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Reticular Access to Highly Porous acs-MOFs with Rigid Trigonal Prismatic Linkers for Water Sorption

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Supporting Information

ABSTRACT: Metal−organic frameworks (MOFs) based on edge-transitive 6-c **acs** nets are well-developed and can be synthesized from trinuclear metal clusters and ditopic ligands, i.e., MOF-235 and MIL-88. The rational design of noncatenated **acs**-MOFs by symmetry-matching between trigonal prismatic organic ligands and trinuclear clusters, however, remains a great challenge. Herein, we report a series of **acs**-MOFs (NU-1500) based on trivalent trinuclear metal (Fe^{3+}, Cr^{3+}, and Sc^{3+}) clusters and a rigid trigonal prismatic ligand courtesy of reticular chemistry. The highly porous and hydrolytically stable NU-1500-Cr can be activated directly from water and displays an impressive water vapor uptake with small hysteresis.

Metal−organic frameworks[1−4] (MOFs) are a class of programmable porous crystalline materials with inorganic nodes linked by organic ligands. On account of their diverse and tunable pore sizes[5−8] and ultrahigh surface areas,[9] MOFs have received an incredible amount of attention from researchers during the past two decades. MOFs have been studied for a wide range of environmental and energy-related applications including, but not limited to, gas storage and separation,[10−12] water capture,[13−17] heterogeneous catalysis,[18,19] and drug delivery.[20,21]

Water vapor capture has emerged as an attractive application for MOFs as a result of the recent discoveries of highly hydrolytically stable MOFs and excellent water sorption performance.[13,14,16,22−25] The high water capture capacity and good recyclability of MOFs make them highly desirable for water vapor sorption-based applications, including water harvesting from low humidity air,[14,26] natural gas dehydration,[15] indoor humidity control,[16,25] and adsorption cooling systems.[27−31] In general, water sorption related applications require a MOF sorbent to meet the following prerequisites: (i) high hydrolytic stability for recycling performance; (ii) reasonably large porosity and surface area for high water vapor uptake; (iii) relatively mild regeneration conditions; (iv) an isotherm with a steep uptake (pore filling or condensation), depending on a specific application (*vide supra*); (v) high deliverable capacity. Nevertheless, it is still demanding to develop highly efficient MOF sorbents that are of interest as alternatives to the current traditional porous silica gels or zeolites suffering from low maximum capacity and high regeneration temperatures.[22]

Reticular chemistry[16,32−36] is a powerful tool for the rational design and synthesis of MOFs with various functionalities and pore architectures. Edge-transitive nets with one type of edge are believed to be the most probable and accessible topologies that commonly exist in MOF structures.[37] The 6-connected (6-c) edge-transitive nets such as **acs** (Figure 1; trigonal prism; e.g., MOF-235[38] and MIL-88[41]), **pcu** (octahedron; e.g., MOF-5[40]), **nia** (trigonal prism and octahedron; e.g., MODF-1,[41] JUC-101,[42] and UTSA-62[43]), and **hxg** (hexagon; e.g., **pbz**-MOF-1[34]) are well established in MOF chemistry. For example, the combination of metal trinuclear clusters (trigonal prismatic nodes) and ditopic ligands can form a 6-c **acs**-MOF.[38,39] In principle, **acs**-MOFs with uniform hexagonal channels can also be synthesized using suitable trigonal prismatic hexatopic organic ligands in the presence of trigonal prismatic trinuclear metal nodes to prohibit the catenation of the frameworks. Noncatenated **acs**-MOFs based on 6-c trigonal prismatic organic ligands, however, have yet to be constructed possibly because of the following limitations: (i) the rigid 6-c trigonal prismatic organic building block is very rare;[42] (ii) the mismatch between hexacarboxylate organic linkers with suitable sizes and inorganic metal trimers could rule out the catenation.[44]

Herein, we report the design and synthesis of a series of 6-c noncatenated M(III)-**acs**-MOFs (NU-1500-M; M(III) = Fe^{3+}, Cr^{3+}, and Sc^{3+}) from a preselected rigid trigonal prismatic triptycene-based organic ligand. Single-crystal X-ray diffraction (SCXRD) studies of NU-1500 allowed us to identify the structures of the MOFs with a 6-c **acs** topology and a pore size of about 1.4 nm. NU-1500 are rigid and microporous with high apparent Brunauer−Emmett−Teller (BET) surface areas ranging from 3580 to 4280 m^2 g^{-1} obtained by thermal

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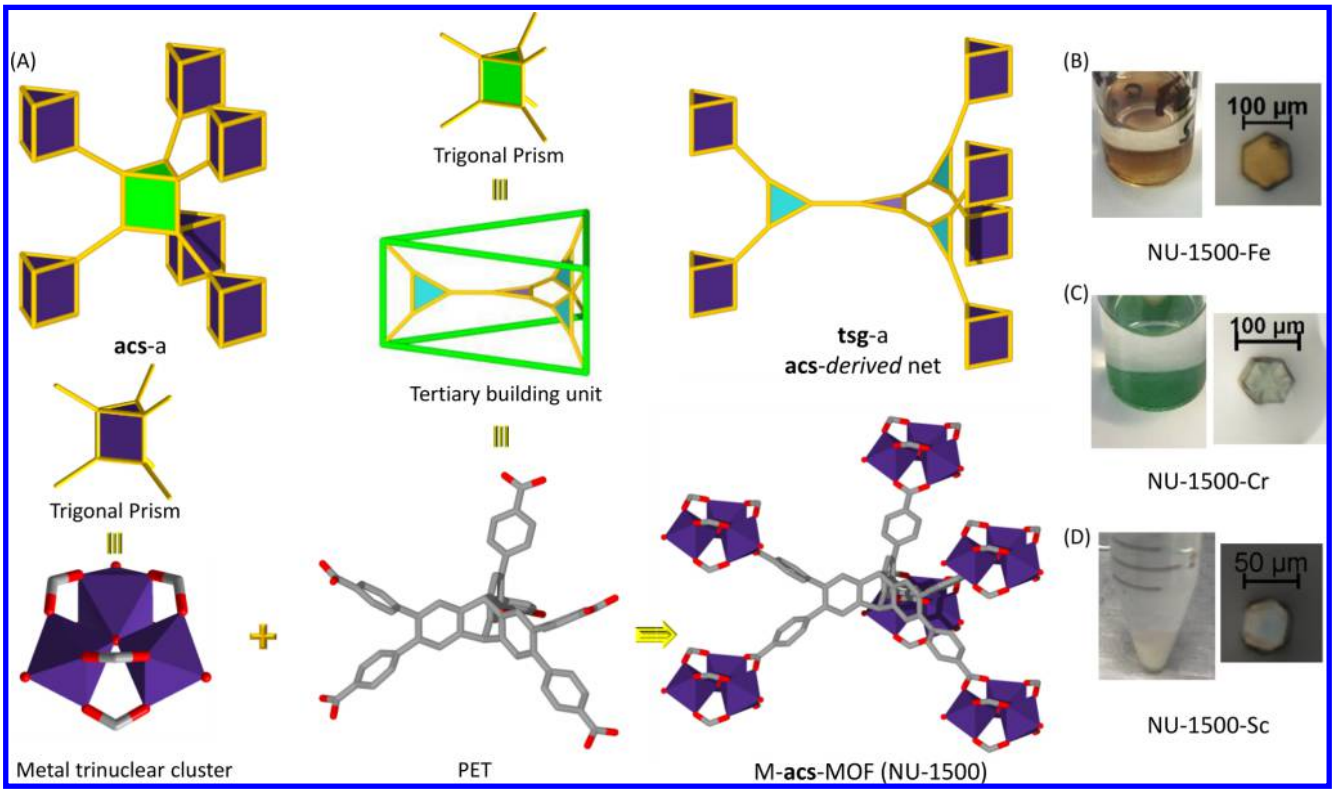


Figure 1. (A) Schematic representation of the design and synthesis of **NU-1500-M** (M = Fe, Cr, and Sc) based on the **acs** net. The 6-c trigonal prismatic organic ligand can also be viewed as a tertiary building unit based on 3-c SBUs, resulting in a (3,3,6)-c **acs**-*derived* **tsg** net. Atom color scheme: C, gray; trivalent metal, polyhedron with Northwestern University (NU) purple; O, red. H atoms are omitted for the sake of clarity. (B–D) Optical images of the single crystals of NU-1500.

activation from volatile solvents such as acetone with no need for supercritical activation (Figure 2).[45] Remarkably, N_2 isotherms at 77 K for NU-1500-Cr activated directly from acetone or water are almost identical, indicating its intrinsically high hydrolytic stability (Figure 3). The water vapor sorption studies of NU-1500-Cr show a high water uptake of 1.09 g g^{-1} at P/P_0 = 0.90 with a step at about P/P_0 = 0.45, which results from continuous pore filling.[17,24] Particularly, the uptake (1.02 g g^{-1}) at 60% relative humidity (RH) outperformed the current benchmark materials such as Co_2Cl_2(BTDD),[17] Cr-soc-MOF-1,[16] Ni-MOF-74-TPP,[29] and MCM-41.[13] The water working capacity of NU-1500-Cr (0.84 g g^{-1}) at room temperature between a RH range of 40–60% is the highest among all solid-state porous materials, making it a promising candidate for water vapor adsorption-based chiller applications.

Inspired by reticular chemistry, the combination of 6-c trigonal prismatic carboxylate ligands and *in-situ*-formed metal oxo trinuclear clusters has led to the rational synthesis of 6-c **acs**-MOFs. Rigid trigonal prismatic hexatopic carboxylic acids are rare in MOF chemistry, however, on account of the synthetic challenges and the flexible nature of dendrimeric carboxylate linkers. Here we utilized a rigid hexacarboxylic acid, peripherally extended triptycene (H_6PET),[46] to build 6-c **acs**-MOFs. The reaction of H_6PET with trivalent metal salts ($FeCl_3$) yielded yellow-orange hexagonal block crystals. SCXRD analysis revealed that this compound (NU-1500-Fe) crystallizes in the hexagonal $P\bar{6}m2$ space group (Table S1). It has a formula of $[Fe_3(\mu_3\text{-}O)(H_2O)_2(OH)(PET)]$ with OH^-, instead of Cl^-, as the charge-balancing anion, as confirmed by the absence of chloride signals from energy-dispersive X-ray spectroscopy (EDS) and X-ray fluorescence (XRF) analyses

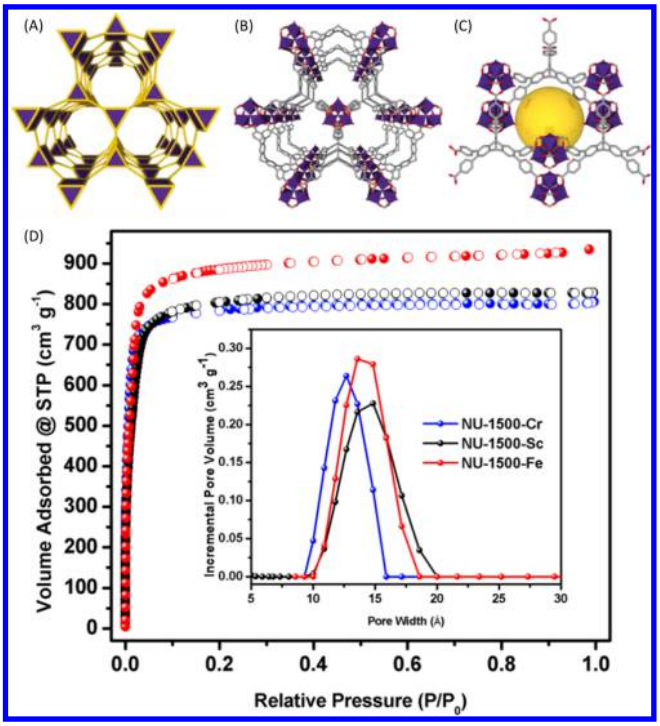


Figure 2. Illustration of one type of hexagonal channel inside **acs-a** net (A) and NU-1500 (B). (C) The pore size of the NU-1500 is about 1.4 nm. (D) N_2 sorption isotherms and DFT pore size distribution (inset) of NU-1500-M (M = Fe, Cr, and Sc) at 77 K. Closed (open) symbols represent adsorption (desorption).

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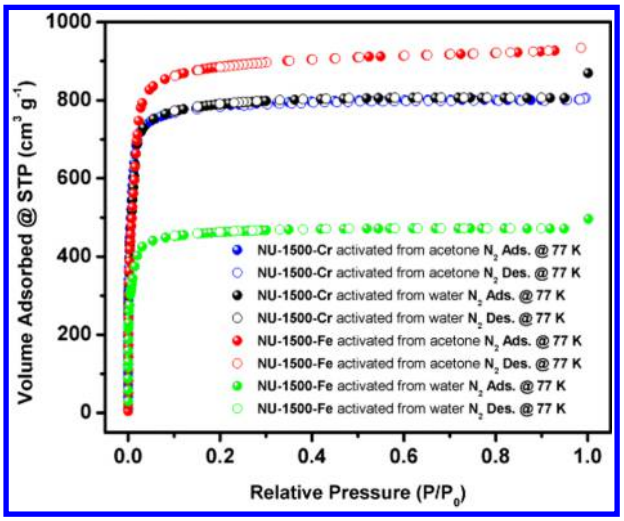


Figure 3. N_2 sorption isotherms at 77 K of NU-1500-Fe and NU-1500-Cr activated from acetone and directly from water, respectively.

(Figures S4 and S9). The crystal structure of NU-1500-Fe reveals a 3-periodic structure constructed from μ_3-oxo-centered trinuclear Fe(III) inorganic building blocks, abbreviated as Fe_3 node. Each Fe(III) cation coordinates to four oxygen atoms from bridging carboxylate groups of four separate ligands, one μ_3-oxo anion, and a terminal water or OH^- anion with an overall octahedral coordination environment.

Topological analysis reveals that the combination of the aforementioned 6-c inorganic node, $[Fe_3(\mu_3\text{-}O)(O_2C-)_6]$, and the 6-c rigid hexacarboxylate building unit resulted in a noncatenated MOF based on the anticipated edge-transitive 6-c **acs** net with transitivity [11].[37] The points of extension of both inorganic Fe_3 nodes and organic hexatopic ligand match the vertex figure of the 6-c trigonal prismatic secondary building unit (SBU) in the **acs** net. The trigonal prismatic ligand can alternatively be viewed as a tertiary building unit composed of two types of interconnected 3-c triangular SBUs, and thus NU-1500-Fe can also be described as having a **tsg** topology: a (3,3,6)-c trinodal net with minimal transitivity [32]. It is worth noting the minimal edge-transitive **tsg** net is derived from the **acs** net.[37,47]

Isoreticular chemistry was applied successfully to isolate M(III)-**acs**-MOF analogues (NU-1500-M; M(III) = Cr^{3+} and Sc^{3+}). The isostructural NU-1500-Cr was obtained by postsynthetic transmetalation from NU-1500-Fe with almost complete exchange of the Fe_3 node by the Cr_3 node as observed by EDS analysis and inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Figure S6 and Table S4).[16,48] The green single crystals of NU-1500-Cr were formed via the reaction of NU-1500-Fe with $CrCl_2$ in dimethylformamide (DMF). SCXRD analysis revealed that NU-1500-Cr was isostructural to NU-1500-Fe (Table S2). NU-1500-Cr has a formula of $[Cr_3(\mu_3\text{-}O)(H_2O)_2(Cl)(PET)]$, as confirmed by EDS, X-ray photoelectron spectroscopy (XPS), and XRF analyses (Figures S7 and S8). NU-1500-Sc was obtained *de novo* from the reaction of the hexatopic acid linker and $ScCl_3$. SCXRD analysis revealed that NU-1500-Sc is an isostructural **acs**-MOF (Table S3 and Figure S5). The phase purity of the bulk NU-1500 was confirmed on the basis of the well-matched simulated and as-synthesized powder X-ray diffraction (PXRD) patterns (Figure S1). It is noted that isolating single crystals of stable MOFs based on trivalent metal ions is a challenging task on account of the strong bonds between the hard metal ions and hard oxygen ions from carboxylates.[4,49]

NU-1500 consists of one type of one-dimensional hexagonal channel along the *c* axis with a pore size of about 1.4 nm as estimated from the relevant crystal structures. The channel of NU-1500 is also correlated to the underlying **acs** net, which contains one kind of hexagonal channel. The permanent porosity of NU-1500-M, after thermal activation from acetone-exchanged samples, has been confirmed by the nitrogen (N_2) adsorption isotherm at 77 K, which displays fully reversible type-I isotherms characteristic of microporous materials with permanent porosity. The apparent BET surface areas of NU-1500-Fe, NU-1500-Sc, and NU-1500-Cr were estimated to be 4280, 3720, and 3580 $m^2\ g^{-1}$, respectively. The volumetric BET areas of NU-1500-Fe, NU-1500-Sc, and NU-1500-Cr were estimated to be 2220, 1890, and 1900 $m^2\ cm^{-3}$, respectively, based on the crystallographic density (Table S5). The experimental total pore volumes of NU-1500-Fe, NU-1500-Sc, and NU-1500-Cr, obtained from the N_2 adsorption isotherms, were estimated to be 1.43, 1.28, and 1.24 $cm^3\ g^{-1}$, respectively. One type of pore was identified for NU-1500-M with pore-size distributions centered at about 1.4−1.5 nm on the basis of a density functional theory (DFT) model, which is in good agreement with the estimated value based on the related crystal structures.

The stability of NU-1500-M was investigated by soaking the MOFs in water for 24 h and activating from water. The PXRD patterns illustrated that NU-1500-Fe and NU-1500-Cr maintain their crystallinity, while NU-1500-Sc becomes almost amorphous (Figure S2). Then, N_2 sorption measurements were conducted on NU-1500-Fe and NU-1500-Cr after the direct activation from water. The experimental total pore volume and BET area of NU-1500-Fe activated from water were estimated to be 1940 $m^2\ g^{-1}$ and 0.73 $cm^3\ g^{-1}$, indicating partial degradation of the MOF structure. Remarkably, the N_2 isotherms of NU-1500-Cr activated from water were nearly identical to those activated from acetone, maintaining its high microporosity and surface area (Table S6). This result suggested that NU-1500-Cr is a highly porous material with ultrahigh hydrolytic stability and could be a promising candidate for water adsorption-based applications.

Inspired by the high pore volume and microporosity, water sorption studies were performed on NU-1500-M to assess their water vapor sorption behavior. The water adsorption isotherms exhibited a steep uptake at about P/P_0 = 0.4−0.6 for the different NU-1500 analogues, showing the pore filling or condensation of H_2O into the pore system (Figure 4 and Figures S10−S12). Porous frameworks of NU-1500-Fe collapsed after the first cycle of water sorption as a consequence of the capillary-force-driven channel collapse,[50] as illustrated in the desorption isotherms. NU-1500-Sc collapsed in the first cycle of water adsorption with a very low water uptake and is the least hydrolytically stable NU-1500 analogue (Figure S3). Owing to the strong and inert bonding of Cr−O, NU-1500-Cr displayed highly repeatable adsorption−desorption cycles with a steep uptake at about P/P_0 = 0.45. Moreover, the water uptake capacity of NU-1500-Cr at P/P_0 = 0.90 and 298 K is about 1360 $cm^3\ g^{-1}$ or 1.09 g g^{-1}, which is among the highest values of MOF-based water sorbents (Table S7).[16] Additionally, the water uptake at P/P_0 = 0.60 (1270 $cm^3\ g^{-1}$ or 1.02 g g^{-1}) outperformed the current top-performing materials, such as Co_2Cl_2(BTDD),[17] Cr-soc-

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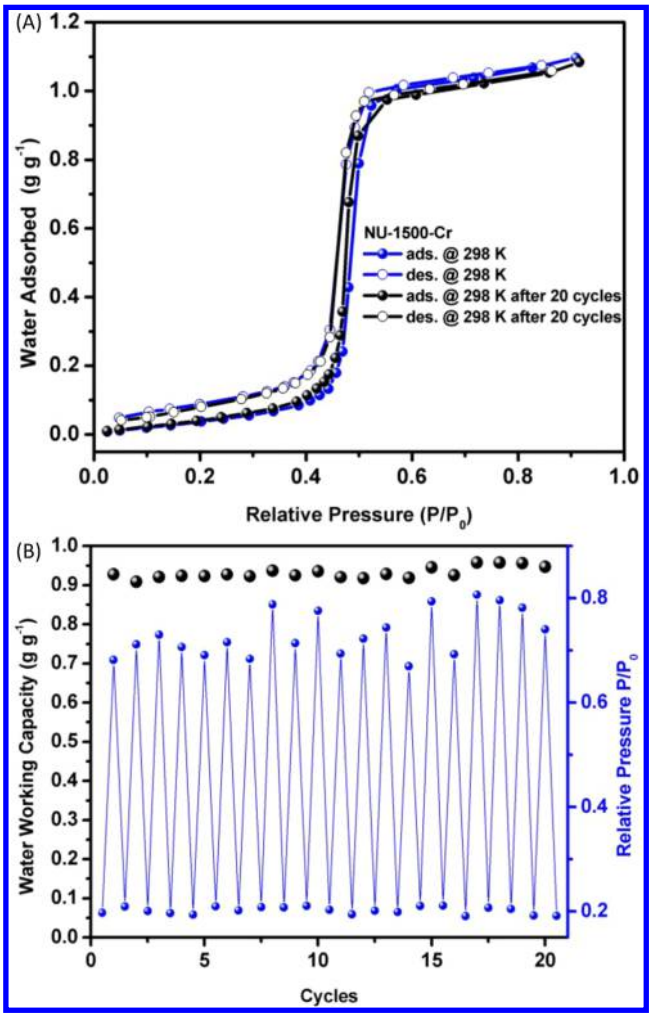


Figure 4. (A) Water sorption isotherms of NU-1500-Cr (1st cycle and after 20 cycles of pressure swing between 20% RH (P/P_0 = 0.2) and 70% RH (P/P_0 = 0.7)) and (B) the cycling test.

MOF-1,[16] Ni-MOF-74-TPP,[29] and MCM-41,[13] and is only slightly lower than MIL-101-Cr.[30,31,51] The unique and small hysteresis between the adsorption and desorption isotherms of NU-1500-Cr affords a water working capacity at 298 K in the relative humidity range of 40−60% (adsorption at P/P_0 = 0.60 and desorption at P/P_0 = 0.40), which is, to the best of our knowledge, the highest among all porous materials including MOFs, carbons, zeolites, and porous silica (Table S8). The durability and cyclability of NU-1500-Cr were evaluated by multiple water adsorption/desorption experiments between the RH range of 20−70%; after 20 cycles, the water sorption isotherms were nearly identical to the first cycle after regeneration at room temperature under vacuum. These results demonstrate that NU-1500-Cr, based on the channel type **acs**-net with a suitable microporous pore size, is a favorable candidate for water vapor sorption based applications such as water adsorption heat transformation.[16,17]

In conclusion, we have designed and synthesized a new series of MOFs with 6-c **acs** topology, based on trinuclear metal clusters and trigonal prismatic hexatopic carboxylate linkers. NU-1500-Cr, a highly stable and highly microporous MOF with uniform hexagonal channels about the size of 1.4 nm, exhibits an exceptionally high water uptake capacity for the reliable delivery of water vapor. The implementation of reticular chemistry for the design of highly stable functional porous MOFs with targeted pore size and geometry will advance the synthesis of next-generation porous water vapor sorbents.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b13710.

Crystallographic data structure (CIF)
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Synthetic procedures of MOF materials, crystallographic data, SEM images, ICP-AES, XPS, XRF, and additional sorption isotherms (PDF)

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Notes

The authors declare no competing financial interest.

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