

# Splitting Mono- and Dibranched Alkane Isomers by a Robust Aluminum-Based Metal–Organic Framework Material with Optimal Pore Dimensions

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**ABSTRACT:** The separation of alkanes with different degrees of branching, particularly mono- and dibranched isomers, represents a challenging yet important industrial process for the production of premium gasoline blending components with high octane number. We report here the separation of linear/monobranched and dibranched alkanes through complete molecular sieving by a robust aluminum-based MOF material, Al-bttotb ( $H_3bttotb = 4,4',4''$ -(benzene-1,3,5-triyltris(oxy))tribenzoic acid). Single- and multicomponent adsorption experiments reveal that the material adsorbs linear and monobranched alkanes, but fully excludes their dibranched isomers. Adsorption sites of alkanes within the MOF channels have been identified by single-crystal X-ray diffraction studies, and the adsorption mechanism was explored through computational calculations and modeling. The highly selective adsorption of the MOF should be attributed to its optimal pore dimensions.

Naphtha streams represent the distillate collected in the range of 35–200 °C during oil refinement in the petrochemical industry. Further distillation of naphtha produces light naphtha streams consisting mostly of C5 and C6 alkanes, which are subject to catalytic isomerization reactions generating isomers with different degrees of branching.<sup>1</sup> The resultant C5 and C6 alkane isomers can be used as valuable gasoline blending components; however, they must undergo further separation so as to guarantee a sufficiently high octane rating.<sup>2,3</sup> Typically, more branched alkanes possess higher research octane number (RON) than their less branched isomers. For example, the RONs for *n*-hexane (nHEX), 2-methylpentane (2MP), 3-methylpentane (3MP), 2,2-dimethylbutane (22DMB), and 2,3-dimethylbutane (23DMB) are 24.8, 73.4, 74.5, 91.8, and 101.7, respectively. Thus, linear alkanes must be removed, or in a more ideal scenario, linear and monobranched alkanes are separated from their dibranched isomers, which have the highest octane number and are premium gasoline blending components.

The separation of alkane isomers represents a challenging process because of their similar chemical and physical properties. Conventional heat-driven distillations could accomplish the separation but with huge capital investment for the equipment and high energy consumption. Alternatively, adsorptive separation technology using porous solids has been proven to be cost efficient and environmentally beneficial, as it would reduce the energy input and suppress carbon dioxide emission. Having the ability to completely separate linear alkanes from their branched isomers, zeolite 5A remains the benchmark material for this separation process.<sup>2,4</sup> However, since zeolite 5A does not adsorb any branched alkanes, it cannot be used to achieve further improved octane number by

differentiating mono- and dibranched isomers, which limits its wider application. To this end, seeking new types of adsorbents with enhanced separation performance is imperative.

Metal–organic frameworks (MOFs) are particularly desirable as adsorbents for industrially challenging separations because of their diverse structures and highly tunable pore systems.<sup>5</sup> MOFs have demonstrated exceptional performance for the separation of hydrocarbons, such as paraffins/olefins and alkane isomers.<sup>6–14</sup> Several MOF materials, including Y-fum,<sup>11</sup>  $Fe_2(BDP)_3$ ,<sup>12</sup> Zr-bptc, Zr-abtc,<sup>13</sup> and Ca-tcpb,<sup>14</sup> have shown similar or even better performance for the separation of alkane isomers compared to zeolite 5A, with respect to adsorption capacity or selectivity. However, to date, none of the reported materials have reached optimum performance. For example,  $Fe_2(BDP)_3$  and Zr-abtc are capable of discriminating mono- and dibranched alkane isomers thermodynamically, but with relatively low selectivity. Ca-tcpb has the ability to separate linear, monobranched, and dibranched alkanes through temperature programming by making use of its structure flexibility.<sup>14</sup> While an ideal size-exclusion-based separation was achieved, it was limited to specific temperature and pressure, which may not represent the ideal conditions under the current industrial setting. In this work, we show that Al-bttotb, an ultramicroporous metal–organic framework with one-dimensional (1D) channels, adsorbs linear and mono-

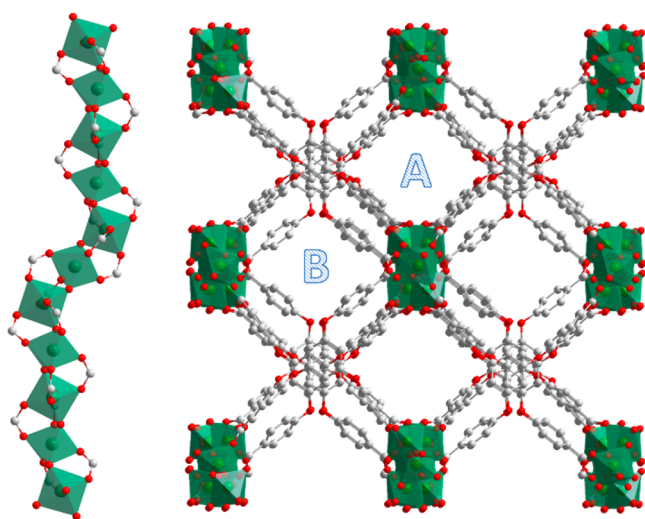
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branched alkanes only and excludes their dibranched isomers. Adsorption sites of linear and monobranched alkanes have been crystallographically identified, and density functional theory (DFT) calculations reveal that the selective adsorption can be attributed to the optimal channel dimension of the MOF.<sup>9</sup>

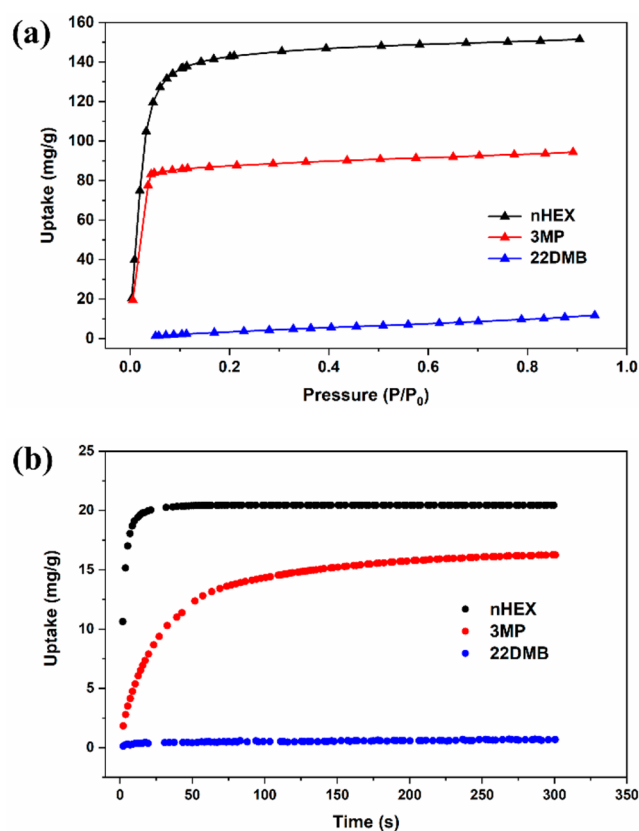
Al-bttotb was prepared solvothermally with  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{H}_3\text{bttotb}$ , and formic acid in DMF at 150 °C. Single-crystal X-ray diffraction reveals the compound crystallizes in the orthorhombic crystal system with a space group of  $Ccca$ .<sup>15</sup> In its crystal structure, each Al(III) center is octahedrally coordinated to O atoms from four carboxylates and two bridging hydroxyl anions, forming a 1D array of corner-sharing  $\text{AlO}_6$  polyhedra (Figure 1). The 1D chains are further



**Figure 1.** Crystal structure of Al-bttotb. Left: 1D array of corner-sharing  $\text{AlO}_6$  polyhedra. Right: 3D structure of Al-bttotb showing two types of channels.

interconnected through  $\text{bttotb}^{3-}$ , forming a 3D network with two types of 1D channels with a square-shaped cross section. Thermogravimetric analysis (TGA) of the as-synthesized material displays a continuous weight loss of 15 wt % up to 180 °C, corresponding to the solvent molecules in the pore (Figure S1). Methanol exchange allows full activation of the material under milder conditions (Figures S1 and S2). Nitrogen adsorption at 77 K of Al-bttotb reveals a typical type I profile, giving a BET surface area of 572  $\text{m}^2/\text{g}$  and a pore volume of 0.22  $\text{cm}^3/\text{g}$  (Figure S3). Pore size distribution shows that the material has a uniform pore size of 5.6 Å (Figure S4). It is well recognized that aluminum-based MOFs are generally robust, attributed to the strong Al–O bonds.<sup>16</sup> Our experiments confirm that the structure of Al-bttotb is well-retained after being heated at 180 °C in open air or being exposed to 90% humidity or boiling water for 1 week (Figure S5).

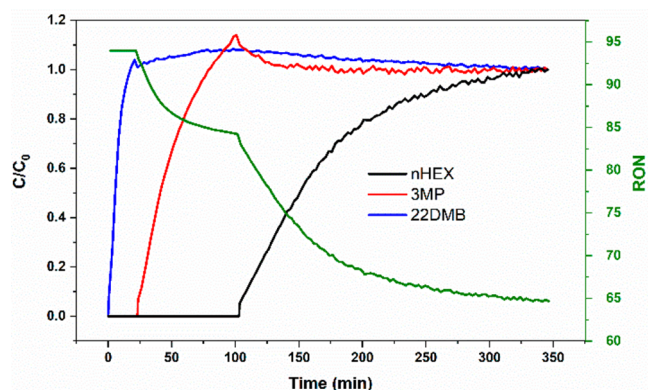
The measured pore size of Al-bttotb falls between the kinetic diameters of mono- and dibranched  $\text{C}_6$  alkanes (3MP: 5.5 Å, 22DMB: 6.2 Å). This encourages us to explore its adsorption properties toward these alkane isomers. Single-component vapor adsorption analysis reveals that the material adsorbs linear and monobranched alkanes (nHEX and 3MP) with uptakes of 151 and 94 mg/g, respectively, at 30 °C (Figure 2a). However, it shows essentially no adsorption toward their dibranched isomer (22DMB). To the best of our knowledge, this represents the first porous material with a rigid framework



**Figure 2.** (a) Adsorption isotherms and (b) adsorption kinetics of nHEX, 3MP, and 22DMB of the first data point from the corresponding adsorption isotherm at 30 °C.

that shows complete separation between mono- and dibranched alkanes, which cannot be accomplished by the benchmark material zeolite 5A. The adsorbed alkanes could be desorbed completely at 120 °C, and no loss of adsorption capacity was observed after six adsorption–desorption cycles (Figure S11 and S12). To confirm it is a case of selective size exclusion rather than kinetic separation due to insufficient equilibration, we looked into the adsorption kinetics. As shown in Figure 2b, nHEX and 3MP reach equilibrium in 20 s and 2 min, respectively, while 22DMB shows no changes in uptake as equilibrium time increases, suggesting the molecule is fully excluded by the MOF.

To evaluate its capability of separating alkane isomers, we performed multicomponent column breakthrough measurements on Al-bttotb with a ternary mixture of equimolar nHEX, 3MP, and 22DMB. The results show that the MOF can well separate the mixture into individual components (Figure 3). 22DMB breaks at the beginning without any retention, confirming the fact that it is not adsorbed by Al-bttotb. In contrast, 3MP and nHEX were retained in the column for 23 and 100 min, respectively, corresponding to dynamic adsorbed amounts of 28 and 129 mg/g. The dynamic adsorption capacity is notably higher than that of zeolite 5A under identical conditions.<sup>13</sup> Real-time RON detection indicates that the initial eluent has a RON of more than 90, well meeting the requirement for gasoline blending components. The notably longer retention of nHEX compared to 3MP could be a result of the combined effect of thermodynamics and kinetics, agreeing with the results from single-component adsorption isotherms. This is also consistent with previously reported



**Figure 3.** Multicomponent breakthrough curves of a ternary mixture of nHEX, 3MP, and 22DMB. Green curve depicts the RON of the eluent.

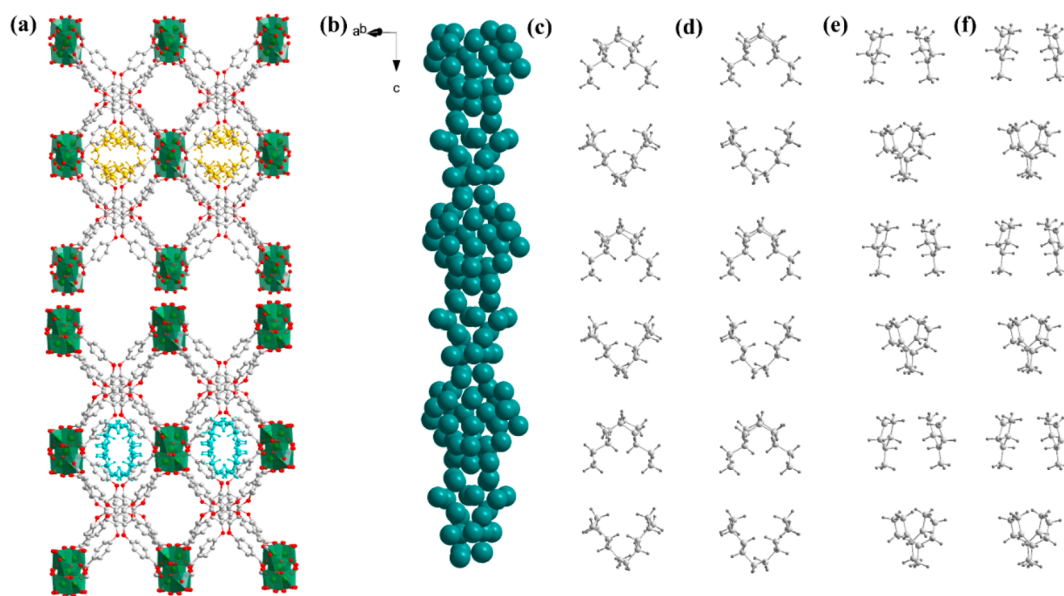
studies that showed that linear alkanes have better contact with 1D channels compared to their branched isomers.

We further expanded the adsorbate mixture from three-component (nHEX, 3MP, 22DMB) to five-component (nHEX, 2MP, 3MP, 23DMB, and 22DMB) to evaluate if the separation ability of the material will be retained under a more complicated scenario. Single-component adsorption measurement indicates that the adsorbed amount and adsorption rate of 2MP fall between nHEX and 3MP and that the material shows moderate adsorption toward 23DMB with a relatively low uptake of 42 mg/g and slow adsorption kinetics (Figures S6 and S7). This is not surprising as the kinetic diameter of 23DMB (5.8 Å) is comparable to the effective pore size of the MOF. Considering the inherent structure flexibility of MOF materials, it is reasonable that it can accommodate 23DMB molecules, but with certain diffusion restrictions. Five-component column breakthrough experiments reveal that the material can well separate the dibranched alkanes from other isomers (Figure S8). This is crucial, as both dibranched isomers (23DMB and 22DMB) have high octane numbers. In

addition, the structure of the material was well-maintained after adsorption/separation measurements (Figures S9 and S10).

To further explore the adsorption behavior of Al-bttob toward alkanes, we studied the shape and dimension of its channels through adsorption simulations. Helium simulation at 1 K and 1 bar was performed to sketch the profile of the channels. The packing of helium atoms reveals that both channels (A and B) are segmented (Figure S13). Adsorption simulation of nHEX and 3MP at 30 °C and 1 bar indicates that the adsorbed alkanes preferentially reside in channel B, leaving channel A unoccupied (Figure 4c and e). This could be attributed to the fact that the smaller chambers in channel B give rise to stronger interaction with nHEX or 3MP molecules.

To experimentally verify the aforementioned adsorption phenomenon, we attempted to resolve the crystal structure of adsorbate-loaded MOF through a single-crystal X-ray diffraction study. This is the most straightforward technique to study the adsorption sites, adsorbate–adsorbent interaction, and adsorption mechanisms. Fortunately Al-bttob is robust and maintains its single crystallinity upon guest removal and inclusion. By exposing an activated MOF sample to nHEX, 3MP, and 22DMB and subsequent single-crystal X-ray diffraction analysis, we were able to determine the crystal structure of nHEX- and 3MP-loaded MOF. In contrast, no sign of 22DMB was detected in the MOF channels, confirming that it is fully excluded by the MOF. Looking into the structure of Al-bttob with nHEX or 3MP adsorbed, we indeed observe that the alkane molecules are packed in channel B, consistent with the simulation results (Figure 4d and f). The adsorbed amount and packing of molecules for nHEX or 3MP agree well with the simulated structures. nHEX (and 3MP) are adsorbed in channel B in pairs, with two molecules residing laterally within each segment. Close contacts of nHEX molecules with the bridging hydroxyl from the MOF have been found, with a H–H distance of 2.19 Å, while the closest H–H distance from 3MP to the MOF is 2.27 Å (Figure S14).



**Figure 4.** (a) Crystal structure of nHEX (top) and 3MP (bottom) loaded Al-bttob. Yellow and cyan molecules represent nHEX and 3MP, respectively. (b) Shape of channel B outlined by adsorption simulation of helium. (c) Simulated and (d) experimentally observed packing of nHEX along channel B. (e) Simulated and (f) experimentally observed packing of 3MP along channel B.



To understand the underlying mechanisms for the experimentally observed preferential adsorption in channel B and its accommodation of nHEX and 3MP but not 22DMB, we perform a computational study at the DFT level.<sup>17–19</sup> To simulate the experimental situation, we model two guest molecules (nHEX, 3MP, 22DMB) in both channel A and B of the Al-MOF and explore the effect on the binding energy. Results for the binding energy per molecule of nHEX, 3MP, and 22DMB are presented in Table S4. Indeed, we observe a preferred channel occupation for both nHEX and 3MP in channel B over channel A, which is in good agreement with our experimental observations. Due to the smaller chamber size of channel B, not only is there an interaction of the guest molecules with the ligands, but the guest molecules are also forced into a significant lateral interaction in-between them due to the tighter confinement. Our results for the binding energy of the 22DMB show that even this molecule theoretically binds in channels A and B with significant binding energy. However, one significant difference for 22DMB as compared to nHEX and 3MP has been observed: We do find that in the case of nHEX and 3MP both molecules also bind to the necks with slightly reduced binding energy (as compared to the values given in Table S4, which show binding in the chambers). However, for 22DMB we find positive binding energies in the necks, i.e., a repulsion of the molecule from the necks. This results in a kinetic barrier for 22DMB—which is not present for nHEX or 3MP—that effectively excludes 22DMB from adsorbing in the MOF, explaining our experimental observation.

Adsorptive separation of similar molecules is challenging, as it requires precise control of the pore structure and/or functionality of the adsorbent. The diversity of MOF pore structures offers an unprecedented opportunity for highly efficient separation of similar molecules, such as alkane isomers. In this work, we show that the separation of monobranched and dibranched alkanes can be accomplished through selective molecular sieving by a robust microporous MOF. The underlying mechanism has been explored through single-crystal X-ray diffraction studies and computational calculation and modeling. The selective adsorption behavior of the material toward alkane isomers should be attributed to its optimal channel dimensions.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c01769>.

Experimental details, synthesis of the MOF, PXRD data, TGA data, and adsorption data (PDF)

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## Notes

The authors declare no competing financial interest.

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