Communication

An Octacarboxylate-Linked Sodium Metal–Organic Framework with High Porosity

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ABSTRACT: Alkali metal-based metal–organic frameworks (MOFs) with permanent porosity are scarce because of their high tendency to coordinate with solvents such as water. However, these MOFs are lightweight and bear gravimetric benefits for gas adsorption related applications. In this study, we present the successful construction of a microporous MOF, designated as HIAM-111, built solely on sodium ions by using an octacarboxylate linker. The structure of HIAM-111 is based on 8-connected Na₄ clusters and exhibits a novel topology with an underlying 3^2 , 4^2 , 8-c net. Remarkably, HAM-111 possesses a robust and highly porous framework with a BET surface area of 1561 m²/g, significantly surpassing that of the previously reported Na-MOFs. Further investigations demonstrate that HIAM-111 is capable of separating C_2H_2/CO_2 and purifying C_2H_4 directly from $C_2H_4/C_2H_2/C_2H_6$ with high adsorption capacities. The current work may shed light on the rational design of robust and porous MOFs based on alkali metals.

M etal-organic frameworks (MOFs) are intricate structures formed by linking polytopic organic linkers with metals or metal clusters through coordination bonds.^{1,2} The number of MOF structures has surpassed 100,000 as reported by the Cambridge Structural Database (CSD). These structures are predominantly based on transition or lanthanide metals.³⁻⁵ In contrast, MOFs based on alkali metals, such as sodium, have been sparingly reported, and the development of such MOFs with permanent porosity remains a significant challenge.⁶⁻⁹ This is primarily due to the tendency of solvent molecules to occupy the coordination sites of alkali metals, resulting in a high ratio of solvent ligands to organic linkers. Consequently, this leads to the formation of coordination polymers with low dimensionality or 3D MOF structures that are delicate and susceptible to pore evacuation.¹⁰⁻¹²

To date, there have been only a few reports on Na-MOFs that can maintain their structure and permanent porosity upon the removal of guest molecules.^{6,13,14} Yaghi and colleagues successfully synthesized two air-stable Na-MOFs, namely, MOF-705 and MOF-706, by utilizing multiple carboxylate functionalities of L-aspartate.⁶ These two MOFs, built on 2D sodium secondary building units (SBUs), demonstrated air stability and permanent porosity upon evacuation with BET surface areas of 132 and 126 m²/g for MOF-705 and MOF-706, respectively. Lin et al. reported a Na-MOF, CYCU-6, employing 4,4'-sulfonyldibenzoate as the linkage, showing a BET surface area of 187.3 m²/g, setting a current record.¹³ The challenges associated with constructing Na-MOFs with extended structures and high porosities have hindered the exploration of their potential uses. However, Na-MOFs are particularly appealing for adsorption-related applications due to the abundance and low toxicity of sodium, as well as their lightweight nature and potential gravimetric benefits.^{15,16} Therefore, it is of great significance, from both a fundamental and practical standpoint, to develop highly porous Na-MOFs and investigate their potential applications in gas adsorption and separation.

In this work, we present the successful synthesis of a robust and highly porous Na-MOF, named HIAM-111, by utilizing the multiple functionalities of an octacarboxylate linker, 4',4''',4'''',4''''''-(Ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-3,5-dicarboxylic acid)) (H₈ETTBPDC). HIAM-111 isstable in various organic solvents and maintains its structuralintegrity upon complete evacuation. Notably, it shows anextraordinarily large BET surface area of 1561 m²/g. Wedemonstrate that HIAM-111 displays a notable preference foradsorbing C₂H₂ and C₂H₆ over C₂H₄, enabling the productionof pure C₂H₄ in a single step from C₂H₂/C₂H₆/C₂H₄ mixtures.Furthermore, we validate the gravimetric advantage of HIAM-111, which leads to relatively high adsorption capacitiescompared to previously reported adsorbents.

Light yellow, block-shaped crystals of HIAM-111 were obtained by solvothermal reaction of NaCl and H₈ETTBPDC in DMF/H₂O at 120 °C for 3 days. (Figure S1, see Supporting Information for synthesis details). Single-crystal X-ray diffraction analysis revealed that HIAM-111 crystallizes in the orthorhombic crystal system with a space group of *Pban* (Table S1). The crystal structure of HIAM-111 consists of 8-connected tetranuclear Na₄(COO)₈ SBUs linked to eight carboxylates from the organic linkers, with the remaining

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Figure 1. Crystal structure of HIAM-111. The tetranuclear Na₄ inorganic building unit, organic linker, and view of the crystal structure are from different directions. Coordinated terminal solvents are omitted for clarity.



Figure 2. (a) N_2 adsorption-desorption isotherms at 77 K of HIAM-111 and its calculated pore size distribution (Insert). (b) Five consecutive measurements of N_2 adsorption-desorption isotherms at 77 K in HIAM-111. (c) Comparison of the BET surface area of HIAM-111 to those of the reported Na-MOFs.

coordination sites occupied by terminal H₂O molecules (Figure S2). The octacarboxylate linker's eight carboxylate groups are connected to Na4 clusters in either monodentate or bidentate modes (Figure S3). The inorganic clusters are interconnected into ladder-shaped 1D arrays, which further propagate to form a 3D framework with 1D channels along the crystallographic *b-axis* (Figure 1). It is noteworthy that MOFs built on octacarboxylate linkers are relatively rare.^{17,18} The overall structure represents a new topology, regardless of the analysis methods.¹⁹ Following the guidelines with ToposPro,^{20,21} in a single node cluster description, the structure can be simplified as 6,7,8-c trinodal net (named hia3), with 6-c and 8-c representing the two distinct organic ligands and 7-c for the Na_4 cluster (Figure S4). When using the all node cluster description, the framework of HIAM-111 can be depicted as a 3⁴,8-c (*hia*2) or 3²,4²,8-c (*hia*1) 5-nodal network (Figure S5). It is worth noting that the structure of HIAM-111 is a single framework without interpenetration with an accessible void space of 45.9% as calculated by PLATON.

The powder X-ray diffraction (PXRD) patterns of the assynthesized HIAM-111 matched well with the simulated patterns, indicating its high crystallinity and phase purity (Figure S6). Thermogravimetric analysis (TGA) displayed a continuous weight loss without a distinct plateau (Figure S7). It is worth noting that alkali metal-based MOFs are commonly sensitive to pore evacuation, with their structures being prone to collapse upon removal of organic solvents from the pores and/or coordinated terminal ligands. However, HIAM-111 stands as a rare example of Na-MOFs that fully retain their crystal structure upon complete activation. Successful solventexchange of HIAM-111 with acetone resulted in a TG curve showing weight loss before 150 °C, followed by a plateau at ~400 °C. Subsequent pore evacuation at 150 °C under dynamic vacuum yielded the activated HIAM-111, with its PXRD pattern remaining unchanged compared to that of the as-synthesized sample, indicating the complete preservation of the structure during thermal activation. Further tests demonstrated the chemical stability of HIAM-111 in common organic solvents, including acetonitrile, n-hexane, ethanol, tetrahydrofuran, and acetone, as the PXRD patterns of the sample after treatment were similar to that of the assynthesized one (Figure S8). Moreover, PXRD measurements

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Figure 3. (a) Adsorption–desorption isotherm of C_2H_2 , C_2H_4 , C_2H_6 , and CO_2 at 298 K on HIAM-111. (b) IAST selectivity of equimolar C_2H_2/C_2H_4 , C_2H_4 , C_2H_6/C_2H_4 and C_2H_2/CO_2 mixtures at 298 K. (c) Comparison of the C_2H_6/C_2H_4 uptake ratio and C_2H_6 adsorption capacity at 298 K for representative adsorbents studied for one-step C_2H_4 purification. (d) Isosteric heat of adsorption (Q_{st}) of CO_2 , C_2H_2 , C_2H_4 , and C_2H_6 on HIAM-111. (e) Breakthrough curve of equimolar $C_2H_2/C_2H_4/C_2H_6$ ternary mixtures at 298 K. (f) Breakthrough curve of the equimolar C_2H_2/CO_2 binary mixtures at 298 K.

confirmed the maintenance of the crystal structure of HIAM-111 up to 200 °C and upon exposure to air, highlighting its high thermal robustness and moisture stability (Figures S9– S10). UV–vis and photoluminescence spectra of HIAM-111 and the organic linker were collected, taking into account the well-studied emissive tetraphenylethylene core (Figure S11). The emission peak of HIAM-111 under excitation of 365 nm was observed at 500 nm, slightly blue-shifted compared to that of the linker, which appeared at 511 nm.

The robust structure of HIAM-111 upon pore evacuation prompted us to assess its permanent porosity. N₂ adsorptiondesorption on HIAM-111 at 77 K displayed a typical Type I profile, with a saturated uptake of 439.6 cm^3/g (Figure 2a). The calculated Brunauer-Emmet-Teller (BET) surface area and pore volume of HIAM-111 were determined to be 1561 m^2/g and 0.56 cm³/g, respectively. The Horvath-Kawazoe pore size distribution curve showed a peak centered at 6.6 Å (inset, Figure 2a). Importantly, the surface area of HIAM-111 was found to be significantly higher than those of previously reported Na-MOFs or alkali metal-based MOFs (Figure 2c).^{6,13,14} This represents an important advancement as constructing alkali metal-based MOFs with high porosity has been a challenging task. We demonstrate that the use of organic linkers with multiple carboxylates could be an effective way to address the challenge. Furthermore, three consecutive adsorption-desorption cycles of N2 at 77 K on HIAM-111 revealed no notable loss of porosity (Figure 2b), indicating its high durability.

We attempted to investigate the potential applications of HIAM-111 in gas adsorption and separation, particularly in the challenging separation of C_2 hydrocarbons in industrial

settings.²²⁻²⁴ Searching for adsorbents that can preferentially adsorb C_2H_6 and C_2H_2 over C_2H_4 affording one-step purification of C_2H_4 from $C_2H_2/C_2H_4/C_2H_6$ mixtures has been an important task and a significant research focus in recent years.²²⁻²⁸ Single-component adsorption isotherms of HIAM-111 for C₂H₂, C₂H₄, and C₂H₆ were collected at 278 and 298 K up to 1 bar (Figure 3a and Figure S13). Notably, at 1 bar and 298 K, the adsorption capacities of HIAM-111 for C_2H_6 and C_2H_2 were 112.17 and 108.88 cm³/g, respectively, noticeably higher than that of C_2H_4 (88.79 cm³/g) under identical conditions. The results indicated the favored adsorption of C₂H₆ and C₂H₂ over C₂H₄ by HIAM-111. It is noteworthy that the adsorption capacities of C_2H_6 and $C_2H_6/$ C₂H₄ uptake selectivity are among the best performing adsorbents for C_2 ternary separation (Figure 3c). CO_2 adsorption on HIAM-111 was also explored as it commonly exits as an impurity along with C_2H_2 . The adsorption capacity of CO₂ at 298 K and 1 bar was 57.22 cm³/g, which was substantially lower than that of C2H2. To quantitatively evaluate the selective adsorption by HIAM-111, ideal adsorbed solution theory (IAST) was applied to calculate the selectivities of C_2H_2/C_2H_4 , C_2H_6/C_2H_4 , and C_2H_2/CO_2 . The calculated selectivities of C2H2/C2H4, C2H6/C2H4, and C_2H_2/CO_2 for equimolar binary mixtures at 298 K and 1 bar were 1.62, 1.23, and 2.42, respectively (Figure 3b, Table S2). The isosteric heats of adsorption (Q_{st}) of C_2H_2 , C_2H_4 , C_2H_6 , CO₂ on HIAM-111 were determined based on the singlecomponent adsorption isotherms at 278 and 298 K (Figure S14).^{23,25,29} The initial Q_{st} followed the sequence of C_2H_2 $(43.8 \text{ kJ/mol}) > C_2H_6 (28.3 \text{ kJ/mol}) > C_2H_4 (25.5 \text{ kJ/mol}) >$ CO₂ (12.4 kJ/mol), in accordance with the single component

adsorption results, confirming that HIAM-111 interacts more strongly to C_2H_2 and C_2H_6 over C_2H_4 (Figure 3d). Ab initio calculations were performed to understand the adsorbate– adsorbent interaction (see Supporting Information for details, Figures S15–S16). It was observed that C_2H_2 binds most strongly with HIAM-111 with a binding energy of 51 kJ/mol. The calculated binding energies for C_2H_6 and C_2H_4 are 39.3 and 34.3 kJ/mol, respectively. The binding energy sequence of $C_2H_2 > C_2H_6 > C_2H_4$ is in accordance with the experimental results.

To further evaluate the feasibility of using HIAM-111 for the separation of C₂ ternary mixtures and C₂H₂/CO₂, multicomponent dynamic breakthrough tests were carried out at 298 K. As depicted in Figure 3e, in the case of an equimolar C_2 ternary mixture, C2H4 was eluted from the column first, followed by C_2H_6 and C_2H_2 with a notably longer retention time. This allowed for the direct production of highly pure (99.95+%) C_2H_4 in a single step. To simulate the gas compositions in practical applications, a breakthrough test of $C_2H_4/C_2H_6/C_2H_2$ (90/9/1, v/v/v) was also performed. The results demonstrated that HIAM-111 retained its capability of separating C_2H_4 from the ternary mixture (Figure S17). Importantly, the adsorbent can be fully regenerated through helium purging at room temperature, and three consecutive breakthrough measurements suggested no notable loss of separation capability of HIAM-111 (Figure S18).³⁰ The ability of HIAM-111 to separate C_2H_2/CO_2 was also confirmed through breakthrough experiments on an equimolar binary mixture (Figure 3f). It was observed that, as anticipated, CO_2 eluted first at the 54th minute, while C₂H₂ did not break out until the 69.6th minute, indicating a clean separation between the two gases.

In conclusion, by employing an octacarboxylate organic linker, we have successfully achieved a Na-MOF, HIAM-111, built on 8-connected tetranuclear Na4 SBU featuring new, complex underlying nets named hia1, hia2, hia3. The newly developed Na-MOF is structurally robust, and resistant to pore evacuation. Its BET surface area of 1561 m^2/g significantly surpasses all previously reported sodium based MOFs. HIAM-111 demonstrates the capability of one-step separation of $C_2H_2/C_2H_4/C_2H_6$ through the favored adsorption of C_2H_2 and C₂H₆ over C₂H₄, leading to direct production of polymergrade C2H4 in one step in multicomponent column breakthrough tests. Gravimetric benefits originating from the relatively low density of Na-MOFs have been validated for HIAM-111, and its C_2H_6 adsorption capacity is among the highest for adsorbents studied for C2 ternary separation. Notably, HIAM-111 can be readily regenerated through room temperature gas purging and exhibits excellent cyclic performance. Our study may provide a new direction in designing robust and highly porous alkali metal-based MOFs for adsorption related applications.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c11260.

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

Accession Codes

CCDC 2282068 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge

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Notes

The authors declare no competing financial interest.

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