

Metal-Organic Frameworks

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High-Capacity Splitting of Mono- and Dibranched Hexane Isomers by a Robust Zinc-Based Metal–Organic Framework

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Abstract: High-efficiency separation of C₆ alkanes, particularly the mono- and dibranched isomers by using porous solids, is of paramount significance in the petrochemical industry and, remains a daunting challenge. In this work, we report the complete separation of linear/monobranched hexanes from their dibranched isomers through selective size-exclusion by a microporous MOF, Zn-tcpt (H₃tcpt = 2,4,6-tris(4-carboxyphenoxy)-1,3,5-triazine), with a two-fold interpenetrated structure of **hms** nets. Importantly, its adsorption capacity and selectivity are notably higher than those of the previously reported adsorbents that can split mono- and dibranched alkane isomers. Dynamic breakthrough measurements verify the excellent separation of C₆ alkane isomers by Zn-tcpt, and the size-exclusion based separation mechanism has been confirmed by *ab initio* materials modeling. The high-efficiency separation of alkane isomers by Zn-tcpt can be attributed to its optimal pore dimensions as well as high porosity.

Industrial chemical separation processes, accounting for 10–15 % of the world's total energy consumption, usually require the discrimination of physically and chemically similar molecules to achieve a high purity of desired components for subsequent applications.^[1] Among them, the separation of alkane isomers (mainly C₅–C₇) is a vital process in the production of polymers and gasoline.^[2] In general, functions of alkanes are closely related to their degrees of branching. For example, the Research Octane

Number (RON) is an indicator to evaluate the magnitude of gasoline's resistance to shock and explosion and gasoline with low RON can cause motor vehicle detonation as well as reduce the engine efficiency. The RON values for n-hexane (nHEX), 3-methylpentane (3MP), and 2,2-dimethylbutane (22DMB) are 30, 75, and 94, respectively. Thus, branched alkanes, in particular the dibranched isomers are premium gasoline components while the linear ones with low RON have to be removed from the mixture when used for gasoline blends. On the other hand, less-branched alkanes, including linear and monobranched isomers are superior ethylene feed through steam/catalytic cracking processes whereas the presence of multi-branched alkanes would lead to a low yield of ethylene.^[3] In this context, the separation of alkane isomers based on different degrees of branching, particularly high-efficiency discrimination of mono- and dibranched isomers represents an important task for the optimization of ethylene feed as well as providing premium gasoline components. Chemical industry currently relies on energy-intensive, heat-driven distillations for the separation of alkane isomers. Adsorptive separation by solid adsorbents is well-recognized as an alternative technique with less energy input. Zeolite 5A has been implemented in industrial separation of linear alkanes from their branched isomers. However, due to its relatively small pore aperture, zeolite 5A does not adsorb any branched alkanes and thus cannot further separate mono- and dibranched isomers, limiting its wider application. ZSM-5 shows kinetic separation of mono- and dibranched alkanes but it suffers from low adsorption capacity.^[4]

Metal-organic frameworks (MOFs) hold particular promise for industrially challenging separations such as the separation of alkane isomers, in light of their structural diversity as well as highly tunable pore dimensions and functionalities.^[5–9] In early studies, thermodynamic separation was the focus where researchers took advantage of the different shapes of alkane isomers which lead to their different contacts with MOF pore surface and different adsorption affinity, as exemplified in Fe₂(BDP)₃ reported by Long and co-workers.^[10] Compared to thermodynamically-driven discrimination, separation by kinetically-driven mechanism, or more ideally, through selective molecular exclusion would render higher selectivity and efficiency.^[4] Thus, recent research efforts have been focused on the development of MOFs with ideal pore dimensions that can fully split mono- and dibranched isomers. Several MOF-based adsorbents with such property have been achieved over the past few years, including Al-bttob,^[11] CAU-10-H/Br,^[12] HIAM-302,^[13] and others.^[3,14] More recently,^[4] we have demon-

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strated that adsorbents with the capability of splitting mono- and di-branched alkane isomers show notably higher efficiency in the separation of naphtha than those showing thermodynamic separation. In addition, adsorption capacities toward linear and monobranched alkanes directly decide the separation efficiency of the adsorbents. We note that the aforementioned adsorbents generally suffer from relatively low porosity which leads to their limited adsorption capacity, although suitable pore dimensions endow them with satisfactory selectivity. Thus, the current challenge remains as the seeking of adsorbents that feature both optimal pore dimensions and high porosity to fully split mono- and dibranched alkanes with high capacity. This seems self-contradictory as generally there is a trade-off between adsorption selectivity and capacity of many previously investigated MOFs. However, such a trade-off can be effectively lifted by utilizing adsorbents that have a suitable pore aperture as well as a high porosity, which has been experimentally demonstrated in this work (Scheme 1).

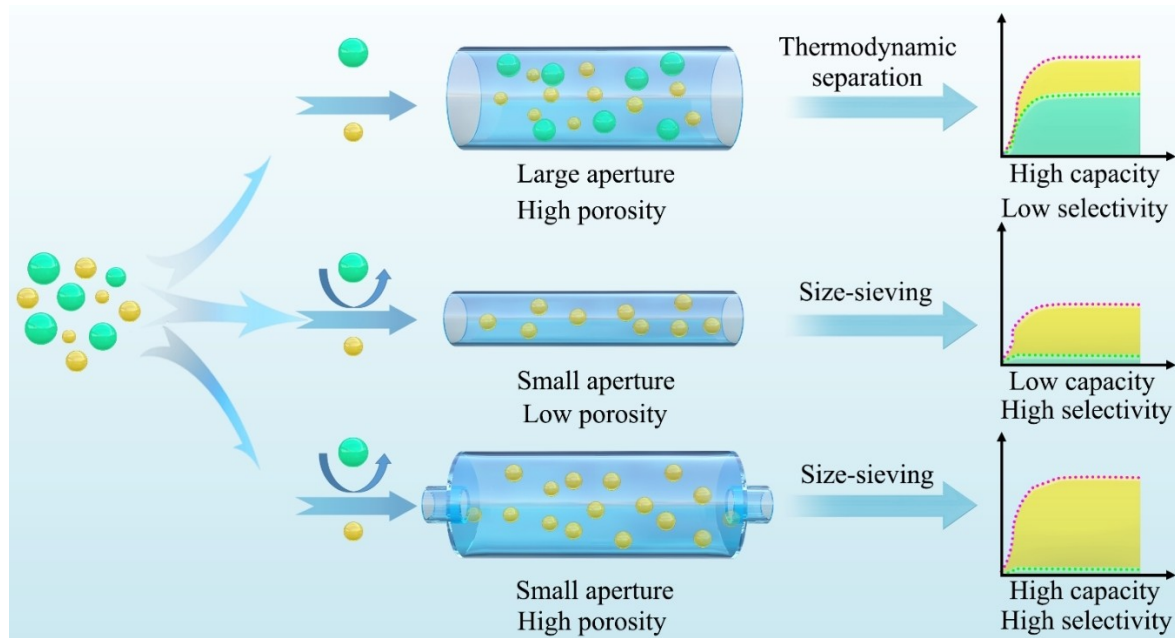
Here we report the efficient splitting of mono- and dibranched C_6 alkane isomers by using a microporous MOF, Zn-tcpt, with excellent thermal and chemical stability. Due to its optimal pore aperture, Zn-tcpt exhibits complete exclusion of dibranched alkanes from its linear and mono-branched isomers. More importantly, its adsorption capacities toward linear and monobranched alkanes are notably higher than those of the previously reported splitters for alkane isomers. Ab initio calculations have confirmed the separation of alkane isomers by Zn-tcpt is a result of selective size-exclusion.

Rectangular-shaped crystals of Zn-tcpt were obtained via solvothermal reactions of $Zn(NO_3)_2 \cdot 6H_2O$ and H_3tcpt in a mixed solvent of DMA/CAN/water with the addition of

HBf_4 at $90^\circ C$ for 2 days (Figure S1). Single-crystal X-ray diffraction analysis revealed that Zn-tcpt crystallizes in hexagonal crystal system with a space group of $P6_3/m$ (Table S1).^[15] A binuclear zinc cluster was formed through coordination with three carboxylates, and the clusters are bridged by hydroxyl groups to form a one-dimensional (1D) chain (Figure 1a and Figure S2). The 1D chains are further interconnected through $tcpt^{3-}$ linkers, forming a 3D **hms**-type network with large hexagonal channels along c axis (Figure 1b). Two identical nets permeate each other forming the resulting doubly interpenetrating structure (Figure 1c). The framework interpenetration results in pore partition of the large hexagonal channels into smaller quadrilateral channels (Figure 1d–e).

Purity of the bulk phase of Zn-tcpt was confirmed by powder X-ray diffraction (PXRD) analysis, where the pattern of the as-synthesized sample matched well with the theoretical one (Figure S3). Thermogravimetric analysis (TGA) of Zn-tcpt displayed a long plateau up to $400^\circ C$, indicating its structural robustness (Figure S4). It should be noted that Zn-tcpt possesses excellent stability. The structure was well-retained after being heated at $180^\circ C$ in open air, exposed to 90 % humidity, or immersed in various organic solvents or hot water for 1 week (Figures S5–S6). Nitrogen adsorption and desorption isotherms of Zn-tcpt at 77 K showed a typical type I profile with saturated uptake of $278\text{ cm}^3\text{ g}^{-1}$, yielding a BET surface area of $1135\text{ m}^2\text{ g}^{-1}$ and a pore volume of $0.43\text{ m}^3\text{ g}^{-1}$ (Figure S7). Its pore size distribution curve centers at $\approx 4.9\text{ \AA}$, consistent with the value calculated by Zeo++ from the crystal structure (Figure S8).

The robust framework, suitable pore dimensions, and high porosity of Zn-tcpt prompted us to evaluate its adsorption and separation toward alkane isomers. Single-



Scheme 1. Schematic representation of the strategy of using adsorbents with small pore size and large porosity for high-efficiency size-exclusion separation.

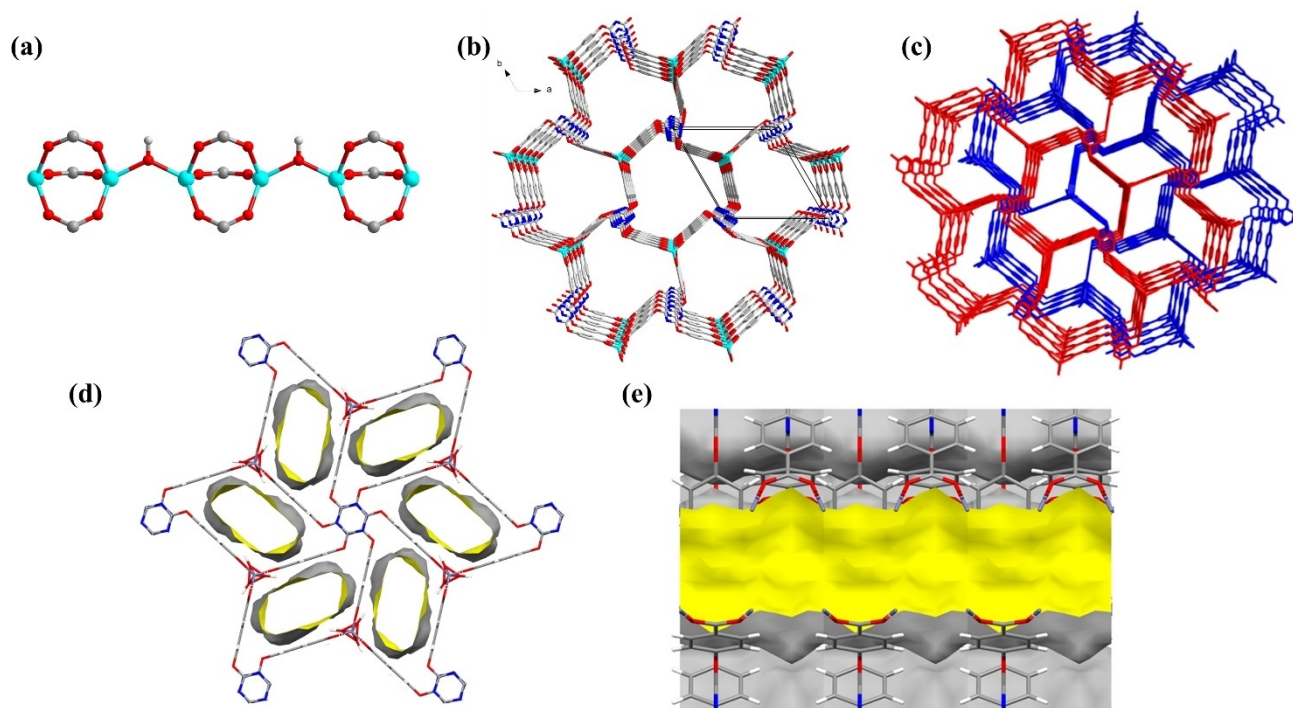


Figure 1. Crystal structure of Zn-tcpt. a) 1D building unit. b) Single network. c) Doubly interpenetrated framework. d) 1D channels. e) Simulated channel shape and dimensions. Color scheme: Zn: cyan, O: red, N: blue, H: light grey. The simulation of the channels and the pore surface was performed by Mercury software with a probe radius of 1 Å.

component adsorption isotherms of nHEX, 3MP and 22DMB were collected at 303 K. The results show that Zn-tcpt completely excludes 22DMB. However, it takes up substantial amounts of nHEX and 3MP, with uptakes of 280 and 184 mg g^{-1} , respectively (Figure 2a and Figure S9). The adsorption capacities of nHEX and 3MP are notably higher than previously reported adsorbents that can split mono-branched and dibranched alkanes, including ZSM-5, Co-FA, Al-bttotb, CAU-10-H/Br, $\text{Ca}(\text{H}_2\text{tcpb})$, and HIAM-302 (Figure 2d). This is significant as improving the adsorption capacity of adsorbents showing selective molecular exclusion is challenging but of high importance in industrial applications. In addition, the uptake ratios of nHEX/22DMB and 3MP/22DMB are 43.3 and 28.5, respectively, which are also markedly higher than that of other adsorbents (Figure 2c). This should be attributed to the high adsorption capacities of nHEX and 3MP, as well as the essentially no uptake of 22DMB. Apparently, optimal pore dimensions, as well as high porosity of Zn-tcpt should account for its excellent separation selectivity and high adsorption capacity. It should be noted that the BET surface area of Zn-tcpt is notably higher than those of the other similar adsorbents (Table S2). Three successive runs of nHEX adsorption by Zn-tcpt at 303 K revealed the compound has good recyclability (Figure S10).

To further evaluate the separation ability of Zn-tcpt for C_6 alkane isomers, column breakthrough experiments with an equimolar mixture of nHEX, 3MP, and 22DMB were conducted. The experimental results show that the material

can well separate the mixture of C_6 alkane isomers into individual components (Figure 2b). 22DMB with a high RON value eluted out from the column at the beginning of the process without any retention, confirming the complete exclusion of 22DMB by Zn-tcpt. In comparison, 3MP was retained in the column for a substantially longer time of 66 min g^{-1} , and nHEX didn't break out until the 128th min g^{-1} . These observations are consistent with the single-component adsorption results, affirming that Zn-tcpt is capable of splitting alkane isomers of different degrees of branching. Real-time RON indicated that the value of the initial eluent was more than 90, well meeting the requirement for gasoline blending components.^[10]

Ab initio calculations were performed to evaluate the separation mechanism of Zn-tcpt for hexane isomers. To investigate the molecular diffusion inside the pore, we carried out transition-state searches with the climbing-image nudged elastic band (cNEB) method.^[16,17] We found very similar diffusion barrier profiles for both nHEX and 3MP, with a slightly higher barrier for the latter (Figure 3). In comparison, the diffusion of 22DMB inside the MOF pore was completely suppressed due to the energetically unfavorable binding of 22DMB. These results are in agreement with the experimental observations that the adsorption amount of 22DMB by Zn-tcpt is negligible while nHEX and 3MP can diffuse into the channel freely. In addition, at the most favorable site (Figures S11, S12), we observed the strongest binding of nHEX with a binding energy of 1.00 eV, notably higher than that for 3MP (0.70 eV). This could explain the

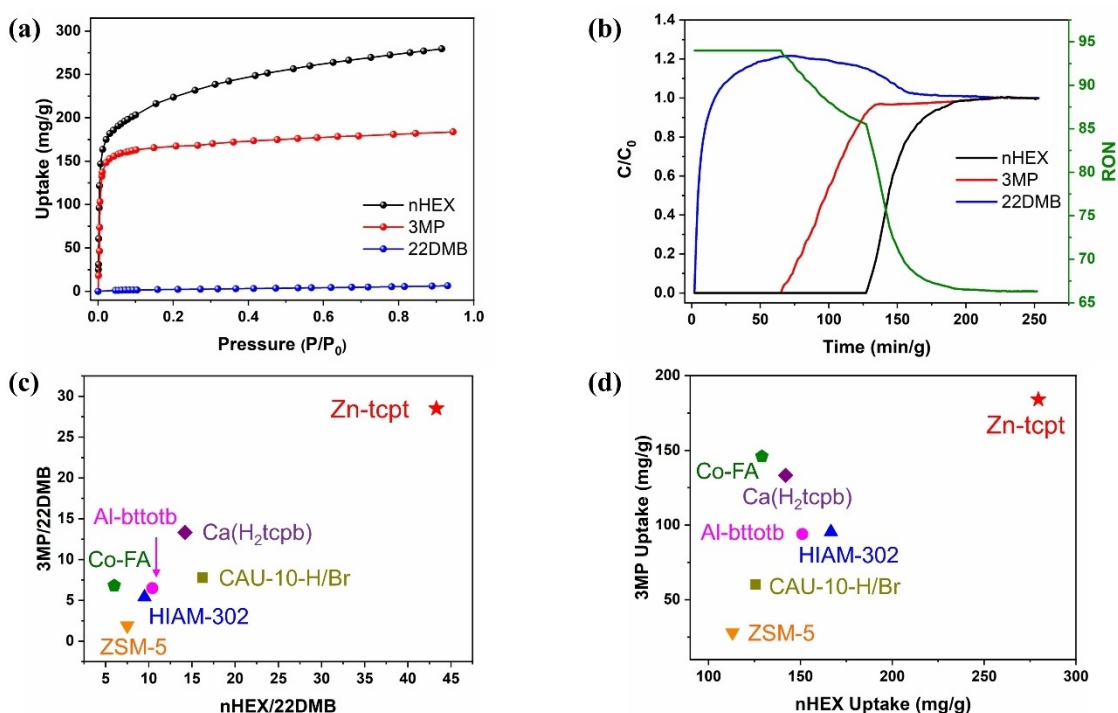


Figure 2. a) Single-component adsorption isotherms of hexane isomers at 303 K. b) Column breakthrough curve of an equimolar ternary mixture of hexane isomers. c) Uptake ratios of 3MP/22DMB and nHEX/22DMB for selected adsorbents that show size-exclusion for mono- and dibranched alkanes. d) Uptake of 3MP and nHEX of selected adsorbents capable of splitting mono- and dibranched alkane isomers. Data were collected at 303 K except for Ca(H₂tcpb) for which data were collected at 333 K.

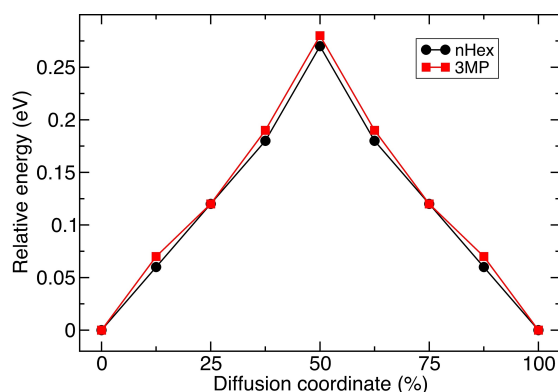


Figure 3. Energy barrier for nHEX and 3MP to diffuse into the channel of Zn-tcpt.

experimentally observed higher adsorption capacity for nHEX than 3MP.

Achieving high-efficiency separation of alkane isomers remains a great challenge in petrochemical industry. In this work we demonstrate the efficient splitting of linear/monobranched and dibranched alkanes by a microporous Zn-based MOF. Due to its large specific surface area and optimal pore aperture, Zn-tcpt exhibits record-high adsorption capacities and separation ratios among all adsorbents showing full splitting of alkane isomers. Multicomponent column breakthrough measurements confirmed its separation capability. The underlying separation mechanism was

further confirmed by computational calculations. Overall, this study presents a new benchmark adsorbent for the separation of alkane isomers as well as some clues for designing porous structures for high-efficiency separations.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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