

Communication

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# Metal-Organic Framework Containing Planar Metal-Binding Sites: Efficiently and Cost-effectively Enhancing the Kinetic Separation of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>

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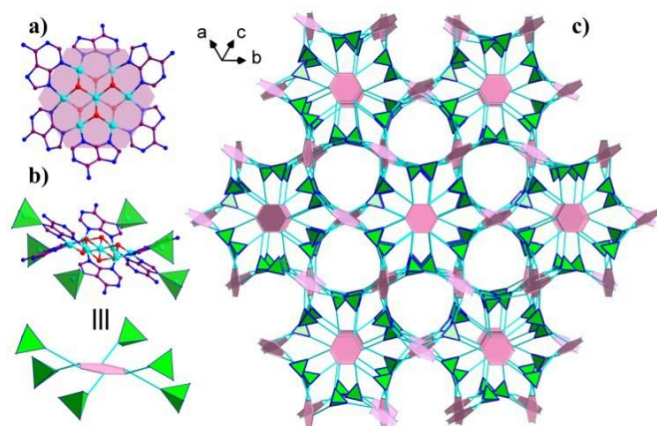
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**ABSTRACT:** One of the emerging problems plaguing the chemical industry today is the efficient and cost-effective separation of C<sub>2</sub> hydrocarbons. In order to help address this problem, we report a new material, **NbU-1**, constructed by the extremely cheap starting materials. The special structural characteristics of **NbU-1** such as the planar, mixed-valence copper clusters and Lewis-basic adsorption channels enforce interactions with acetylene molecules that lead to the highest kinetic separation efficiency for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>. Via DFT-D calculations, it is indicated that C<sub>2</sub>H<sub>2</sub> molecules are adsorbed onto the two adjacent Cu(I) centers, but not the usual single open metal sites of Cu centers. The reported results not only provide information for a deep investigation into the separation mechanism, but also offer an alternative strategy for preparing the cost-effective materials that can perform highly-efficient separations of light hydrocarbons.

Purification of ethylene from C<sub>2</sub> mixtures is an extremely important industrial process that plays a major role in the chemical and polymer industry. Due to the close-boiling points and small differences between their condensabilities, cryogenic distillation is the current state of the art process used for C<sub>2</sub> separation, even though it is an extremely high energy-cost process.<sup>1</sup> Inversely, non-thermally driven separations such as adsorption processes using porous

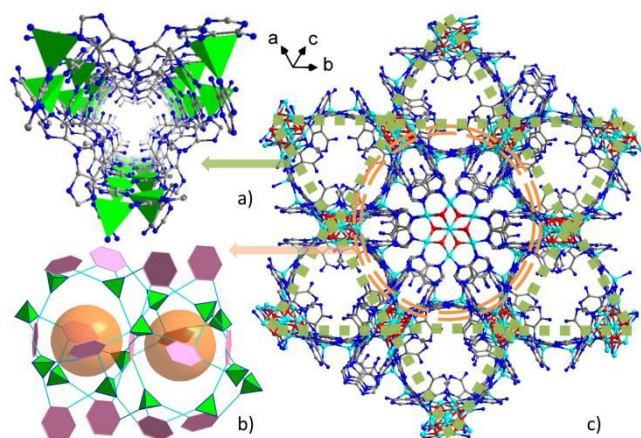
materials have been receiving widespread attention from academia and industry over the last two decades.<sup>2</sup>

Metal-Organic Frameworks (MOFs), which are renowned for their tunable porous structure and functional surfaces, have exhibited great potential as the efficient separation materials.<sup>3-8</sup> However, several fatal weaknesses still block the practical application of MOFs-based separation, such as the lack of the effective interaction sites, low thermal or chemical stability and the contradiction between the low separation efficiency and high cost of the starting materials. In order to surmount these defects, lots of research work has focused on increasing the effective open sites in MOFs separation. For example, the MOF-74 series illustrated that the presence of open metal within MOFs play a critical role in the identification of similar C<sub>2</sub> molecules.<sup>4a</sup> In response to this work, the pursuit of materials with additional open metal sites has become more intense as well as significantly more challenging.<sup>9</sup> Due to the limitation of coordination habits, spatial hindrance, high cost of the starting materials and synthesis process, the pursuit of larger high-nuclearity cluster-based MOFs has encountered a bottleneck, and the related research work still focused on the several star MOFs templates. In order to inject new vitality, highly efficient and cost-effective synthesis strategies and models are urgently required.



**Figure 1.** Perspective view of the six-connected heptanuclear  $\text{Cu}_7(\text{OH})_6(\text{Ad})_6$  planar and 4-connected single Cu (a, b); Three-dimensional structure of **NbU-1** composed of simplified nodes (c).

Planar, high-nuclearity M-O based complexes have attracted increasing attention due to their fascinating properties.<sup>10-12</sup> Each metal center in the planar core tends to generate two perpendicular open sites, which could be conjugated into two metal-active-surfaces used to enhance the related properties of the planar complexes. With the consideration of the complementarity and structural advantages, the materials integrated planar high-nuclearity node into MOFs could generate unprecedented separation performances, such as metal-active-surfaces within pores that exert strong binding interactions with specific guest molecules. In order to validate the effectiveness of this constructive strategy, a novel MOF,  $(\text{NH}_4)_3[\text{Cu}^{\text{II}}_3[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}_6(\text{OH})_6(\text{Ad})_6]_2] \cdot (\text{H}_2\text{O})_x$  (**NbU-1** = **Ningbo University-1**, Ad = adenine), has been directly constructed from the cheap starting materials via one-step synthesis (see ESI<sup>†</sup>). **NbU-1** exhibits not only high chemical stabilities, but also the highest efficient kinetic selectivity of  $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ .



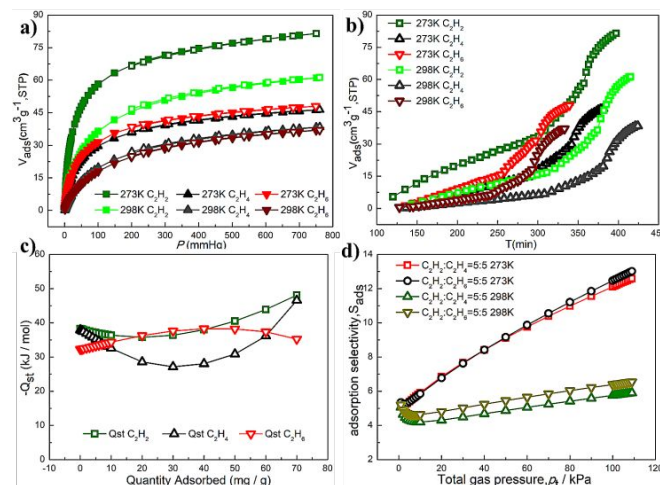
**Figure 2.** The basic adsorption channel (a) and cavities (b) in the three-dimensional structure (c) of **NbU-1**.

Single-crystal X-ray diffraction analysis revealed that **NbU-1** presents a 3D porous structure based on heptanuclear  $\text{Cu}_7(\text{OH})_6$  clusters and single Cu ions linked by adenine ligands (Figure 1). In the heptanuclear cluster, the central Cu1 ion and Cu2 ring are co-planar. Cu1 exhibits a distorted octahedral geometry with six  $\mu_3\text{-OH}^-$  groups, which are distributed equally between the two sides of the heptanuclear plane. Cu2 atoms reside in a four-coordinated coordination mode with two  $\mu_3\text{-OH}^-$  groups and two N donors from different adenine ligands. One Cu1 and two Cu2 atoms are bound together via one  $\mu_3\text{-OH}^-$  group to form the  $\text{Cu}_3(\text{OH})$  triangle. Through sharing two isosceles edges, six triangles are fused into the heptanuclear planar, whose periphery is decorated by six adenine ligands that further separately coordinate with Cu3 atoms. Each Cu3 atom is surrounded by four adenine units via N2 atom. For Cu1 and Cu3, the Cu-O and Cu-N distances fall in the range of Cu(II) state, but for Cu2, the related values indicate Cu(I) state (Table S2). Furthermore, the existence and proportion of two different of copper states was also validated by X-ray photo-electron spectroscopy (XPS) (Figure S2). The  $2p_{3/2}$  peak is characterized by doublets with the energies of 934.6 and 932.5 eV, corresponding to  $\text{Cu}^{\text{II}}$  and  $\text{Cu}^{\text{I}}$ , respectively.<sup>13</sup> The integral areas of two peaks yield  $\text{Cu}^{\text{I}}:\text{Cu}^{\text{II}}$  in a ratio of 70:30, in consistent with the crystallographic studies of  $12\text{Cu}^{\text{I}}:5\text{Cu}^{\text{II}}$ .

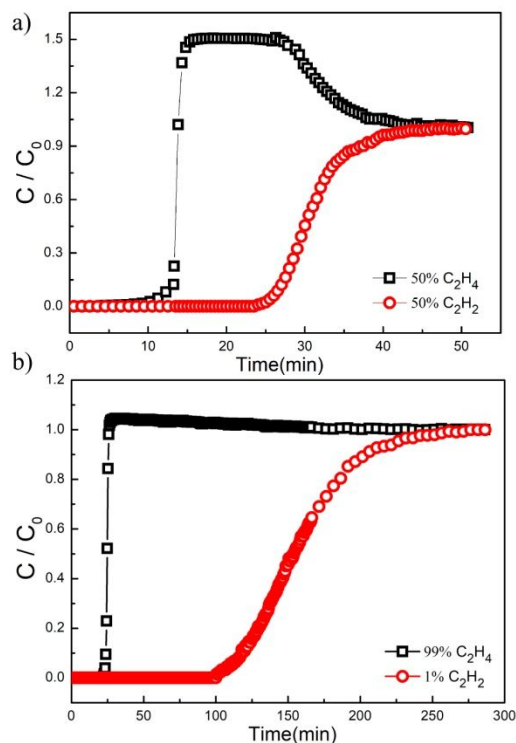
From a topological point of view, **NbU-1** can be described as a (4,6)-connected 3D *gar* topological network (Figure S3) with the point (Schläfli) symbol  $\{4^4 \cdot 6^2\}_3\{4^6 \cdot 6^6 \cdot 8^3\}_2$ .<sup>14</sup> Meanwhile, 3D framework presents irregular void, featuring rich open channels and cavities (54.9% of the unit cell volume, Figure 2). The channels have trigonal windows, which are functionalized with the Lewis-basic adsorption sites such as the uncoordinated pyridyl and amino-groups of Adenine on the inner surface. Furthermore, the surface of irregular pores is decorated with planar metal-binding sites created by the heptanuclear clusters which supply the exceptional number of open metal sites. Therefore, in terms of structural characteristics, the dual adsorption active sites of **NbU-1** could synergistically enforce the specific host-guest interactions with  $\text{C}_2\text{H}_2$ .

Powder XRD studies displayed **NbU-1** not only possesses high thermal stability under the wet and vacuum condition, but also exhibits outstanding chemical stability in both boiling acidic and alkaline conditions even for one week,

which means **NbU-1** is more stable than the most MOFs with exceptional gas separation performances.<sup>4</sup> N<sub>2</sub> adsorption of activated **NbU-1** at 77 K shows a reversible type-I isotherm, giving Langmuir surface area of 538.6 m<sup>2</sup> g<sup>-1</sup> (BET surface area of 368.2 m<sup>2</sup> g<sup>-1</sup>). The Horvath–Kawazoe method shows a well uniform pore distribution of about 4Å, indicating the ultra-microporous structure of **NbU-1**.



**Figure 3.** (a) C<sub>2</sub>H<sub>x</sub> sorption isotherms for **NbU-1** at 273 K and 298K; (b) The isotherms of the relationship between the adsorption amount and the equilibrium time; (c) The C<sub>2</sub>H<sub>x</sub> isosteric heats of adsorption for **NbU-1**; (d) IAST adsorption selectivities for **NbU-1** of equimolar C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>x</sub> mixtures.



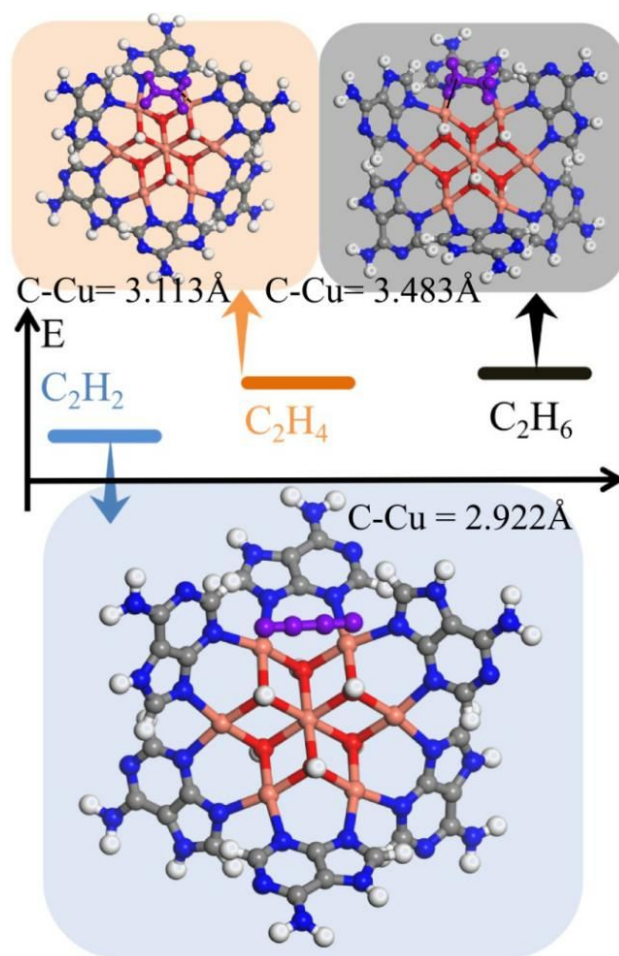
**Figure 4.** Breakthrough curves for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separations (50/50) (a) and (1/99) (b).

The stable, ultra-microporous structure and functionalized porous surface prompted us to further examine the capacities of **NbU-1** for the adsorption of small C<sub>2</sub> hydrocarbons. Single component adsorption isotherms for C<sub>2</sub> hydrocarbons were measured at 273 and 298K, respectively, which shows **NbU-1** exhibits adsorption capacities with the trend of C<sub>2</sub>H<sub>2</sub> > C<sub>2</sub>H<sub>4</sub> ≈ C<sub>2</sub>H<sub>6</sub>, and the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> uptake ratio of **NbU-1** were estimated to be 1.76 and 1.69 at 273K, which is notably larger than the values for MOF-74 series separation with the value range of 1.21–1.36.<sup>4c</sup> According to the virial equation (Figure 3c), the heat of adsorption values at zero loading for C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> are 38.3, 37.9 and 32.2 kJ mol<sup>-1</sup> respectively. Therefore, the remarkable adsorption enthalpies, which have a trend of C<sub>2</sub>H<sub>2</sub> ≈ C<sub>2</sub>H<sub>4</sub> > C<sub>2</sub>H<sub>6</sub>, must be attributed to the specific structural characteristics of the Lewis-basic sites and the planar metal-binding sites. Simultaneously, the similar adsorption enthalpies for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> manifest **NbU-1** might be not suitable for thermodynamic separation of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>.

Due to this, kinetic adsorption behavior was carefully studied because gas separation is the process of non-equilibrium adsorption, which is related not only to the interactions between the host and the guest, but also the kinetic diffusion rate of the gas molecules themselves within the material.<sup>15</sup> The relationship between the adsorption amount and equilibrium time gives a time sequence of T(C<sub>2</sub>H<sub>2</sub>) << T(C<sub>2</sub>H<sub>6</sub>) < T(C<sub>2</sub>H<sub>4</sub>) (especially the lower adsorption amounts 0–0.5bar) (Figure 3b). The shortest equilibrium time not only indicate the fastest diffusion rate within **NbU-1** for C<sub>2</sub>H<sub>2</sub>, but also theoretically endows **NbU-1** with the separation potential of C<sub>2</sub>H<sub>2</sub> based on a combination of kinetic diffusion rates and enthalpies of adsorption.

In order to evaluate the real gas separation abilities of **NbU-1**, ideal adsorbed solution theory (IAST) was performed on 50–50 C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> binary mixtures, which yield the separation selectivity values for **NbU-1** of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> under 100kPa to be 12.1, 12.5 at 273 K, and 5.9, 6.5 at 298K, respectively (Figure 3d). The relatively high selectivity value of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> for **NbU-1** is greater than that the presented star MOFs (Table S4), illustrating the great potential of **NbU-1** as the efficient separation material for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>. Prompted by the results of theoretical calculation, the experimental breakthrough studies were further performed for the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures that were flowed over a packed bed of activated **NbU-1** at

293K and 1bar. Two different ratios of  $C_2H_2/C_2H_4$  mixture (50:50 and 1:99, v/v) were conducted and clear separations curves were realized (Figure 4). It was found that **NbU-1** displays a remarkable separation of the 1:99 mixtures, where the breakthrough of  $C_2H_2$  occurs at 93 min after dosing the gas mixture. Furthermore, an extremely high purity of  $C_2H_4$  that was greater than 99.997% had been obtained (the detection limit of the GC, 0.003%). Moreover, based on the breakthrough curve, the amounts of  $C_2H_2$  adsorbed by **NbU-1** during the time  $0 \sim t_{break}$  can be calculated as 1.2 and  $27.6 \text{ cm}^3 \text{ g}^{-1}$  from 1/99 and 50/50  $C_2H_2/C_2H_4$  mixture respectively, which are 13.2% and 52.0% of the values obtained from the single component adsorption isotherms ( $9.1$  and  $53.1 \text{ cm}^3 \text{ g}^{-1}$  at  $T=298\text{K}$ ,  $P_{C_2H_2}=0.01$  bar and  $0.5$  bar). Compared to the performance of other MOFs-based separation materials (Table S4), it is worth noting that **NbU-1** exhibits the longest dimensionless breakthrough time ( $\tau_{break}$ ) of  $C_2H_2$  for the 50/50 mixtures with the specific constant flow rate of  $2\text{ml/min}$ , and for the 1/99 mixtures, the  $\tau_{break}$  of  $C_2H_2$  only lower than UTSA-200a<sup>4d</sup>, and illustrates the excellent kinetic-factors, especially the fastest diffusion rate of  $C_2H_2$ , and excellent stability promoted **NbU-1** to be an extremely practical material for  $C_2H_2/C_2H_4$  separations. There is no obvious enhancement for the separation of acetylene/ethane compared to acetylene/ethylene. For ethylene/ethane, there is no separation effect for **NbU-1**, which was also caused by the faster diffusion rate of ethane than ethylene (Figure S15 , S16).



**Figure 5.** DFT-D calculated  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$  adsorption binding sites on  $Cu_7(OH)_6(adenine)_6$  unit.

Additionally, spin-polarized density function theory calculations were carried out to investigate the role of planar metal-binding sites in **NbU-1**. The extended **NbU-1** can be simplified as the effective moiety of  $Cu_7(OH)_6(Ad)_6$  to highlight the crucial role of the planar metal-binding sites in the process of separation. Different from the normal adsorption mechanism, in **NbU-1**, the series of  $C_2$  molecules prefer to bind onto the open metal sites via dangling bonds between the  $d$  block-electrons-rich regions of two adjacent  $Cu^I$  atoms (Figure 5, S1). Furthermore, the adsorption energy has been calculated as  $-13.07 \text{ kcal/mol}$  for  $C_2H_2$ ,  $-12.57 \text{ kcal/mol}$  for  $C_2H_4$  and  $-12.01 \text{ kcal/mol}$  for  $C_2H_6$ , meaning the weak adsorption of these  $C_2$  molecules onto metal-active surface. The average C-Cu bond lengths of  $2.922 \text{ \AA}$  for  $C_2H_2$ ,  $3.113 \text{ \AA}$  for  $C_2H_4$ , and  $3.483 \text{ \AA}$  for  $C_2H_6$ , indicate the important role of the weak Van der Waals force between gas molecules and planar unit. The different bond characteristic of  $C_2$  molecules must be responsible for the origination of different weak C-Cu interactions. Observed

from the theoretical investigation, the planar, open metal sites of the four-coordinated Cu<sup>I</sup> atoms, especially through conjugated with each other, play an important role in the selective adsorption of different C<sub>2</sub> light hydrocarbons.

In conclusion, **NbU-1** exhibits the several advantages as the multiple Cu<sup>I</sup> open metal-binding sites, extreme chemical stability and the best price-performance ratio (Table S3) compared to the reported MOFs-based separations. Via breakthrough experiments, **NbU-1** clearly illustrates the excellent kinetic parameters for the separation of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures. The out-standing and record-breaking separation abilities of **NbU-1** are ascribed to the affluent basic adsorption sites and special planer, open metal binding sites. Therefore, the related research results illustrate an important and significant advancement on the design and preparation of MOF materials for practical C<sub>2</sub> separations and can provide a model for further MOF development.

## ASSOCIATED CONTENT

### Supporting Information

Information of experimental details, materials and measurements, synthesis and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1)(a) Kerry, F.G. *Industrial Gas Handbook Gas Separation and Purification*, CRC Press, Boca Raton, **2007**; (b) Sholl, D. S.; Lively, R. P. Seven chemical separations to change the world, *Nature*, **2016**, 532, 435-437
- (2) Bereciartua, P. J.; Cantn ,  .; Corma, A.; Jord , J. L.; Palomino, M.; Rey, F.; Valencia, S.; Corcoran, E. W.; Kortunov, P.; Ravikovitch, P. I.; Burton, A.; Yoon, C.; Wang, Y.; Paur, C.; Guzman, J.; Bishop, A. R.; Casty, G. L. Control of zeolite framework flexibility and pore topology for separation of ethane and ethylene. *Science*, **2017**, 358, 1068-1071.
- (3) (a) Kirchon, A.; Feng, L.; Drake, H. F.; Josepha, E. A.; Zhou, H.-C. From fundamentals to applications: a toolbox for robust and multifunctional MOF materials. *Chem. Soc. Rev.*, **2018**, 47, 8611;(b) Bai, Y.; Dou, Y.; Xie, L.-H.; Rutledge, W.; Li, J.-R.; Zhou, H.-C. Zr-based metal-organic frameworks: design, synthesis, structure, and applications. *Chem. Soc. Rev.*, **2016**, 45, 2327-2367.
- (4) (a) Bloch, E. D.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. Hydrocarbon Separations in a Metal-Organic Framework with Open Iron(II) Coordination Sites. *Science*, **2012**, 335, 1606-1610; (b) Hu, T. L.; Wang, H.; Li, B.; Krishna, R.; Wu, H.; Zhou, W.; Zhao, Y.; Han, Y.; Wang, X.; Zhu, W.; Yao, Z.; Xiang, S.; Chen, B. Microporous metal-organic framework with dual functionalities for highly efficient removal of acetylene from ethylene/acetylene mixtures. *Nat. Commun.*, 2015, 6, 7328; (c) Cui, X.; Chen, K.; Xing, H.; Zaworotko, M. J.; Chen, B. Pore chemistry and size control in hybrid porous materials for acetylene capture from ethylene. *Science*, **2016**, 353, 141-144; (d) Li, B.; Cui, X.; O'Nolan, D.; Wen, H.-M.; Jiang, M.; Krishna, R.; Wu, H.; Lin, R.-B.; Chen, Y.-S.; Yuan, D.; Xing, H.; Zhou, W.; Ren, Q.; Qian, G.; Zaworotko, M. J.; Chen, B. An Ideal Molecular Sieve for Acetylene Removal from Ethylene with Record Selectivity and Productivity. *Adv. Mater.* **2017**, 29, 1704210;(e) Hao, H. -G.; Zhao, Y. -F.; Chen, D. -M.; Yu, J. -M.; Tan, K.; Ma, S. -Q.; Chabal, Y.; Zhang, Z. -M.; Dou, J. -M.; Xiao, Z. -H.; Day, G.; Zhou, H. -C. and Lu, T. -B. Simultaneously Trapping C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> into a Robust MetalOrganic Framework from a Ternary Mixture of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> for Purification of C<sub>2</sub>H<sub>4</sub>. *Angew. Chem., Int. Ed.*, **2018**, 57, 16067-16071; (f) Peng, Y.-L.; Pham, T.; Li, P.; Wang, T.; Chen, Y.; Chen, K.-J.; Forrest, K. A.; Space, B.; Cheng, P.; Zaworotko, M. J.; Zhang, Z. Robust Ultramicroporous Metal-Organic Frameworks with Benchmark Affinity for Acetylene. *Angew. Chem., Int. Ed.*, **2018**, 57, 10971-10975.
- (5) (a) Liao, P. -Q.; Zhang, W.-X.; Zhang, J.-P.; Chen, X.-M. Efficient purification of ethene by an ethane-trapping metal-organic framework. *Nat. Commun.*, 2015, 6, 8697;(b) Li, L.; Lin, R.-B.; Krishna, R.; Li, H.; Xiang, S.; Wu, H.; Li, J.; Zhou, W.; Chen, B. Ethane/ethylene separation in a metal-organic framework with iron-peroxo sites. *Science*, **2018**, 362, 443;(c) Lin, R.-B.; Li, L.; Zhou, H.-L.; Wu, H.; He, C.; Li, S.; Krishna, R.; Li, J.; Zhou, W.; Chen, B. Molecular sieving of ethylene from ethane using a rigid metal-organic framework. *Nat. Mater.*, DOI: 10.1038/s41563-018-0206-2.
- (6) (a) Kim, J. Y.; Balderas-Xicoht catl, R.; Zhang, L.; Kang, S. G.; Hirscher, M.; Oh, H.; Moon, H. R. Exploiting Diffusion Barrier and Chemical Affinity of Metal-Organic Frameworks for Efficient

Hydrogen Isotope Separation. *J. Am. Chem. Soc.*, **2017**, *139*, 15135–15141;(b) Xiao, D. J.; Gonzalez, M. I.; Darago, L. E.; Vogiatzis, K. D.; Haldoupis, E.; Gagliardi, L.; Long, J. R. Selective, Tunable O<sub>2</sub> Binding in Cobalt(II)–Triazolate/Pyrazolate Metal–Organic Frameworks. *J. Am. Chem. Soc.*, **2016**, *138*, 7161–7170.

(7) A. Cadiau, K. Adil, M. Eddaoudi et al. A metal-organic framework–based splitter for separating propylene from propane. *Science*, **2016**, *353*, 137–140.

(8) (a) Liao, P.-Q.; Chen, H.; Zhou, D.-D.; Liu, S.-Y.; He, C.-T.; Rui, Z.; Ji, H.; Zhang, J.-P.; Chen, X.-M. Monodentate hydroxide as a super strong yet reversible active site for CO<sub>2</sub> capture from high-humidity flue gas. *Energy Environ. Sci.*, **2015**, *8*, 1011–1016; (b) Jiang, J.; Lu, Z.; Zhang, M.; Duan, J.; Zhang, W.; Pan, Y.; Bai, J. Higher Symmetry Multinuclear Clusters of Metal–Organic Frameworks for Highly Selective CO<sub>2</sub> Capture. *J. Am. Chem. Soc.*, **2018**, *51*, 17825–17829.

(9) Li, J.; Tao, J.; Huang, R.-B.; Zheng, L.-S. Magnetic Nanosized (MII<sub>24</sub>)-Wheel-Based (M = Co, Ni) Coordination Polymers. *Inorg. Chem.*, **2012**, *51*, 5988–5990.

(10) (a) Pérez-Aguirre, R.; Beobide, G.; Castillo, O.; Pedro, I. d.; Luque, A.; Pérez-Yáñez, S.; Rodríguez Fernández, J.; Román, P. 3D Magnetically Ordered Open Supramolecular Architectures Based on Ferrimagnetic Cu/Adenine/Hydroxide Heptameric Wheels. *Inorg. Chem.* **2016**, *55*, 7755–7763;(b) Liu, Z.-Y.; Zhang, H.-Y.; Yang, E.-C.; Liu, Z.-Y.; Zhao, X.-J. A (3,6)-connected layer with an unprecedented adeninate nucleobase-derived heptanuclear disc. *Dalton Trans.*, **2015**, *44*, 5280–5283;(c) Leite Ferreira, B.J.M.; Brandão, P.; Dos Santos, A.M.; Gai, Z.; Cruz, C.; Reis, M.S.; Santos T.M.; Félix, V. Heptacopper(II) and dicopper(II)-adenine complexes: synthesis, structural characterization, and magnetic properties. *J. Coord. Chem.*, **2015**, *68*, 2770–2787.

(11)(a) Armentano, D.; Mastropietro, T. F.; Julve, M.; Rossi, R.; Rossi, P.; Munno, G. D. A New Octanuclear Copper(II)–Nucleoside Wheel. *J.*

*Am. Chem. Soc.* **2007**, *129*, 2740–2741;(b) Chang, C. -H.; Hwang, K. C.; Liu, C. -S.; Chi, Y.; Carty, A. J.; Scoles, L.; Peng, S. -M.; Lee, G. -H.; Reedijk, J. Formation and Stabilization of a Decanuclear CuII Wheel Linked by Chloride and O···H–N Hydrogen Bonds. *Angew. Chem., Int. Ed.* **2001**, *40*, 4651–4653.

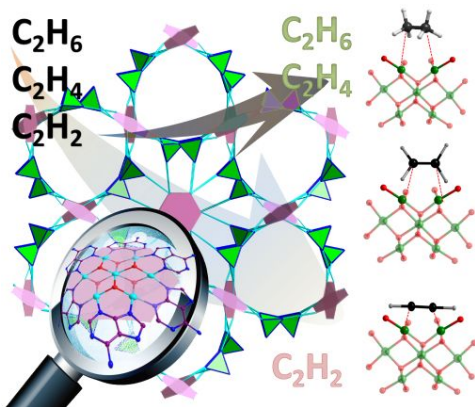
(12) (a) Deng, Y.-K.; Su, H.-F.; Xu, J.-H.; Wang, W.-G.; Kurmoo, M.; Lin, S.-C.; Tan, Y. -Z.; Jia, J.; Sun, D.; Zheng, L.-S. Hierarchical Assembly of a {MnII<sub>15</sub>MnIII<sub>4</sub>} Brucite Disc: Step-by-Step Formation and Ferrimagnetism. *J. Am. Chem. Soc.* **2016**, *138*, 1328–1334;(b) Guo, L.-Y.; Su, H.-F.; Kurmoo, M.; Tung, C.-H.; Sun, D.; Zheng, L.-S. Core–Shell {Mn<sub>7</sub>C(Mn,Cd)<sub>12</sub>} Assembled from Core {Mn<sub>7</sub>} Disc. *J. Am. Chem. Soc.* **2017**, *139*, 14033–14036.

(13) (a) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.*, **1968**, *10*, 247–422; (b) Yu, F.; Kurmoo, M.; Zhuang, G.-L.; Zuo, J.-L. Hierarchical tandem assembly of planar [3×3] building units into {3×[3×3]} oligomers: mixed-valency, electrical conductivity and magnetism. *Chem. Sci.*, **2018**, *9*, 7498–7504.

(14) Blatov, V. A. IUCr CompComm Newsletter, 2006, 7, 4; see also <http://www.topos.ssu.samara.ru>.

(15) (a) Li, K.; Olson, D. H.; Seidel, J.; Emge, T. J.; Gong, H.; Zeng, H.; Li, J. Zeolitic Imidazolate Frameworks for Kinetic Separation of Propane and Propene. *J. Am. Chem. Soc.*, **2009**, *131*, 10368–10369; (b) Lee, C. Y.; Bae, Y.-S.; Jeong, N. C.; Farha, O. K.; Sarjeant, A. A.; Stern, C. L.; Nickias, P.; Snurr, R. Q.; Hupp, J. T.; Nguyen, S. T. Kinetic Separation of Propene and Propane in MetalOrganic Frameworks: Controlling Diffusion Rates in Plate-Shaped Crystals via Tuning of Pore Apertures and Crystallite Aspect Ratios. *J. Am. Chem. Soc.* **2011**, *133*, 5228–5231.

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