

Size-Exclusion Separation of Hexane Isomers by a Y-MOF Built on $\{Y(COO)_3\}_n$ Chains

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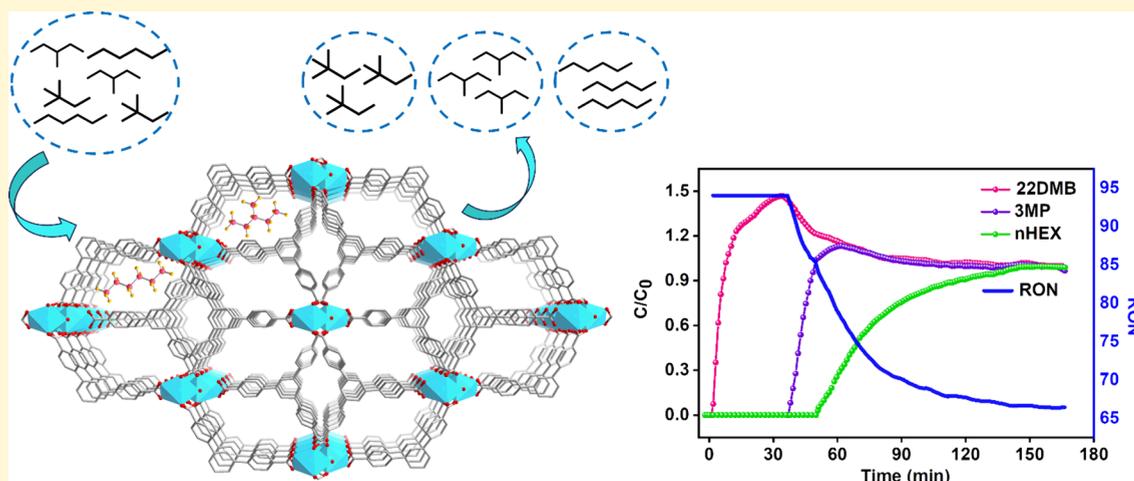
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ABSTRACT: Due to the similar physicochemical properties, the separation of hexane isomers is a challenging task, but it is, however, of high importance in the petrochemical industry. In this study, we present a three-dimensional (3D) Y-based MOF, Y(BTB) (denoted as HIAM-318, $H_3BTB = 1,3,5$ -tri(4-carboxyphenyl)benzene), with a rarely reported bnn topology. HIAM-318 possesses one-dimensional (1D) channels with appropriate pore size, leading to size-exclusion-based separation of hexane isomers. It adsorbs linear *n*-hexane (nHEX) and monobranched 3-methylpentane (3MP) but can barely accommodate dibranched 2,2-dimethylbutane (22DMB). Multicomponent breakthrough experiments confirmed the separation capability. DFT calculations and computational modeling verified the size-sieving separation mechanism and revealed the domains of guest–host interactions.

Separation of alkane isomers according to their degree of branching represents an important process in petrochemical industry because each of the individual isomers is of high value as chemical feedstock.¹ In general, linear alkanes are ideal ethylene feed, while dibranched alkanes are optimal gasoline blends for RON (research octane number) enrichment. For example, the RON of hexane isomers follows the sequence of nHEX (30) < 3MP (75) < 22DMB (94).² Conventional separation of alkane isomers was dominated by heat-driven distillations, which are undoubtedly energy-intensive.³ Selective physisorption by porous materials under mild conditions has emerged as a promising alternative approach and has been implemented in the separation industry. The currently used adsorbent, zeolite 5A, adsorbs linear alkanes but fully excludes their branched isomers because of its limiting pore aperture. However, the incapability of separating between branched alkanes limits its wider applications. In this context, the separation of monobranched

and dibranched alkane isomers, which is crucial for producing pure dibranched isomers with sufficiently high RON and for optimizing ethylene feed, remains to be solved.⁴ Thus, it is imperative to develop new adsorbents with optimal pore structure to meet this separation need.

Among various porous adsorbent materials, metal–organic frameworks (MOFs) have garnered significant attention due to their large surface area, structural diversity, tunable pore size, and modifiable pore environment.^{5–12} The unique features of MOFs have enabled their efficient separation of various

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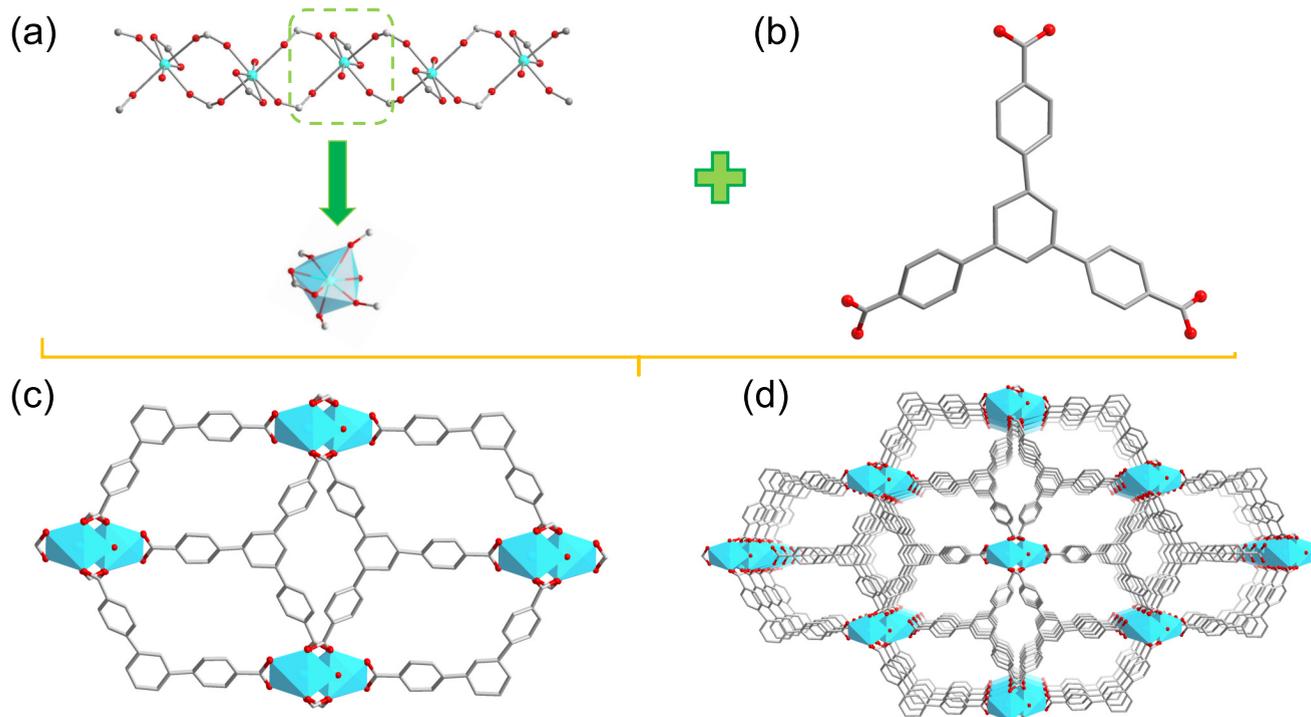


Figure 1. Crystal structure of HIAM-318. (a) The coordination environment of Y^{3+} and the 1D $\{Y(COO)_3\}_n$ chain. (b) Molecular structure of the organic linker BTB^{3-} . (c) Presentation of the pore structure of HIAM-318. (d) View of the 3D structure of HIAM-318. Color scheme: Y: cyan polyhedra, O: red, C: gray. Hydrogen atoms have been omitted for clarity.

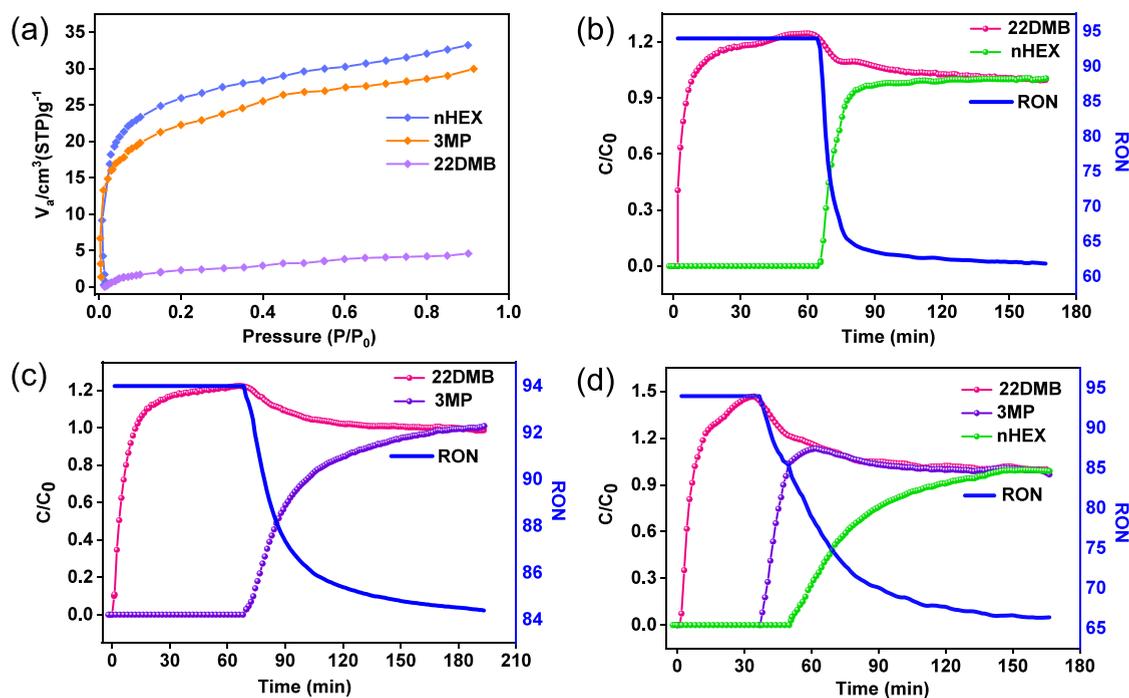


Figure 2. (a) Single-component adsorption isotherms of hexane isomers at 303 K. Breakthrough curves of the equimolar binary mixture of nHEX and 22DMB. (b) Equimolar binary mixture of 3MP and 22DMB (c) and equimolar ternary mixture of nHEX, 3MP, and 22DMB. (d) Blue curve describes the real-time RON of eluted alkanes.

hydrocarbons, including alkane isomers.¹³ Different separation mechanisms, including thermodynamically driven separation, kinetic separation, and size-exclusion, have been practiced in MOFs with varied pore shapes and pore dimensions. Long et al. reported an Fe-MOF showing different adsorption strength

toward hexane isomers with different degrees of branching, resulting in thermodynamic separation.¹⁴ Mendes et al. documented a case of kinetically controlled separation of hexane isomers using modified MIL-53(Fe)-(CF₃)₂.¹⁵ In comparison, separation through size-exclusion is more optimal,

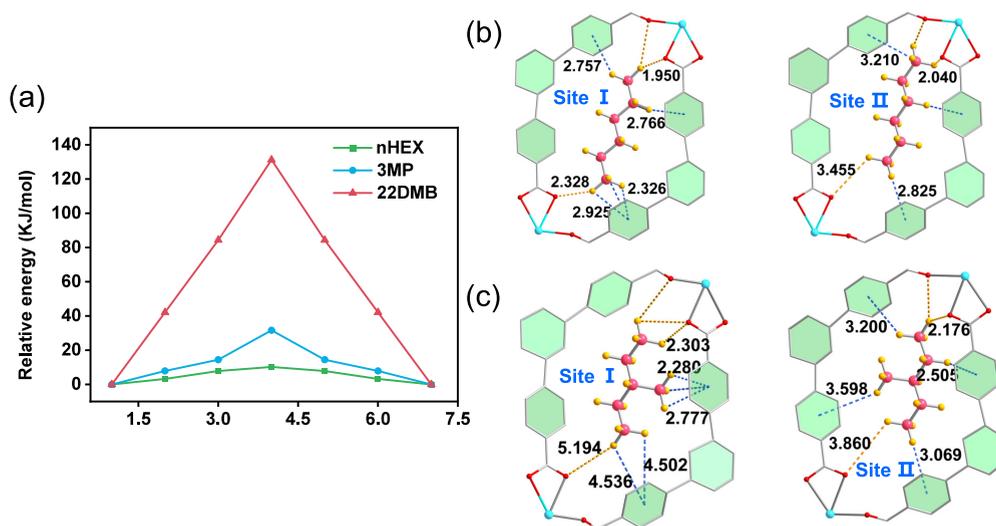


Figure 3. (a) Energy barrier for nHEX, 3MP, and 22DMB to diffuse into the channels of HIAM-318. Binding configurations of (b) nHEX and (c) 3MP in the pore cavity.

as it may render high adsorption selectivity and separation efficiency. In 2018, we demonstrated the size-exclusion separation of linear and branched hexane isomers through topology-directed pore size engineering of Zr-MOFs.¹⁶ And later in 2020, we reported the full separation of monobranched and dibranched hexane isomers by an Al-MOF with optimal pore size.¹⁷ Over the past few years, a series of MOFs have been reported with high efficiency for the separation of alkane isomers (Table S3).^{18–28} However, adsorbents that are capable of complete separation between mono- and dibranched are still relatively rare. Thus, developing new structures that can meet such a need and understanding the underlying separation mechanism remains an important task.

In this work, we report a new Y-based MOF, HIAM-318, with an optimal pore size of 5.4 Å that allows the size-exclusion separation of monobranched and dibranched hexane isomers. HIAM-318 was facilely synthesized at 120 °C by utilizing $Y(NO_3)_3 \cdot 6H_2O$ and the organic ligand H_3BTB in DEF. Single crystal X-ray diffraction analysis revealed that HIAM-318 crystallizes in orthorhombic crystal system with a space group of $Cmcm$. The structure is built on $\{Y(COO)_3\}_n$ chains where each Y^{3+} atom is seven-coordinated to six carboxylate oxygen atoms from BTB^{3-} and one terminal water (Figure 1a). The Y–O bond lengths in the structure of HIAM-318 range from 9.045 to 10.223 Å. The adjacent 1D $\{Y(COO)_3\}_n$ chains extend through the connection by BTB^{3-} ligands, forming a 3D framework containing 1D channels along the c -axis (Figure 1c,d). The overall structure exhibits a rarely reported **bn** topology.^{29,30}

Powder X-ray diffraction (PXRD) analysis confirmed the phase purity of HIAM-318, showing excellent agreement between the experimental and simulated patterns (Figure S6). Thermogravimetric analysis (TGA) revealed an ~30% weight loss before 200 °C followed by a long plateau up to 550 °C (Figure S3). HIAM-318 can undergo vacuum activation at a temperature of 180 °C and retains its crystallinity after adsorption (Figure S6).

To evaluate the porosity of HIAM-318, N_2 adsorption at 77K was performed (Figure S4). The obtained adsorption isotherm displayed a Type I profile with a maximum uptake of

168 $cm^3 g^{-1}$, yielding a BET surface area of 599 $m^2 g^{-1}$ and a pore volume of 0.25 $cm^3 g^{-1}$. According to the DFT model, the pore size distribution curve of HIAM-318 was centered approximately at 5.4 Å, similar to the kinetic diameter of 3MP (5.5 Å). Considering the intrinsic structure flexibility of MOFs, HIAM-318 holds the potential for separating monobranched and dibranched hexane isomers. Single-component adsorption isotherms of hexane isomers, including nHEX, 3MP, and 22DMB on HIAM-318, were subsequently tested (Figure 2a). It showed substantial adsorption of 33.3 $cm^3 g^{-1}$ for nHEX and 30.0 $cm^3 g^{-1}$ for 3MP at 30 °C. In contrast, the uptake for 22DMB was negligible (<5 $cm^3 g^{-1}$). This is not surprising considering the molecular dimensions of the isomers and the pore size of HIAM-318. The results indicated that HIAM-318 is capable of effectively separating nHEX/3MP and 22DMB at 30 °C through selective molecular exclusion. We further evaluated the durability of the material by collecting three consecutive adsorption isotherms of nHEX, and the results indicated no notable loss of adsorption capacity after three runs, demonstrating its good cycle stability (Figure S9).

The separation capability of HIAM-318 was further assessed by multicomponent column breakthrough measurements. To fully evaluate the separation performance, we first conducted two-component breakthrough tests with equimolar binary mixtures of 22DMB/nHEX and 22DMB/3MP (Figure 2b,c). For the 22DMB/nHEX mixture, 22DMB eluted initially without notable retention, while nHEX was retained in the column for as long as 65 min. Similarly, in the test of the 22DMB/3MP mixture, 22DMB eluted at the beginning, whereas 3MP did not break out until the 70th minute. These experiments indicated the ability of HIAM-318 to effectively discriminate between dibranched 22DMB and its linear or monobranched isomers. To further assess the separation capability of HIAM-318, breakthrough measurements of an equimolar ternary mixture of nHEX/3MP/22DMB were performed (Figure 2d). The results demonstrated the immediate elution without any retention, which is consistent with the findings of single-component adsorption isotherms and breakthrough curves of binary mixtures. In

contrast, the retention times for 3MP and nHEX were determined to be 38 and 51 min, respectively. These results confirmed that HIAM-318 is capable of separating the dibranched 22DMB from its linear and monobranched isomers, which is aligned with our expectations considering its optimal pore size. Real-time RON of the breakthrough tests demonstrated that the initial eluate had an RON value exceeding 90, meeting the crucial specifications for gasoline blending components.

In order to gain deeper insights into the selective adsorption behavior of HIAM-318 toward nHEX and 3MP, we employed density functional theory (DFT) calculations based on first principles.³¹ The exchange-correlation potential was described using the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE), and Grimme's DFT-D3 methodology was utilized to describe dispersion interactions among all the atoms in the adsorption models.^{32,33} These calculations aimed to explore the interaction between hexane isomers and the HIAM-318 framework and to assess their transport capabilities within the channels. Density functional theory (DFT) calculations unveiled an energy barrier of only 10.21 kJ mol⁻¹ for nHEX and 31.62 kJ mol⁻¹ for 3MP, indicating their free passage along the HIAM-318 channels without significant limitations (Figure 3). However, when it comes to 22DMB, it encounters a substantial adsorption barrier of 131.27 kJ mol⁻¹, hindering its ability to enter the channels by surmounting the energy barrier.

To further study the domains of guest–host interactions, we modeled the guest molecules (nHEX, 3MP) within the channels of HIAM-318 and examined the binding energy. Indeed, we observed preferential occupation of the channels by both nHEX and 3MP, aligning well with our experimental observations. The results unequivocally indicate the presence of two binding sites for each isomer, where the guest molecules assume distinct configurations at each site. Due to the constrained pore environment, the guest molecules engage in robust interactions with the organic linkers. A detailed examination of nHEX configurations at site I reveals its entrapment through multiple C–H···O hydrogen bonds, with the shortest distance of 1.950 Å, alongside the shortest C–H··· π distance of 2.326 Å. At site II, the head –CH₃ group of nHEX is ensnared by the BTB linkers' oxygen atoms, primarily through potent C–H···O hydrogen bonds (2.040 Å) and C–H··· π interactions (2.655 Å) with the benzene rings (Figure 3b). The calculated binding energies (ΔE) for two nHEX molecules are 83 kJ mol⁻¹ at site I and 75 kJ mol⁻¹ at site II, respectively. Similarly, 3MP at site I was grasped by multiple C–H···O hydrogen bonds and C–H··· π interactions with the shortest distances of 2.303 and 2.280 Å. For site II, 3MP was captured in a perpendicular fashion by the pore windows, primarily through C–H···O hydrogen bonds and C–H··· π interactions, and the shortest distances are 2.176 and 2.505 Å (Figure 3c). The pore cavity shows a similar binding energy for two 3MP molecules, measuring 59 and 52 kJ mol⁻¹ for sites I and II, lower than those of nHEX, explaining the higher adsorption capacity of HIAM-318 for nHEX compared to 3MP. These results are in agreement with the experimental observations. Thus, the remarkable combination of molecular recognition and size-sieving effects endows HIAM-318 with outstanding separation performance for hexane isomers.

In summary, we report a Y-MOF (HIAM-318) with an optimal pore aperture that adsorbs nHEX and 3MP but excludes 22DMB. Single-component adsorption isotherms and

multicomponent breakthrough experiments confirmed the high efficiency of HIAM-318 for the separation of hexane isomers under mild conditions. Theoretical calculations provide important insights into the underlying separation mechanism of HIAM-318 in the sieving of hexane isomers. This study presents an excellent adsorbent for the separation of hexane isomers and offers valuable insights into material design for targeted separations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.4c00113>.

Experimental methods, TGA, nitrogen adsorption results, PXRD, adsorption kinetics, adsorption cycles (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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