

A Robust Ca-Based Microporous Metal–Organic Framework for Thermodynamic Separation of Hexane Isomers

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ABSTRACT: Adsorptive separation of alkane isomers, especially the efficient separation of mono- and dibranched alkanes, remains challenging in the petrochemical industry. We report here the discrimination of alkane isomers through a thermodynamically driven mechanism by a highly stable calcium-based metal–organic framework. This newly developed 3D structure is built on a tetracarboxylate linker, featuring 1D channels with optimal pore dimensions to discriminate alkane isomers.

The manufacture of widely demanded commodities such as polymers, plastics, and gasoline relies heavily on the

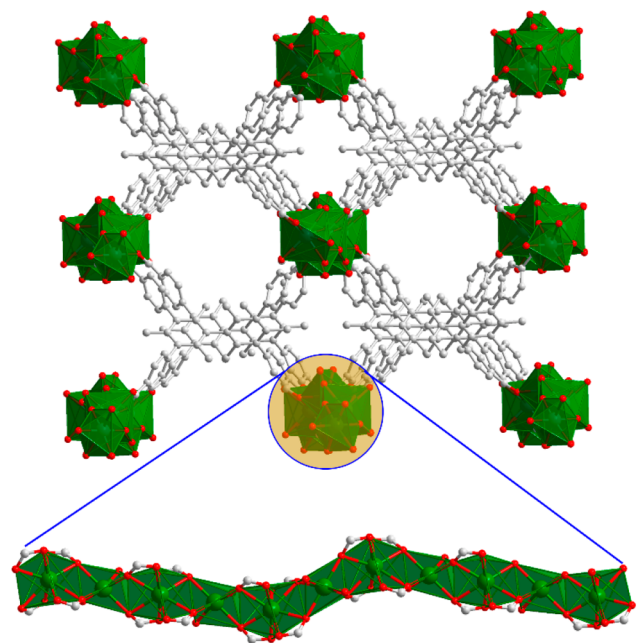


Figure 1. 3D crystal structure of HIAM-202 showing open channels and the inorganic building units of the 1D chain. Color scheme: Ca: green polyhedra, O: red, C: gray. Hydrogen atoms and coordinated terminal solvents are omitted for clarity.

separation of hydrocarbons. In petrochemical industry, separation of alkane isomers is of particular significance, as it produces feed for ethylene production by steam cracking as well as gasoline blends with a high research octane number (RON).¹ The current technology of separating alkane isomers as a function of different degrees of branching relies on heat-driven distillations, which are undoubtedly energy and capital intensive.² Adsorptive separation by porous solids, which could potentially lower the energy input and suppress carbon

emission, has been applied in industrial scale for the separation of alkane isomers using zeolite 5A as the adsorbent.³ Zeolite 5A adsorbs normal alkanes only and fully excludes all branched isomers as a result of its restricted pore aperture.⁴ However, the adsorption capacity of zeolite 5A is relatively low, limiting its separation efficiency. Moreover, it is incapable of splitting monobranched and dibranched alkanes, which is much needed to produce sufficient ethylene feed as well as gasoline blends with high RON.

Metal–organic frameworks (MOFs) are particularly promising to address challenging separations thanks to their structural diversity and highly tunable pore dimensions.^{5–12} A number of MOFs have been evaluated for the separation of alkane isomers, and some of them outperform traditional adsorbents such as zeolites. Long et al. reported the thermodynamic separation of hexane isomers by $\text{Fe}_2(\text{BDP})_3$ featuring triangular channels.¹³ More recently, Li et al. developed a series of MOFs, including Zr-bptc,¹⁴ Al-bttoh,¹⁵ Co-FA,¹⁶ and so on, that can either split linear and branched alkanes or separate linear/monobranched and dibranched alkane isomers. However, adsorbents that can separate monobranched and dibranched alkanes with high adsorption capacity are still rare and much needed. In this work, we report the thermodynamic separation of hexane isomers, in particular monobranched and dibranched isomers, by a new microporous calcium-based MOF with high uptake capacity.

Calcium-based MOFs (Ca-MOFs) feature certain advantages for adsorptive separation in light of their gravimetric benefits as well as framework robustness. However, it remains a challenge to construct permanently porous Ca-MOFs, as they tend to form nonporous coordination polymers with 1D or 2D networks (Table S1).¹⁷ The MOF compound we report in this

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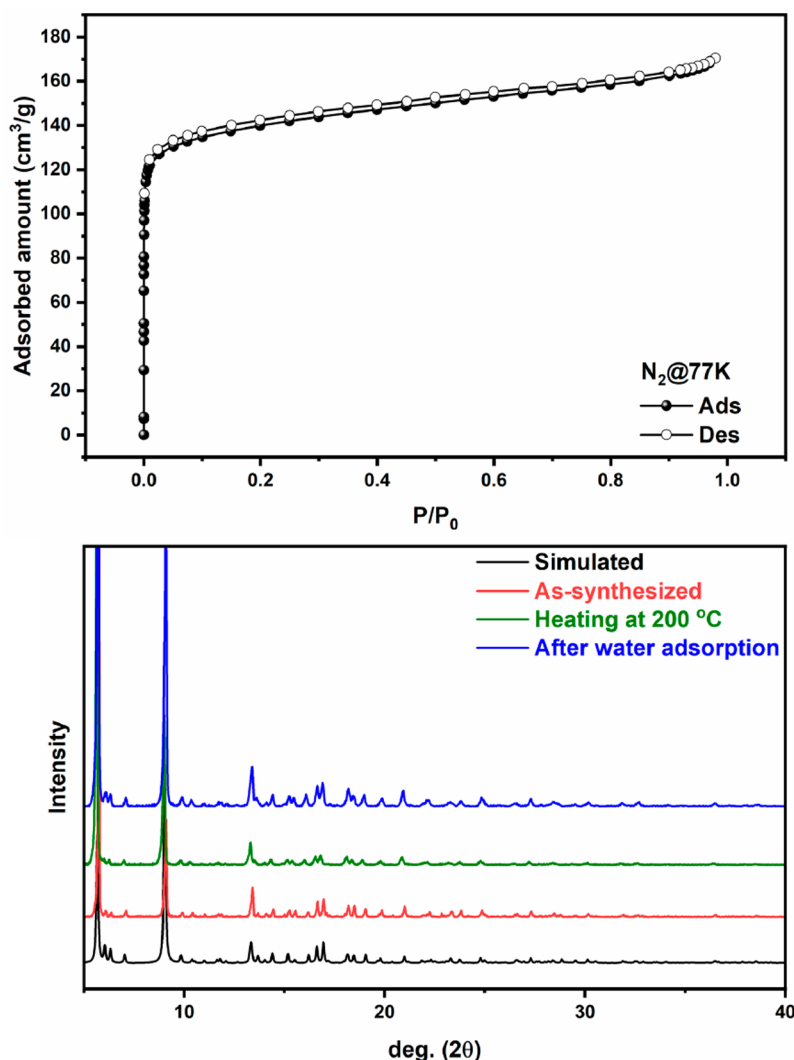


Figure 2. Nitrogen adsorption isotherm 77 K (top) and PXRD patterns (bottom) of HIAM-202.

work, Ca_2L (denoted as HIAM-202, HIAM stands for Hoffmann Institute of Advanced Materials), is built on a methyl functionalized tetracarboxylate linker H_4L (Figure S1). HIAM-202 was solvothermally prepared with CaCl_2 and H_4L in ethanol (95%) at 150 °C for 2 days, and block shaped colorless crystals were obtained (Figure S2, see Supporting Information for synthesis details). The structure of HIAM-202 was determined by single-crystal X-ray diffraction analysis, which features a space group of $I2$ in the triclinic crystal system (Table S2). There are four independent calcium(II) centers in its crystal structure (Figure S3). $\text{Ca}1$ and $\text{Ca}4$ are eight-coordinated to four carboxylates from four different organic linkers. $\text{Ca}2$ and $\text{Ca}3$ are octahedrally connected to four carboxylates from organic linkers, and the remaining two sites are occupied by terminal solvent molecules (water or ethanol). The one-dimensional (1D) arrays of calcium centers are further interconnected through the 4-c organic struts to form the resultant 3D network featuring 1D channels with a diameter of around 7 Å (Figure 1). Upon simplification, it is revealed that the overall structure adopts a *cao* topology (Figure S4).

N_2 adsorption at 77 K was performed to evaluate the porosity of HIAM-202. The adsorption isotherm features a

Type I profile, and a saturation capacity of $170 \text{ cm}^3 \text{ g}^{-1}$ was achieved, giving a BET surface area of $543 \text{ cm}^2 \text{ g}^{-1}$ and a pore volume of $0.26 \text{ cm}^3 \text{ g}^{-1}$ (Figures 2 and S5). The pore volume is consistent with the theoretical value ($0.28 \text{ cm}^3 \text{ g}^{-1}$) calculated by Materials Studio by using a probe molecule. The surface area of HIAM-202 is comparable to Ca-MOFs with the highest porosity such as Ca-BTB¹⁸ and HIAM-201¹⁹ (Table S1). Pore size distribution analysis revealed the pore size of HIAM-202 is around 6–7 Å, consistent with its crystal structure (Figure S6).

The bulk phase purity of HIAM-202 was confirmed by powder X-ray diffraction (PXRD) analysis where the diffraction pattern of the as-made sample matches well with the simulated pattern (Figure 2). Thermogravimetric analysis (TGA) displayed a ~10% weight loss before 180 °C, followed by a plateau up to 500 °C (Figure S7). The framework stability of HIAM-202 was evaluated upon various treatments. The compound remained intact after being heated in open air at 180–200 °C (Figures 2 and S8), after the water adsorption experiment (Figure 2) or being treated with various organic solvents (Figure S9). In addition, upon exposure to 90% relative humidity, no loss of crystallinity was observed (Figure S10). These results suggest that the structure of HIAM-202 is robust and resistant to moisture. Furthermore, HIAM-202 can

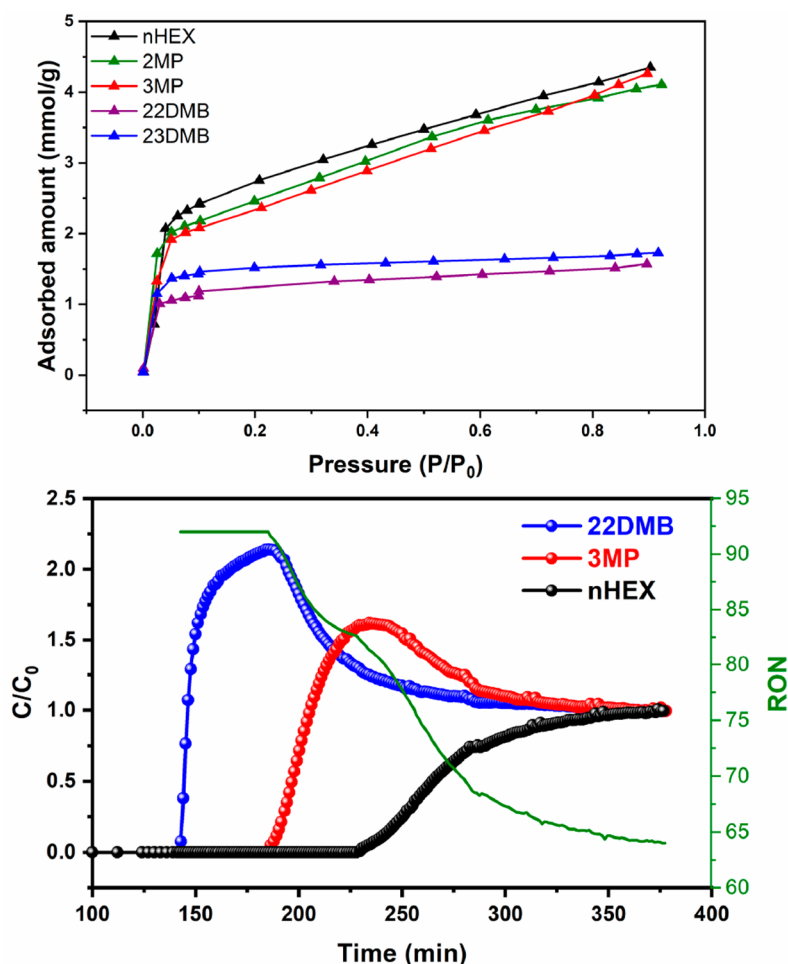


Figure 3. Single-component adsorption isotherms of all five hexane isomers at 30 °C (top) and column breakthrough curves of three-component hexane isomers at 303 K (bottom). Green curve describes the real-time RON of eluted alkanes.

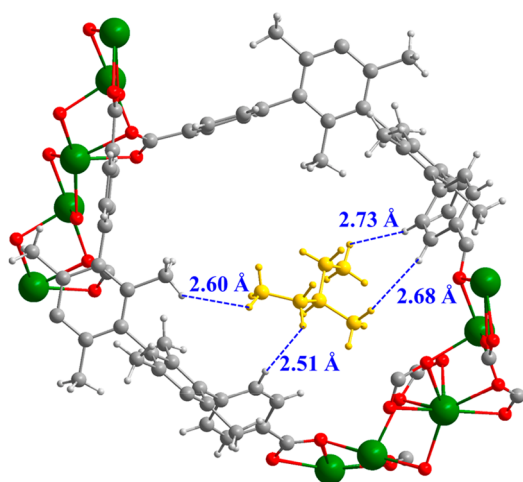


Figure 4. Single-crystal structure of 3MP loaded HIAM-202.

be easily synthesized by 10× scale in lab reactions with high crystallinity (Figure S11).

Single-component adsorption isotherms of all five hexane isomers (*n*-hexane: nHEX, 2-methylpentane: 2MP, 3-methylpentane: 3MP, 2,3-dimethylbutane: 23DMB, 2,2-dimethylbutane: 22DMB) were collected at 30 °C (Figures 3 and S12). As shown in Figure 3, HIAM-202 can accommodate all five

isomers, including the bulkiest 22DMB. This is not surprising considering its relatively large pore aperture. However, it is observed that HIAM-202 preferentially adsorbs linear and monobranched isomers compared to their dibranched isomers. Its adsorption capacities toward nHEX, 2MP, and 3MP are 4.35, 4.11, and 4.26 mmol/g, respectively. These values are much higher than those of MOFs showing selective size exclusion behavior, including Zr-bptc,¹⁴ Al-bttotb,¹⁵ Co-FA,¹⁶ of which the adsorption amounts are ~2 mmol/g. In contrast, HIAM-202 adsorbs much less dibranched hexane isomers, with uptake capacities of 1.73 and 1.57 mmol/g for 23DMB and 22DMB. The adsorption preference of HIAM-202 toward linear and monobranched alkanes over their dibranched isomers should be attributed to the fact that the former molecules may have better contacts with the 1D channels, leading to higher adsorption affinity. This has also been observed in previous reports where MOFs featuring 1D channels generally favor linear and monobranched alkanes compared to their bulkier isomers.¹³

The high adsorption capacities of HIAM-202 for hexanes as well as its distinct adsorption behaviors toward linear/monobranched and dibranched isomers indicate that it may be potentially suitable for the separation of hexane isomers, especially for the discrimination of monobranched and dibranched alkanes. We thus evaluated its separation capability by multicomponent column breakthrough measurements with

a feed of an equimolar ternary mixture of nHEX, 3MP, and 22DMB at 30 °C. It can be seen from the breakthrough curve that HIAM-202 exhibits a clear separation of hexane isomers as a function of different degrees of branching (Figure 3). 22DMB eluted out first, in accordance with the single-component adsorption results that it is the least adsorbed isomer among all three components. In contrast, 3MP exhibited a much longer retention compared to 22DMB, indicating the capability of HIAM-202 for the full separation of monobranched and dibranched isomers. The breakthrough curve suggests that the material can also separate nHEX and 3MP apart, that is, it is capable of separating the ternary mixture as a function of different degrees of branching. While the adsorption selectivity of HIAM-202 is not comparable to those showing full molecular exclusion, our experiments reveal it is capable of completely separating hexane isomers, in particular, monobranched and dibranched alkanes. It is noteworthy that HIAM-202 also holds the advantage of high adsorption capacity. PXRD analysis after breakthrough measurements confirmed that the adsorbent retained its crystallinity (Figure S13).

To further gain insights into the adsorbate–adsorbent interactions, we attempted to obtain the crystal structures of HIAM-202 loaded with each adsorbate molecules. While the attempts failed for nHEX and 22DMB, we managed to achieve the structure of 3MP loaded HIAM-202 (3MP@HIAM-202) through single-crystal X-ray diffraction analysis. It is observed that the adsorbed 3MP molecules interact with the framework (predominantly the organic linker) through van der Waals forces with the closest H...H distance of 2.51 Å (Figure 4). To simulate the interaction between the framework and different alkane isomers, density functional theory (DFT) calculations were performed. We start by optimizing the empty MOF followed by the C₆ loading at various positions to find the optimum binding site. A strong binding for nHEX and 3MP is noted with binding energies of 80 and 75 kJ/mol, respectively. Nevertheless, a moderate binding energy of 55 kJ/mol was calculated for 22DMB. To further visualize the C₆ interactions with the MOF, induced charge densities were calculated (Figure S14). A similar strong interaction is observed for nHEX and 3MP—the former being the strongest—which is in accordance with their binding energies. A relatively weaker interaction of 22DMB with the MOF is noticed. Furthermore, all the C₆ isomers interact mainly with the organic linkers via H...H bonding, consistent with single-crystal X-ray diffraction results.

Adsorptive separation of hexane isomers is challenging but industrially important. Their efficient separation has stringent requirements with respect to the pore structure of the adsorbents. We demonstrated here that a newly developed calcium-based microporous MOF, HIAM-202, with a 3D framework containing 1D channels, shows highly efficient separation of hexane isomers. In particular, it exhibits full separation of monobranched and dibranched alkane isomers with high adsorption capacities, which is much needed for industrial separation of alkane isomers.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01024>.

Detailed synthesis; crystal data and structure refinement of MOFs; PXRD and TGA results of MOFs; water adsorption isotherm; porosity characterization of MOFs; stability test, etc. (PDF)

■ Accession Codes

CCDC 2159611 and 2159614 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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