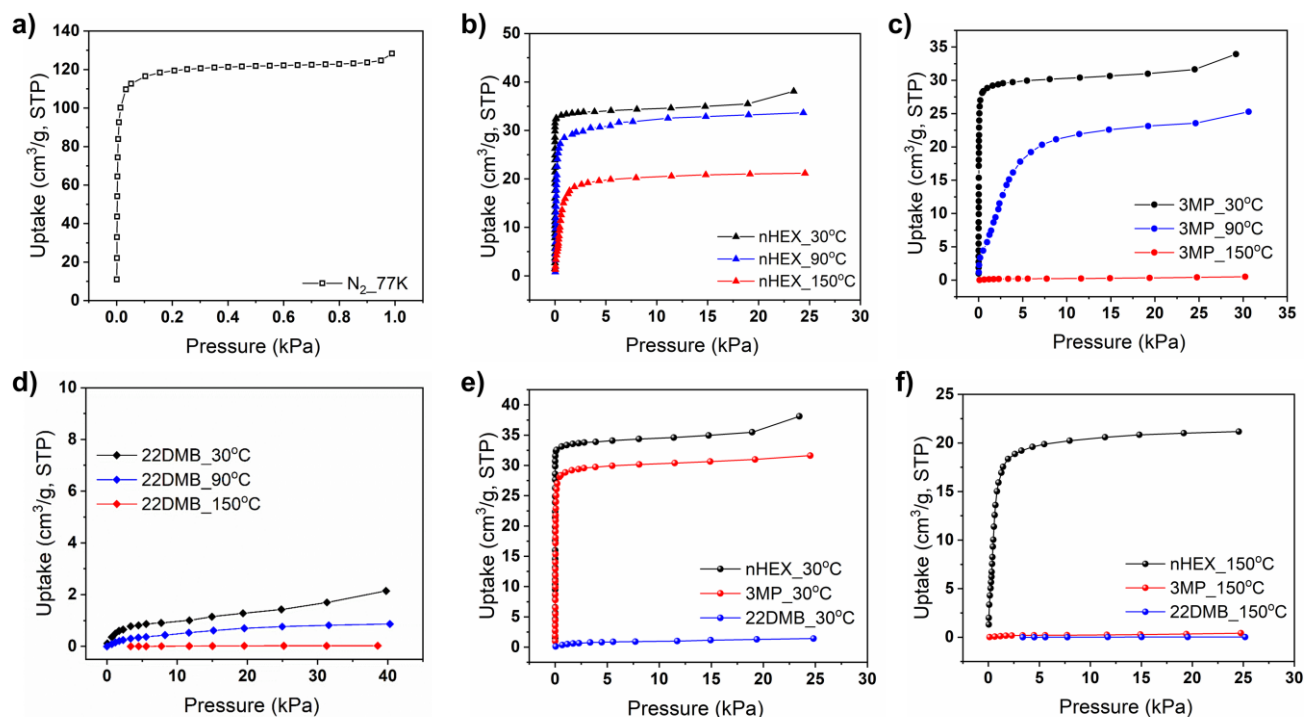
Phase purity of HIAM-203 was confirmed by powder X-ray diffraction (PXRD) analysis where the as-synthesized pattern matched well with the simulated one (Figure 2). Thermogravimetric analysis (TGA) of the compound displays a

Figure 3. Gas/vapour adsorption on HIAM-203. (a) N_2 adsorption at 77 K, (b) nHEX, (c) 3MP, and (d) 22DMB adsorption isotherms at 30, 90, and 150 °C, (e) comparison of adsorption isotherms of nHEX, 3MP, and 22DMB at 30 °C, (f) comparison of adsorption isotherms of nHEX, 3MP, and 22DMB at 150 °C.

Porosity of HIAM-203 was evaluated by nitrogen adsorption at 77 K. The result shows a typical Type I adsorption profile with a saturation capacity of 128.3 cm^3/g (Figure 3a), yielding a BET surface area of 499 m^2/g and a pore volume of 0.19 cm^3/g. Calcium-based MOFs possessing permanent porosity are relatively rare and the surface area of HIAM-203 is among the highest of all Ca-MOFs reported to date.[22] Interestingly, CO_2

adsorption on HIAM-203 at 273 K was negligible up to 1 bar (Figure S3). This reminded us of the structural flexibility of the compound which may not undergo a gating process upon CO_2 adsorption under such condition. The subsequent measurement of CO_2 adsorption at 195 K verified our hypothesis (Figure S4). At 195 K, the adsorption of CO_2 displayed a Type I profile, with a saturation capacity of 113.4 cm^3/g at P/P_0 = 1. Further

exploration of the adsorption of various light gases, including C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 (isobutene), C_4H_{10} (isobutane), Xe, and Kr confirmed the adsorbate- and temperature-dependent adsorption behavior (Figure S5-S9). For example, HIAM-203 adsorbed essentially no Kr at 298 K up to 1 bar but a steep increase of Xe adsorption isotherm was observed at 0.4 bar reaching an uptake of 74.1 cm³/g at 1 bar (Figure S9). This should be attributed to the gas-framework interaction, which is not surprising and has been observed in other flexible MOFs.[23]
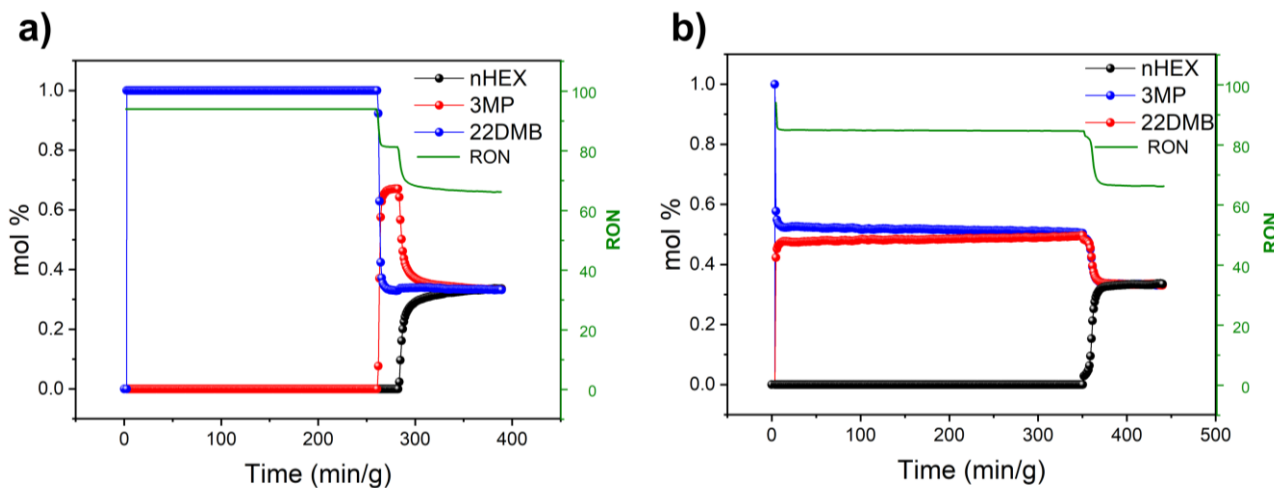

Figure 4. Breakthrough curves of nHEX, 3MP, and 22DMB at (a) 30 °C and (b) 150 °C on HIAM-203. Green curves are the real-time RON of the eluent.

Single-component adsorption of hexane isomers of different degrees of branching, including n-hexane (nHEX), 3-methylpentane (3MP), and 2,2-dimethylbutane (22DB) were evaluated at 30, 90, and 150 °C (Figure 3b-f). The adsorption of nHEX on HIAM-203 at all three temperatures followed Type I profile and reached saturation at low partial pressure (< 2 kPa). Its adsorption capacity for nHEX at 150 °C (21.2 cm³/g) was slightly lower than that at 30 °C (38.1 cm³/g) and 90 °C (33.7 cm³/g). In contrast, the adsorption behavior for 3MP was distinctly different (Figure 3c). While the adsorption isotherms at 30 and 90 °C are Type I with capacities slightly lower than those of nHEX at the same temperatures, we observed essentially no adsorption of 3MP at 150 °C at identical pressure range. More importantly, the compound showed negligible adsorption of 22DMB at all three temperatures up to 40 kPa (Figure 3d). Based on the above observations, it is clear that at 30 °C HIAM-302 adsorbs nHEX and 3MP only but fully excludes 22DMB, and when temperature increases to 150 °C only nHEX can be accommodated (Figure 3e-3f).

The aforementioned single-component adsorption results suggested that HIAM-203 is capable of splitting nHEX/3MP and 22DMB at 30 °C through selective molecular exclusion, and full separation of nHEX and 3MP/22DMB at 150 °C.[24] This is significant as the complete separation of monobranched and dibranched alkanes by simple, easily attainable MOFs has been a great challenge. In addition, the compound could realize the full splitting of alkane isomers as a function of different degrees of branching. To verify the separation capability of HIAM-203 under conditions mimicking industrial separation processes, we performed multicomponent column breakthrough measurements with a feed of a mixture of nHEX, 3MP, and 22DMB at different temperatures according to the single-component adsorption results (Figure 4). At 30 °C, 22DMB eluted out from the column at the beginning of the measurement, without notable retention in the column (Figure 4a), consistent with the single-component adsorption isotherms that 22DMB was fully excluded by the adsorbent at 30 °C. In contrast, 3MP and nHEX did not break through the column until the 262nd and 283rd min/g, suggesting they are substantially adsorbed by the adsorbent. The results confirmed that at ambient conditions HIAM-203 can fully separate 22DMB from its linear and monobranched isomers. This type of complete size-exclusion would maximize the working capacity and separation efficiency. At an elevated temperature of 150 °C, multicomponent column breakthrough measurements revealed neither 3MP nor 22DMB showed notable retention in the column (Figure 4b), in accordance with the single-component adsorption results that they are excluded by the adsorbent at this temperature. In contrast, nHEX was substantially retained, consistent with the adsorption isotherm at 150 °C.

The aforementioned single-component adsorption results and column breakthrough curves suggest that by programming temperature HIAM-203 may be able to split hexane isomers as a function of different degrees of branching and produce pure individual components. To experimentally verify this hypothesis, a temperature-programmed two-column system was established (Figure 5a). The ternary mixture passed first through a column at 150 °C and then the other column at 30 °C. The resulting breakthrough curves demonstrate the three components could be fully separated (Figure 5b). 22DMB eluted out from the column at the beginning, indicating it was excluded by both column which is consistent with single-component adsorption results. 3MP eluted out the next as it was adsorbed in the second column but not the first one while nHEX eluted out the last as it was adsorbed in both columns. The results confirmed pure individual alkanes could be obtained through the temperature-programmed two-column breakthrough system.
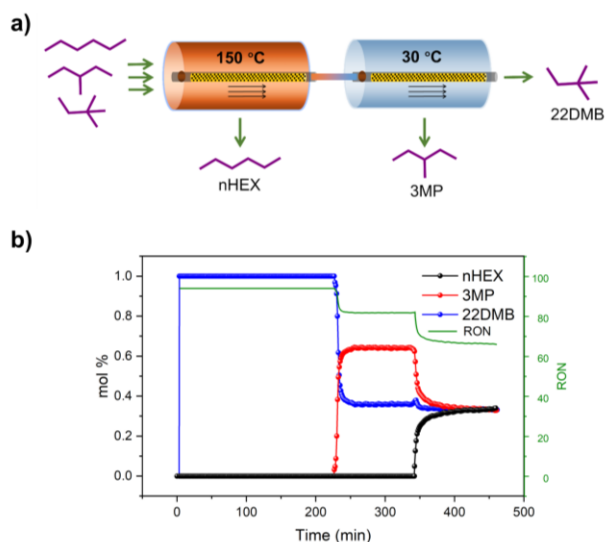
4

Figure 5. (a) Schematic representation of temperature-programmed two-column system (150 °C and 30 °C) for the separation of hexane isomers. (b) Experimental breakthrough curves for the two-column experiments. The green curve is the real-time RON of the eluent.

In order to gain an in-depth understanding of the guest-framework interactions at the molecular-level, *ab initio* calculations were performed.[25, 26] While HIAM-203 undergoes a structural transformation upon activation, the framework returns
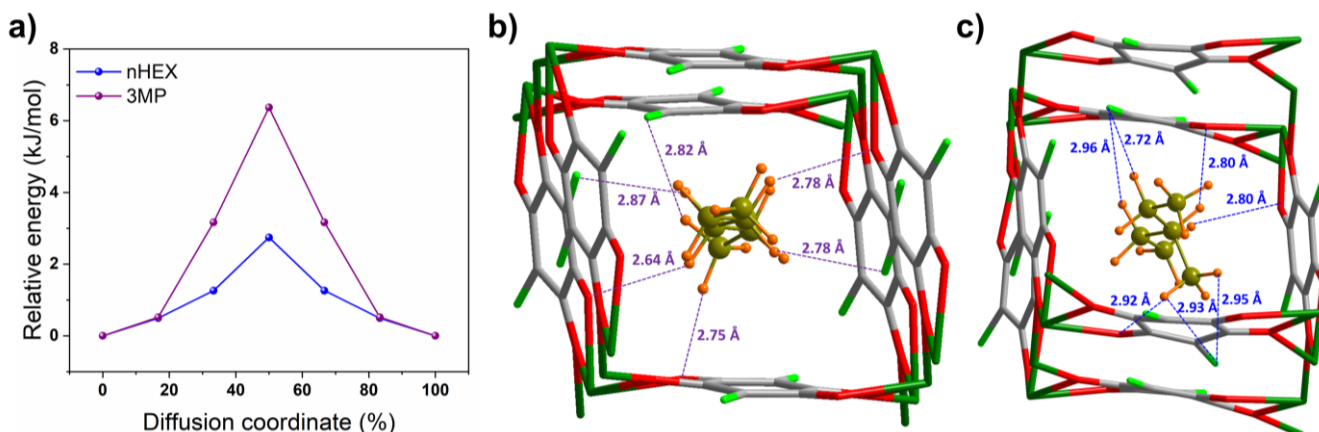
back to the as-synthesized form with guest molecules loaded. Thus it is reasonable to use the initial structure for the calculation and acquire adsorption thermodynamics and kinetics. Hexane isomers were loaded at various positions in the pore of HIAM-203 to find the corresponding optimum binding sites. At full loading, we find the binding energy of nHEX and 3MP to be 116 and 67 kJ/mol, respectively, in agreement with the experimental adsorption results of a higher uptake for nHEX. This also agrees with the fact that MOFs with 1D open channels generally interact more favorably with linear alkanes than their branched isomers as the former have more contacts with the channel. For molecular diffusion within the MOF, a transition-state search was carried out using the climbing-image nudged elastic band (cNEB) method. Interestingly, we find quite low barriers for nHEX and 3MP (Figure 6a), indicating both molecules can diffuse inside the channels of the open-state MOF framework. However, visible changes to the position of the linkers were observed due to the incorporation of the larger-sized 3MP. To visualize the host-guest interactions, we calculated the induced charge density-i.e., the charge rearrangement upon bond formation (Figure S10). We find that both nHEX and 3MP interact quite similarly with the MOF's linker-mostly with Cl and O via hydrogen bonding (Figure 6b-c). In contrast, when 22DMB molecules were placed in the channel, the incremental binding energy quickly becomes repulsive. Thus, the MOF has size exclusion for 22DMB and therefore no noticeable uptake is recorded for 22DMB.

Figure 6. Energy barrier experienced by nHEX and 3MP during diffusion within the MOF (a) and DFT calculated optimum binding sites for nHEX (b) and 3MP (c).

Conclusion

Hexane isomers are valuable industrial feedstock/commodities such as ethylene feed or gasoline components, depending on their degrees of branching. However, their separation remains challenging due to the similar physical properties of the isomers. In this work we report the development of a novel coordination network, calcium chloranilate, featuring 1D channel and a flexible framework. It exhibits temperature- and adsorbate-dependent adsorption profiles. At 150 °C, only linear nHEX can be adsorbed, whereas both nHEX and monobranched 3MP can enter the channel at 30 °C. Thus, the compound can separate

the mixture into individual isomers through temperature-programmed selective molecular exclusion. The material reported here is simple, easily attainable, and promising for the industrial separation processes.

Acknowledgements

RESEARCH ARTICLE

[1] H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444.

[2] L. Li, L. Guo, D. H. Olson, S. Xian, Z. Zhang, Q. Yang, K. Wu, Y. Yang, Z. Bao, Q. Ren, J. Li, *Science* **2022**, *377*, 335-339.

[3] A. Cadiau, K. Adil, P. M. Bhatt, Y. Belmabkhout, M. Eddaoudi, *Science* **2016**, *353*, 137-140.

[4] X. Cui, K. Chen, H. Xing, Q. Yang, R. Krishna, Z. Bao, H. Wu, W. Zhou, X. Dong, Y. Han, B. Li, Q. Ren, M. J. Zaworotko, B. Chen, *Science* **2016**, *353*, 141-144.

[5] S. J. Datta, C. Khumnoon, Z. H. Lee, W. K. Moon, S. Docao, T. H. Nguyen, I. C. Hwang, D. Moon, P. Oleynikov, O. Terasaki, K. B. Yoon, *Science* **2015**, *350*, 302-306.

[6] A. R. Millward, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 17998-17999.

[7] M. J. Kalmutzki, C. S. Diercks, O. M. Yaghi, *Adv. Mater.* **2018**, *30*, 1704304.

[8] N. Hanikel, M. S. Prévot, O. M. Yaghi, *Nat. Nanotechnol.* **2020**, *15*, 348-355.

[9] E. J. Carrington, C. A. McAnally, A. J. Fletcher, S. P. Thompson, M. Warren, L. Brammer, *Nat. Chem.* **2017**, *9*, 882-889.

[10] V. Guillerm, D. Maspoch, *J. Am. Chem. Soc.* **2019**, *141*, 16517-16538.

[11] L. Yu, X. Han, H. Wang, S. Ullah, Q. Xia, W. Li, J. Li, I. da Silva, P. Manuel, S. Rudić, Y. Cheng, S. Yang, T. Thonhauser, J. Li, *J. Am. Chem. Soc.* **2021**, *143*, 19300-19305.

[12] Y. Jiang, J. Hu, L. Wang, W. Sun, N. Xu, R. Krishna, S. Duttwyler, X. Cui, H. Xing, Y. Zhang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202200947.

[13] W. Lou, J. Li, W. Sun, Y. Hu, L. Wang, R. F. Neumann, M. Steiner, Z. Gu, B. Luan, Y. Zhang, *Chem. Eng. J.* **2023**, *452*, 139296.

[14] H. Wang, J. Li, *Acc. Chem. Res.* **2019**, *52*, 1968-1978.

[15] L. Yu, X. Dong, Q. Gong, S. R. Acharya, Y. Lin, H. Wang, Y. Han, T. Thonhauser, J. Li, *J. Am. Chem. Soc.* **2020**, *142*, 6925-6929.

[16] Q. Gong, L. Yu, J. Ding, S. Zhang, Y. Bo, K. Chi, H. Wang, Q. Xia, S. He, J. Li, *Sep. Purif. Technol.* **2022**, *294*, 121219.

[17] D. Peralta, G. Chaplais, A. Simon-Masseron, K. Barthelet, G. D. Pirngruber, *Ind. Eng. Chem. Res.* **2012**, *51*, 4692-4702.

[18] Z. R. Herm, B. M. Wiers, J. A. Mason, J. M. van Baten, M. R. Hudson, P. Zajdel, C. M. Brown, N. Masciocchi, R. Krishna, J. R. Long, *Science* **2013**, *340*, 960-964.

[19] H. Wang, X. Dong, J. Lin, S. J. Teat, S. Jensen, J. Cure, E. V. Alexandrov, Q. Xia, K. Tan, Q. Wang, D. H. Olson, D. M. Proserpio, Y. J. Chabal, T. Thonhauser, J. Sun, Y. Han, J. Li, *Nat. Commun.* **2018**, *9*, 1745.

[20] L. Yu, S. Ullah, K. Zhou, Q. Xia, H. Wang, S. Tu, J. Huang, H.-L. Xia, X.-Y. Liu, T. Thonhauser, J. Li, *J. Am. Chem. Soc.* **2022**, *144*, 3766-3770.

[21] H. Wang, X. Dong, J. Ding, K. Wang, L. Yu, S. Zhang, Y. Han, Q. Gong, A. Ma, J. Li, *Chem. Eur. J.* **2021**, *27*, 11795-11798.

[22] Y. Lin, J. Zhang, H. Pandey, X. Dong, Q. Gong, H. Wang, L. Yu, K. Zhou, W. Yu, X. Huang, T. Thonhauser, Y. Han, J. Li, *J. Mater. Chem. A* **2021**, *9*, 26202-26207.

[23] H. Wang, M. Warren, J. Jagiello, S. Jensen, S. K. Ghose, K. Tan, L. Yu, T. J. Emge, T. Thonhauser, J. Li, *J. Am. Chem. Soc.* **2020**, *142*, 20088-20097.

[24] H. Wang, X. Dong, E. Velasco, D. H. Olson, Y. Han, J. Li, *Energy Environ. Sci.* **2018**, *11*, 1226-1231.

[25] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169-11186.

[26] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758-1775.

RESEARCH ARTICLE

Entry for the Table of Contents
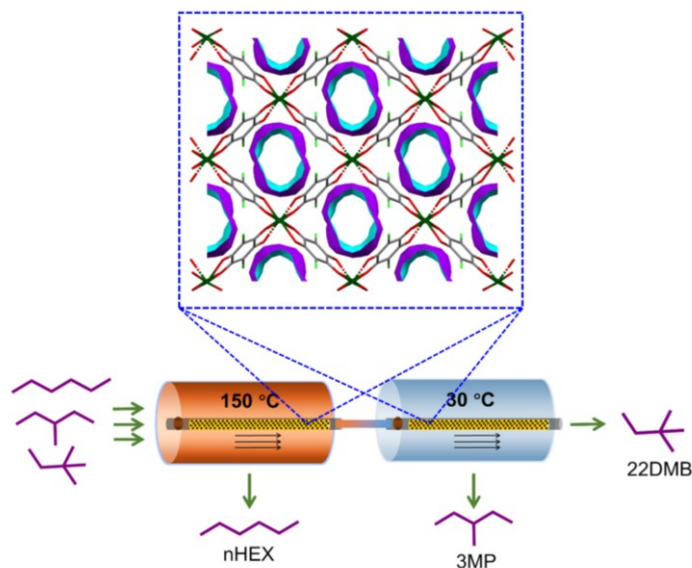
A novel calcium-based metal-organic framework shows temperature- and adsorbate-dependent adsorption of hexane isomers with different branching, leading to temperature-programmed separation of the isomers as a function of different degrees of branching.