

A Microporous Metal–Organic Framework Incorporating Both Primary and Secondary Building Units for Splitting Alkane Isomers

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ABSTRACT: We demonstrate the assembly of a mononuclear metal center, a hexanuclear cluster, and a V-shaped, trapezoidal tetracarboxylate linker into a microporous metal–organic framework featuring an unprecedented 3-nodal (4,4,8)-c **lyu** topology. The compound, HIAM-302, represents the first example that incorporates both a primary building unit and a hexanuclear secondary building unit in one structure, which should be attributed to the desymmetrized geometry of the organic linker. HIAM-302 possesses optimal pore dimensions and can separate monobranched and dibranched alkanes through selective molecular sieving, which is of significant value in the petrochemical industry.

Metal–organic frameworks (MOFs) represent an intriguing class of multifunctional materials not only because they hold potential value for various applications, particularly in addressing industrial challenges related to energy and the environment, but also because they are fundamentally interesting as a result of the underlying rich chemistry.¹ On one hand, MOFs with specific features may be achieved through rational design following reticular chemistry, pioneered by Yaghi et al., as successfully practiced in different series of materials, including IRMOFs,² MOF-74 and its analogues,^{3–5} and UiO-type structures,⁶ to name a few. This is of great significance for precise control of structural features of MOFs so as to optimize their performance for a target application. On the other hand, however, MOFs are sometimes unpredictable because of the various geometry and connectivity of the metal nodes and organic linkers. This is also an important aspect in the development of MOFs, as it has led to the discovery of a number of structures with new topologies that have not been observed for other crystalline materials.^{7,8} The quest for novel MOF structures represents an essential component in MOF research for enriching the structural complexity and diversity as well as for discovering new materials for applications including separation and catalysis.

Typically, MOFs built on well-defined secondary building units (SBUs) and rigid organic linkers with high symmetry feature commonly observed, largely predictable topology. For example, 6-connected tetranuclear Zn_4O and 12-connected hexanuclear Zr_6 usually form **pcu** and **fcu** topologies with linear dicarboxylate linkers, respectively. Another well-explored family of MOFs are those built on hexanuclear M_6 SBUs ($M = Zr, RE$, etc.) and planar tetratopic organic linkers, as they exhibit tremendous structural diversity and are topologically tunable.^{9–14} The combination of Zr or rare-earth (RE) elements with square-shaped tetratopic linkers would likely form **ftw** or **shp** nets built on 12-connected hexanuclear clusters. When incorporating rectangular linkers with high aspect ratio, Zr-MOFs tend to adopt nets with reduced SBU

connectivity, such as (8,6,4)-c Zr_6 clusters, which lead to **scu**/**csq**/**sqc**, **soc**, and **lvt** topology, respectively.¹² In contrast, multinuclear RE clusters with reduced connectivity have been rarely observed, despite the introduction of a rectangular linker with high aspect ratio. This has been attributed to the variable coordination mode of RE cations which allows for multiple directionality of the coordinated linkers so as to form thermodynamically favored structures with fully connected SBUs.^{7,15}

Complementary to reticular chemistry, which tends to precisely connect the structure and functionality of compounds with regular topologies, the pursuit of non-default nets originates from the geometry mismatch of seemingly incompatible building blocks.¹⁶ Li, Zhou, and Trikalitis recently reported a series of RE-MOFs built on less connected hexanuclear clusters by the incorporation of desymmetrized, highly distorted tetrahedral linkers.^{7,15} However, these structures are still built on exclusively hexanuclear RE_6 building blocks.

In this work we report a novel microporous Y-based MOF, $Y_6(\mu_3-OH)_8(adip)_2(HCOO)_4(H_2O)_4Y_2(adip)_2 \cdot [(CH_3)_2NH_2]_4(DMF)_7(H_2O)_8$ (HIAM-302, where HIAM stands for Hoffmann Institute of Advanced Materials; $H_4adip = 5,5'$ -azanediyl-diisophthalic acid). Built on such a linker, HIAM-302 is made of an 8-connected hexanuclear $Y_6(OH)_8(COO)_2$ SBU and a mononuclear $Y(COO)_4$ primary building unit (PBU), featuring an unprecedented 3-nodal (4,4,8)-c **lyu** topology. The compound possesses 1D channels

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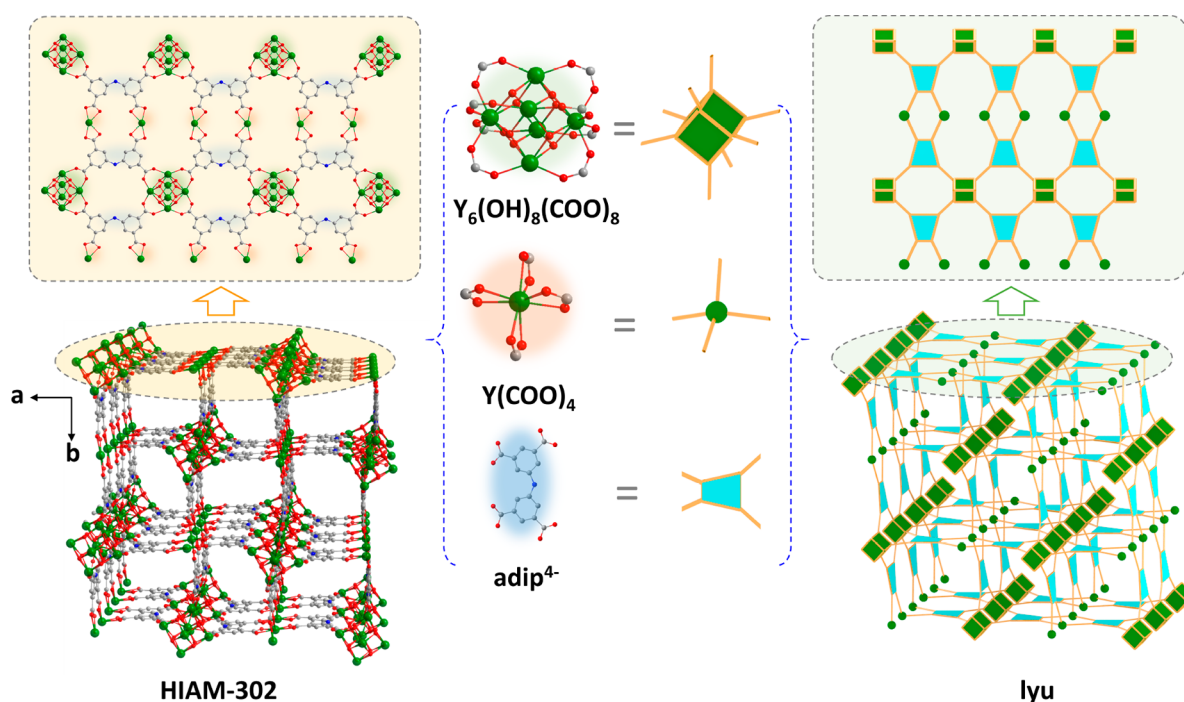


Figure 1. Crystal structure and topology of HIAM-302, and the inorganic and organic building blocks comprising the framework. Coordinated terminal solvents are omitted for clarity.

and is capable of splitting monobranched and dibranched alkane isomers.

In our previous study, we developed a series of MOFs built on Zr_6 or Y_6 and isophthalate-derived tetracarboxylates. These rigid, rectangle-shaped tetra-topic linkers generally form (4,12)-c **ftw** structures in Y-MOFs with cubic or slightly distorted cages. It was noted that with the increase of aspect ratio of the organic linkers from $bptc^{4-}$ to abt^{4-} , the cage in Y- abt^{4-} was severely distorted compared to that in Y- $bptc^{4-}$.¹³ In this context, it is not unexpected that the incorporation of the V-shaped, trapezoidal $adip^{4-}$ would lead to a Y-MOF that is not a **ftw**-type structure, and even not built on pure hexanuclear Y_6 SBUs.

HIAM-302 was solvothermally synthesized at 120 °C by reacting $Y(NO_3)_3 \cdot 9H_2O$ and H_4adip in DMF/ H_2O with the addition of 2-fluorobenzoic acid as a modulator. Single-crystal X-ray diffraction analysis of the block-shaped crystals reveals that it crystallizes in the space group $I4/m$ (Figure S1 and Table S1). The structure is built on both hexanuclear SBU $Y_6(OH)_8(COO)_8$ and mononuclear PBU $Y(COO)_4$, with a ratio of 1:2 (Figure 1). The former is 8-connected, rather than 12-connected as is commonly observed in Y-MOFs built on Y_6 clusters. The remaining four extending sites of the Y_6 core are terminated by formate. In contrast, the mononuclear Y center is fully coordinated to four carboxylates from four different $adip^{4-}$ linkers, and each of the carboxylates is coordinated to the metal center in a bidentate mode. This represents a rare example of a MOF structure incorporating both PBUs and hexanuclear SBUs and a single organic linker.¹⁷ These usual structural features should be attributed to the desymmetrized geometry of the organic linker that probably does not fit into 12-connected SBUs.

HIAM-302 possesses an 8-connected $Y_6(OH)_8(COO)_8$ SBU, a 4-connected $Y(COO)_4$ PBU, and a 4-connected organic linker, $adip^{4-}$. It is thus a 3-nodal (4,4,8)-connected network with stoichiometry of 4:2:1 ($adip^{4-}$:PBU:SBU). The

point symbol for the net is $\{4^{12} \cdot 6^4 \cdot 8^{12}\} \cdot \{4^2 \cdot 6^2 \cdot 8^2\}_4 \cdot \{4^2 \cdot 6^4\}_2$, which represents a new topology and is denoted as **lyu** here. This indicates that the quest for Y-MOFs (or analogously Zr/Hf/RE-MOFs) with novel topology may be accomplished by incorporation of organic linkers with uncommon and less symmetric geometry, such as the V-shaped, trapezoidal $adip^{4-}$ used in this work (Figure S2).

The three-dimensional (3D) crystal structure of HIAM-302 displays one-dimensional (1D) open channels along the crystallographic c axis (Figure 1). The compound retains its crystallinity upon treatment of various organic solvents or water/moisture (Figures S3–S7). This is encouraging, as one would expect that the existence of PBUs and SBUs of lower connectivity would lead to an unstable framework. No noticeable adsorption of nitrogen was observed at 77 K. In contrast, notable carbon dioxide adsorption was observed at 195 K, revealing a BET surface area of 388 m^2/g for HIAM-302 (Figures S8 and S9). The optimal pore dimension of HIAM-302 encourages us to explore its adsorption and separation of alkanes. The separation of alkanes as a function of their degree of branching is of paramount significance for upgrading the octane rating of gasoline and for optimizing feedstock for ethylene production. To date, a number of MOFs have been evaluated for the adsorptive separation of alkanes.^{18–20} However, adsorbents that can efficiently separate monobranched and dibranched alkane isomers have been rarely reported, as such a separation has stringent requirements for the pore size.²¹ Nevertheless, such adsorbents are critically needed for industrial applications.

Adsorption and separation of linear, monobranched, and dibranched hexane isomers, which have been commonly used to evaluate the separation capability of an adsorbent for alkane isomers, were carried out on HIAM-302. Single-component vapor adsorption isotherms at 30 °C revealed that the compound adsorbs a substantial amount of *n*-hexane (*n*HEX; kinetic diameter = 4.3 Å) and 3-methylpentane (3MP; kinetic

diameter = 5.5 Å), with saturated values of 165 and 94 mg/g, respectively (Figure 2). In contrast, its adsorption capacity for

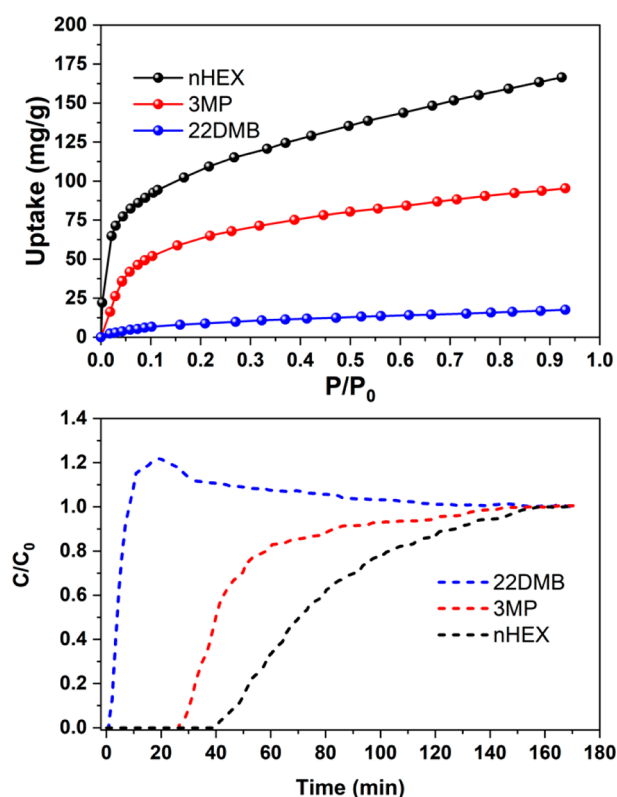


Figure 2. (Top) Single-component adsorption isotherms of hexane isomers at 298 K. (Bottom) Column breakthrough curve of an equimolar ternary mixture of hexane isomers at 298 K.

2,2-dimethylbutane (22DMB; kinetic diameter = 6.2 Å) is negligible. Adsorption kinetics indicates a similar trend: nHEX showed no noticeable diffusion restriction, and 3MP showed a slightly lower adsorption rate, while 22DMB was barely adsorbed (Figure S11). These results suggest that HIAM-302 adsorbs both linear and monobranched hexanes but fully excludes their dibranched isomer, thus acting as a molecular sieve for splitting monobranched and dibranched alkanes, which has been rarely reported.^{21–24} The separation capability of HIAM-302 was further confirmed by multicomponent column breakthrough measurements of an equimolar ternary mixture of nHEX, 3MP, and 22DMB (Figure 2). The breakthrough curve shows that 22DMB eluted out from the column at the very beginning, without any retention in the column, suggesting its complete exclusion by the adsorbent. In contrast, 3MP and nHEX were retained in the column for 25 and 38 min, respectively, before breaking out, indicating they were substantially adsorbed by HIAM-302.

To gain further insight into the selective adsorption behavior of HIAM-302, first-principles-based density functional theory (DFT) calculations—with the aid of the vdW-DF functional—were performed to study the interaction of hexane isomers with the framework and to assess their transport within the channels.^{25–30} Our cNEB diffusion-based calculations (see Supporting Information) indicate an energy barrier of only 9.29 kJ/mol for nHEX, suggesting its rapid loading into the channels of HIAM-302 without notable limitations (Figure 3). This is in good agreement with our experimental adsorption

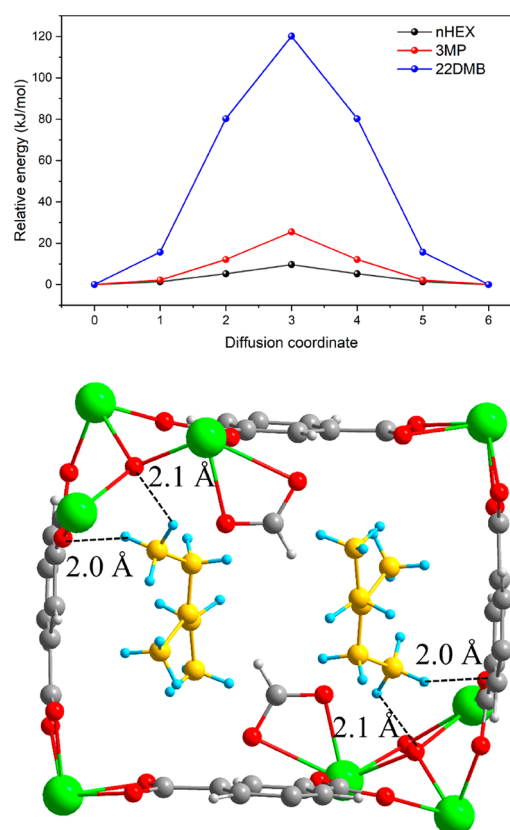


Figure 3. (Top) Energy barrier for nHex, 3MP, and 22DMB to diffuse into the channels of HIAM-302. (Bottom) Single-crystal structure of 3MP-loaded HIAM-302.

results. The energy barrier for 3MP is 24.50 kJ/mol, which can still be overcome at room temperature. This higher barrier explains the slightly lower adsorption rate of 3MP compared to nHEX. In contrast, 22DMB has an energy barrier well above 100 kJ/mol, thus prohibiting its entering into the pore, which is in good agreement with our adsorption experiments showing that 22DMB is fully excluded by the adsorbent. The adsorption affinity of nHEX and 3MP was then evaluated by binding energy calculations. At the most favorable site (Figure S13), nHEX binds to the framework with a binding energy of 91 kJ/mol, slightly higher than that of 3MP, which is 82 kJ/mol. This suggests that nHEX is slightly favored over 3MP by HIAM-302 thermodynamically.

Finally, with numerous trials, we were able to obtain the single-crystal structure of 3MP-loaded HIAM-302 (3MP@HIAM-302), which provides a direct visualization of the adsorption site of adsorbates as well as guest–framework interactions; nevertheless, the attempt to refine the nHEX-loaded structure was unsuccessful.³¹ Two 3MP molecules were identified in each channel segment of HIAM-302 (Figure 3), with one occupying a location similar to the preferred adsorption site from our *ab initio* calculations. It was noted that the adsorbed 3MP has close contacts with the Y_6 cluster, with the shortest H...O distance of 2.0 Å. This explains the relatively high binding energy of the guest molecules.

In summary, we report in this work a novel Y-MOF built on 8-connected hexanuclear SBUs, 4-connected PBUs, and 4-connected tetratopic organic linkers. The overall framework features the *Iyu* topology that has not been observed before. We reason that it is the desymmetrized linker that leads to the

coexistence of SBUs and PBUs in one MOF structure. The compound exhibits optimal micropores, showing efficient separation of branched alkane isomers. We believe this work may shed light on the quest for MOFs with non-default topology for fundamental study as well as for potential applications in adsorption, separation, and catalysis. More systematic investigation of RE/Zr-MOFs with various unusual geometries is currently ongoing.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c12068>.

Experimental details, synthesis of the MOF, PXRD data, TGA data, and adsorption data, including Figures S1–S13 and Tables S1 and S2 (PDF)

Accession Codes

CCDC 2109593 and 2109594 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.

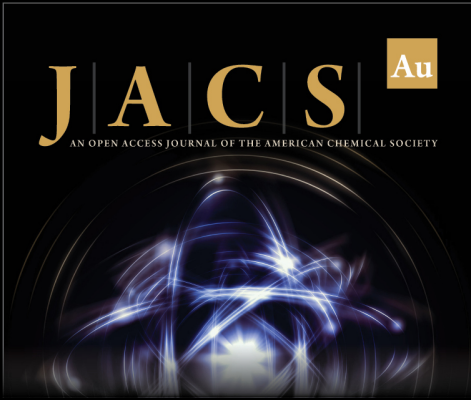
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