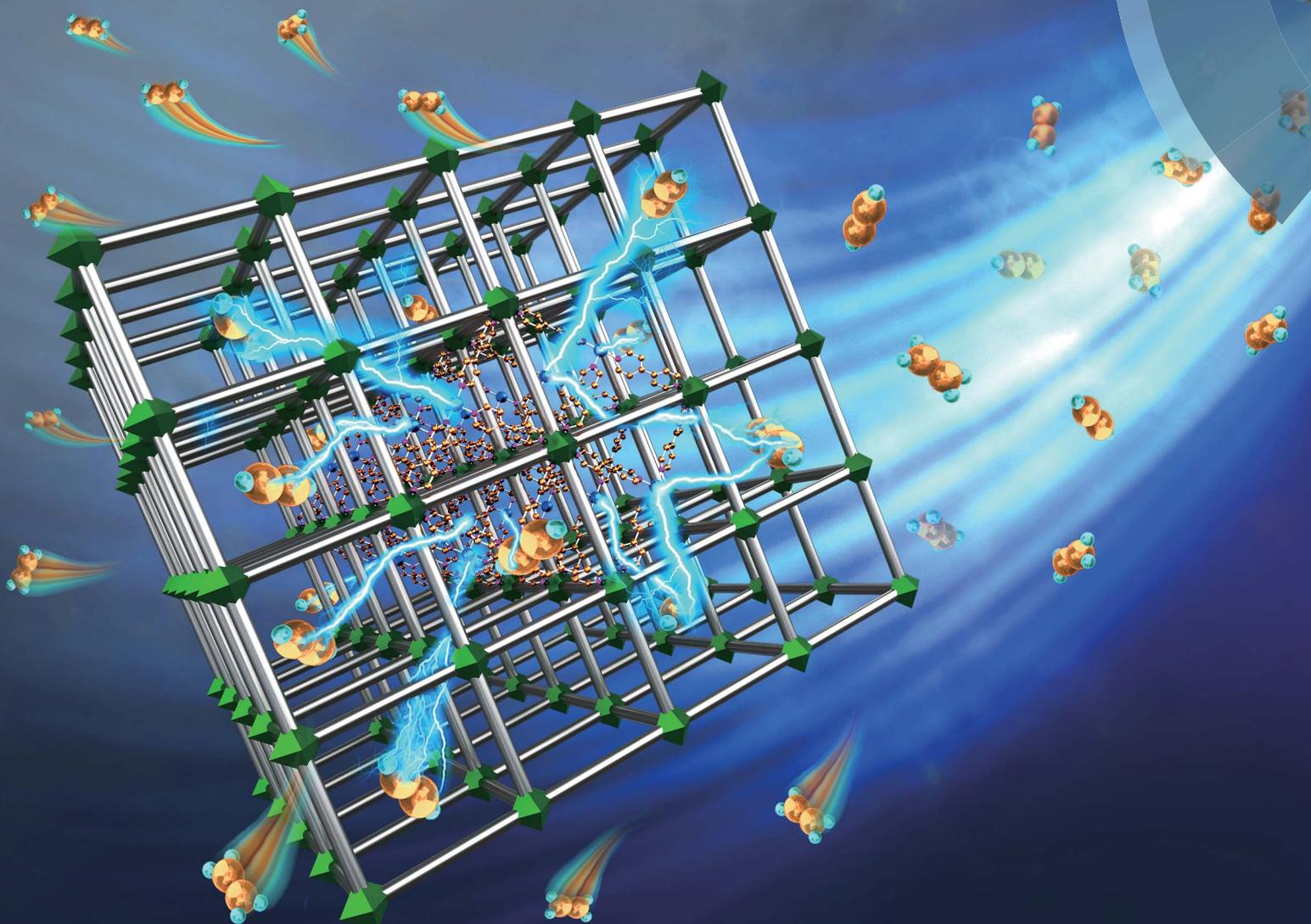


# Journal of Materials Chemistry A

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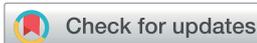
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**PAPER**

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Efficient separation of ethylene from acetylene/ethylene mixtures  
by a flexible-robust metal-organic framework

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## Efficient separation of ethylene from acetylene/ethylene mixtures by a flexible-robust metal–organic framework†

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During the production of polymer-grade ethylene, trace amounts of acetylene (about 1%) in the ethylene feed need to be reduced to 40 parts per million (ppm). We herein report a metal–organic framework (MOF) of flexible-robust nature for the efficient removal of acetylene from acetylene/ethylene mixture to meet such a challenging separation need. Neutron powder diffraction studies reveal that its specific binding sites and unique pore structure collectively enable this MOF (ELM-12) to efficiently and selectively adsorb acetylene over ethylene under ambient conditions, making it feasible for this challenging separation. The purity of obtained ethylene is over 99.999%, as demonstrated by experimental breakthrough curves of 1/99 acetylene/ethylene mixture.

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### Introduction

Nowadays, oil and natural gas resources are supplying human needs worldwide. Large quantities of chemicals in the petrochemical industry are produced and purified into purer forms, and these separation processes account for 10–15% of the world's energy consumption.<sup>1</sup> Ethylene (C<sub>2</sub>H<sub>4</sub>), one of the most widely used organic chemicals in the world, is produced by steam cracking in the petroleum refining process. In the production of polymer-grade C<sub>2</sub>H<sub>4</sub>, the removal of trace acetylene (C<sub>2</sub>H<sub>2</sub>) (about 1%) from C<sub>2</sub>H<sub>4</sub> gas must meet the requirement of ≤40 parts per million (ppm) C<sub>2</sub>H<sub>2</sub> for the downstream polymerization reaction.<sup>2,3</sup> Traditional methods, such as cryogenic distillation and partial hydrogenation of C<sub>2</sub>H<sub>2</sub>, are energy intensive, so there is an urgent need to develop efficient adsorbents for C<sub>2</sub>H<sub>2</sub> capture from C<sub>2</sub>H<sub>4</sub>.

In recent years, metal–organic frameworks (MOFs) with porous structures and designable frameworks have received considerable attention, as they offer great opportunities for revolutionizing some industrial applications, especially in the storage, separation and purification of gases.<sup>4–12</sup> Indeed, based on their sieving and preferential binding effects, a number of microporous MOFs have shown great promise for effective C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation *via* pore tuning and functionalization. In 2011, Xiang *et al.* reported the first example of microporous MOFs for the efficient separation of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures.<sup>13</sup> Based on the sieving effect, M'MOF-3a enabled the full entrance of the smaller-sized C<sub>2</sub>H<sub>2</sub> and basically blocked C<sub>2</sub>H<sub>4</sub> molecules, exhibiting high C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> selectivity, but the relatively low uptake of C<sub>2</sub>H<sub>2</sub> restricted its separation capacity. Later, Hu *et al.* reported a microporous MOF UTSA-100 which can exhibit highly efficient removal of acetylene from C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99) mixtures.<sup>3</sup> UTSA-100 has the special zigzag narrow channels (window opening 3.3 Å) and –NH<sub>2</sub> functionalized pore channels, which collaboratively enabled high C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> selectivity and high C<sub>2</sub>H<sub>2</sub> uptake capacity at low pressure, based on both sieving and preferential binding effects.<sup>3</sup> Very recently, the report of SIFSIX materials represented great progress in C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation, where the preferential binding and orderly assembly of C<sub>2</sub>H<sub>2</sub> molecules through cooperative host–guest and/or guest–guest interactions allow unprecedented performance in the separation of trace amounts of C<sub>2</sub>H<sub>2</sub> from C<sub>2</sub>H<sub>4</sub> gas mixtures.<sup>2</sup> Hence, strong binding sites and suitable pore size in robust MOFs are considered to be useful for C<sub>2</sub>H<sub>2</sub> separation. Note, however, that higher adsorption affinity (isosteric heat of adsorption) will lead to greater energy costs during the regeneration process.<sup>14,15</sup> Therefore, generally, ideal porous materials for gas separation should exhibit high

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† Electronic supplementary information (ESI) available: Powder XRD patterns, adsorption selectivities of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (50/50) predicted by IAST at 298 K, regenerability and structural stability data of ELM-12. CCDC 1545783. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ta05598f

adsorption selectivity and large adsorption capacity for the target gas molecules,<sup>16–23</sup> as well as relatively low adsorption heat for easy regeneration.

Herein, we report a microporous MOF [Cu(bpy)<sub>2</sub>(OTf)<sub>2</sub>]<sup>24–26</sup> (ELM-12, bpy = 4,4'-bipyridine, OTf<sup>−</sup> = trifluoromethanesulfonate) with a flexible-robust structure for the efficient removal of trace C<sub>2</sub>H<sub>2</sub> from C<sub>2</sub>H<sub>4</sub> mixtures. This type of flexible-robust MOF is different from traditional flexible and robust MOFs in that their guest-free phases or intermediate phases possess robust pore structures. At relative low pressure, such flexible-robust MOFs will exhibit adsorbate-dependent gas sorption isotherms and thus can be theoretically applied to gas separation, which has basically been overlooked. ELM-12 exhibits high C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> selectivity and low C<sub>2</sub>H<sub>2</sub> adsorption heat, which is very good for practical gas separation applications. The special binding affinity and suitable pore confinement for C<sub>2</sub>H<sub>2</sub> account for its high C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> selectivity, as clearly evidenced by neutron powder diffraction studies. Its separation potential has been further established by IAST calculations and transient separation experiments. The trace amounts of C<sub>2</sub>H<sub>2</sub> can be readily removed from a C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99) mixture to produce high-purity C<sub>2</sub>H<sub>4</sub> (over 99.999%) under ambient conditions.

## Experimental section

### Materials

[Cu(bpy)<sub>2</sub>(OTf)<sub>2</sub>] (ELM-12): the synthetic method described by Kondo *et al.* was improved as follows:<sup>25</sup> A solution of bpy (10.0 mmol L<sup>−1</sup>, 10.0 mL) in ethanol was carefully layered onto an aqueous solution of Cu(OTf)<sub>2</sub> (5.0 mmol L<sup>−1</sup>, 10.0 mL) in a watch glass with no stirring. Then, the mixture was placed in a 298 K incubator for 7 days to give sheet crystals as [Cu(bpy)<sub>2</sub>(OTf)<sub>2</sub>]·2EtOH·H<sub>2</sub>O. Then, the crystals were collected and activated under 10<sup>−6</sup> bar at 393 K until no further weight loss was observed, to give [Cu(bpy)<sub>2</sub>(OTf)<sub>2</sub>] as a guest-free material.

### Characterization

The crystallinities and phase purities of the samples were measured by powder X-ray diffraction (PXRD) with a Rigaku Mini Flex II X-ray diffractometer employing Cu K<sub>α</sub> radiation operated at 30 kV and 15 mA, scanning over the range of 5–40° (2θ) at a rate of 1° min<sup>−1</sup> (Fig. S1†).

### Single-component adsorption measurements

Ultrapure-grade C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> were used for all measurements. Their adsorption isotherms were collected with an Intelligent gravimetric analyser (IGA 001, Hiden, UK). Samples were activated overnight under reduced pressure at 393 K or until no further weight loss was observed.

### Neutron diffraction experiment

Powder neutron diffraction data were collected using the BT-1 neutron powder diffractometer at the National Institute of Standards and Technology (NIST) Center for Neutron Research.

To probe the C<sub>2</sub>H<sub>2</sub> adsorption locations, fully activated ELM-12 sample was loaded in a vanadium can, and a pre-determined pressure (1 bar) of C<sub>2</sub>D<sub>2</sub> was loaded into the sample at room temperature. Diffraction data were then collected on the C<sub>2</sub>D<sub>2</sub>-loaded MOF sample, and Rietveld structural refinement was performed on the data. Both the ELM-12 building block and C<sub>2</sub>D<sub>2</sub> molecules were treated as rigid bodies in Rietveld refinement (to limit the number of variables), with the molecule orientation and centre of mass freely refined. Refinement on lattice parameters, atomic coordinates, thermal factors, gas molecule occupancies, background, and profiles all converge with satisfactory *R*-factors. CCDC 1545783† contains the supplementary crystallographic data of C<sub>2</sub>D<sub>2</sub>-loaded ELM-12. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Breakthrough separation experiments and procedures

The experimental setup consisted of two fixed-bed stainless steel reactors (Fig. S2†), each with inner dimensions of ϕ9 × 150 mm, connected in parallel.<sup>26,27</sup> The horizontal reactors were placed in a temperature-controlled environment maintained at 298 K. The gas flow and pressure were set and controlled at the outlet and inlet by a pressure controller valve and a mass flow meter, and a gas chromatograph continuously monitored the effluent gas from the adsorption bed. For practical considerations, powder samples of ELM-12 were pelletized into particles of a certain size (220–320 μm), and the column was loaded with particles of ELM-12 (4.1380 g). To ensure the homogeneous nature of the synthesized materials, samples from all batches were tested by powder X-ray diffraction.

## Result and discussion

### Adsorption performance of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> on ELM-12

We examined the C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> gas adsorption isotherms of ELM-12 at ambient temperatures of 273 and 298 K under 1 bar in order to figure out its potential for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation. As shown in Fig. 1, ELM-12 rapidly adsorbs C<sub>2</sub>H<sub>2</sub> at low pressure (≤0.1 bar), and its C<sub>2</sub>H<sub>2</sub> uptake reaches 30.1 cm<sup>3</sup> g<sup>−1</sup> (298 K) and 38.3 cm<sup>3</sup> g<sup>−1</sup> (273 K) at 0.1 bar. With increasing pressure, stepwise adsorption appears at 0.25 bar for 298 K and 0.11 bar for 273 K (Fig. 1a and c), which indicates a slight structural transformation during C<sub>2</sub>H<sub>2</sub> adsorption because of the certain flexibility of this MOF.<sup>28–34</sup> At 1 bar and 298 K, the uptake of ELM-12 for C<sub>2</sub>H<sub>2</sub> is up to 57.3 cm<sup>3</sup> g<sup>−1</sup>. Surprisingly, ELM-12 adsorbs much smaller amounts of C<sub>2</sub>H<sub>4</sub> (5.9 cm<sup>3</sup> g<sup>−1</sup> at 0.1 bar and 22.5 cm<sup>3</sup> g<sup>−1</sup> at 1 bar) at 298 K, which implies weaker interactions between the C<sub>2</sub>H<sub>4</sub> molecule and ELM-12. The obvious difference between C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> adsorption indicates that ELM-12 is very promising for the removal of C<sub>2</sub>H<sub>2</sub> from C<sub>2</sub>H<sub>4</sub> mixtures.

To predict the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation performance of ELM-12 and compare it with other materials, ideal adsorbed solution theory (IAST) calculations were conducted on the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99 and 50/50) mixtures (Fig. 1b and S3†). Fig. 1d shows the

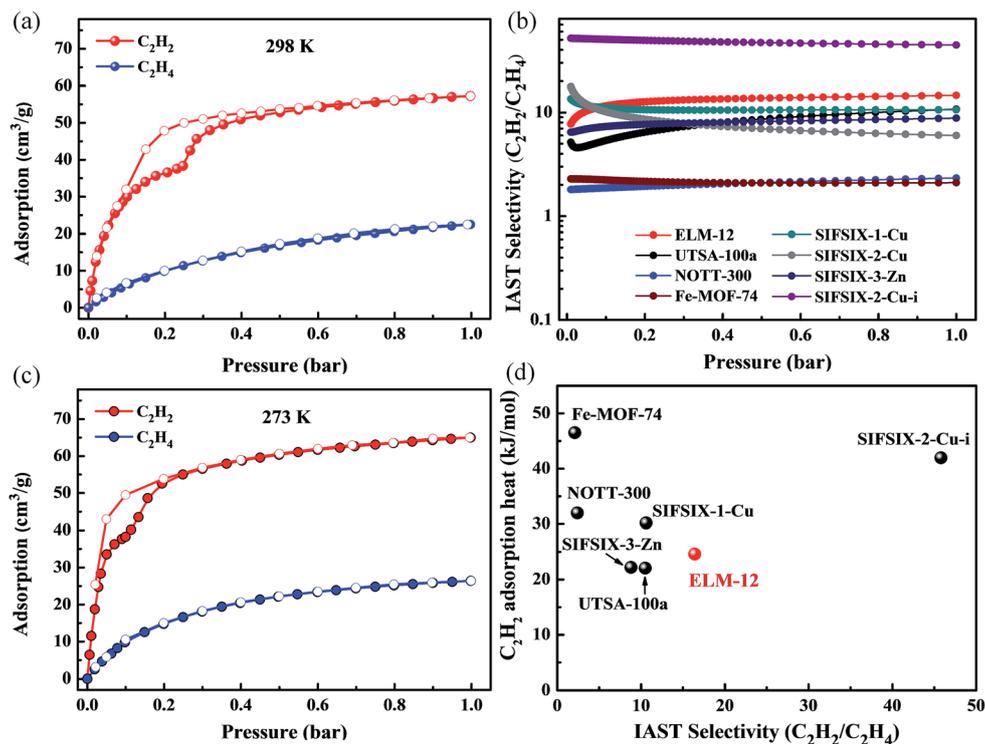


Fig. 1 C<sub>2</sub>H<sub>2</sub> (red) and C<sub>2</sub>H<sub>4</sub> (blue) sorption isotherms for ELM-12 at (a) 298 K and (c) 273 K. (b) Comparison of the IAST selectivities in C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99) mixtures and (d) adsorption heat of ELM-12 versus those of previously reported best-performing materials for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation.

comparison of IAST selectivity and adsorption enthalpy calculated for ELM-12 and other reported materials. The C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> adsorption selectivity of ELM-12 was calculated to be 14.8 at 1 bar, which is higher than those of previously reported MOFs except SIFSIX-2-Cu-i.

IAST separation selectivity values of the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99) mixture at 1 bar decrease in the order of SIFSIX-2-Cu-i > ELM-12 > SIFSIX-1-Cu > UTSA-100a > SIFSIX-3-Zn > SIFSIX-2-Cu > NOTT-300 > Fe-MOF-74. Other than gas separation selectivity, the energy required to regenerate the sorbent during the regeneration process is also very important for practical applications. Interestingly, compared to other materials, ELM-12 exhibits a quite modest adsorption enthalpy ( $Q_{st}$ ) of 25.4 kJ mol<sup>-1</sup> at zero-coverage (Fig. 1d), which is significantly lower than those of SIFSIX-2-Cu-i (42.0 kJ mol<sup>-1</sup>) and Fe-MOF-74 (46.5 kJ mol<sup>-1</sup>). This indicates that the interactions between C<sub>2</sub>H<sub>2</sub> molecules and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anions in ELM-12 are comparatively weak and not as strong as those between C<sub>2</sub>H<sub>2</sub> molecules with SiF<sub>6</sub><sup>2-</sup> in SIFSIX-2-Cu-i or open Fe(II) sites in Fe-MOF-74. Overall, ELM-12 stands out as one of the best materials for the separation of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>, given the fact that it exhibits moderately high C<sub>2</sub>H<sub>2</sub> uptake and selectivity, but also low adsorption enthalpy.

### High-resolution neutron powder diffraction

In order to understand the exceptional performance of C<sub>2</sub>H<sub>2</sub> adsorption in ELM-12, we performed high-resolution neutron powder diffraction on C<sub>2</sub>D<sub>2</sub>-loaded ELM-12. The Rietveld

structural refinements were successfully performed to give a detailed structure of the C<sub>2</sub>D<sub>2</sub> adsorption (Fig. 2). As shown in Fig. 2a, two preferential C<sub>2</sub>H<sub>2</sub> adsorption sites were identified from the data. On site I, two C<sub>2</sub>D<sub>2</sub> molecules are restricted in the pore centre, and each C<sub>2</sub>D<sub>2</sub> is bound by two CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anions from different nets through cooperative C–D⋯O H-bonding (2.43 and 2.44 Å; Fig. 2b), which enables the high C<sub>2</sub>H<sub>2</sub> adsorption observed in ELM-12 at low pressure. On site II, the C<sub>2</sub>D<sub>2</sub> molecule shows slightly weaker binding affinity as implied by its lower occupancy, with a C–D⋯F H-bonding from 2.29 Å to 3.31 Å (Fig. 2d). On both sites, the appropriate pore space provides a geometric optimal cage to restrict the linear C<sub>2</sub>D<sub>2</sub> (3.3 × 3.3 × 5.7 Å<sup>3</sup>) molecule. Thus, we can conclude that the exceptional performance of C<sub>2</sub>H<sub>2</sub> adsorption in ELM-12 is attributed to its optimal pore sizes and polar functional moieties for binding C<sub>2</sub>H<sub>2</sub>. Structure comparison between bare ELM-12 and the C<sub>2</sub>D<sub>2</sub>-loaded structure reveals that the dynamic OTf<sup>-</sup> accordingly adjusts its position/orientation upon C<sub>2</sub>H<sub>2</sub> loading (Fig. S1†), while the overall crystal lattice stays nearly unchanged (the average interlayer distance increasing by only ~1.7%). Also, the geometric pore volume (0.141 cm<sup>3</sup> g<sup>-1</sup>) remains almost the same as that of guest-free ELM-12 (0.138 cm<sup>3</sup> g<sup>-1</sup>). The crystallographic data of C<sub>2</sub>D<sub>2</sub>-loaded ELM-12 is shown in Table S2.†

### Dynamic separation of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures in ELM-12

Furthermore, we performed an actual breakthrough experiment to establish the feasibility of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separations, in which

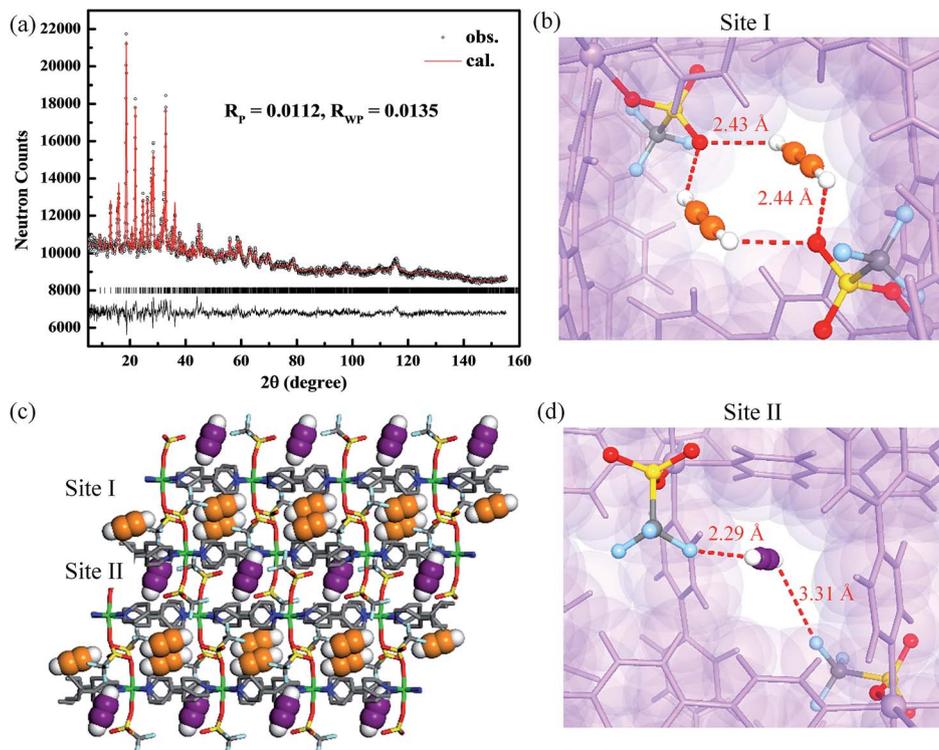


Fig. 2 (a) and (c) Rietveld refinement of the neutron powder diffraction ELM-12  $\supset$  2.5C<sub>2</sub>D<sub>2</sub> at 298 K (Cu, green; C, gray; O, red; S, yellow; F, light blue). (b) and (d) The two preferential binding sites for C<sub>2</sub>D<sub>2</sub> adsorption (sites I and II) in ELM-12.

C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99 and 50/50) mixtures were used as feeds to mimic the industrial process conditions (Fig. 3 and S4<sup>†</sup>). As shown in Fig. 3, C<sub>2</sub>H<sub>4</sub> firstly eluted through the bed to yield a polymer-grade gas, then, after a long period of time, C<sub>2</sub>H<sub>2</sub> broke through from the adsorption bed. The capacity of C<sub>2</sub>H<sub>2</sub> captured from the 1/99 mixture in ELM-12 was as high as 175 mmol per liter, and the concentration of C<sub>2</sub>H<sub>4</sub> obtained from the outlet reached higher than 99.999%. Clearly, the C<sub>2</sub>H<sub>2</sub> was efficiently removed by the ELM-12 material, reducing impurity concentration to lower than 10 ppm. In addition, ELM-

12 exhibits excellent separation performance on the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (50/50) mixture (Fig. S4<sup>†</sup>), and the concentration of C<sub>2</sub>H<sub>4</sub> can be upgraded to higher than 99.995%.

In normal industrial environments, an adsorbent should also possess good structural stability and regenerability. To ensure the cycling performance and regenerability of the ELM-12, we performed C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> adsorption and C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99) cycling experiments at 1 bar and 298 K. As shown in the ESI (Fig. S5 and 6<sup>†</sup>), all C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> adsorption processes are completely reversible, and the adsorption cycling experiments further indicate no performance loss in C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> adsorption cycles. The cycling column breakthrough curves also show that ELM-12 can keep its separation ability for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99) separation mixtures over 20 cycles. Because of the low C<sub>2</sub>H<sub>2</sub> adsorption heat, ELM-12 can be easily regenerated after the breakthrough experiments, and the adsorbed C<sub>2</sub>H<sub>2</sub> can be fully removed under He flow for 30 minutes at 373 K. Furthermore, an aged sample was evaluated through PXRD and C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99) separation at 298 K (Fig. S7<sup>†</sup>). The results showed that ELM-12 material possesses excellent structure stability, and its crystal structure and adsorption ability remain unchanged after two years of storage in regular sample vials.

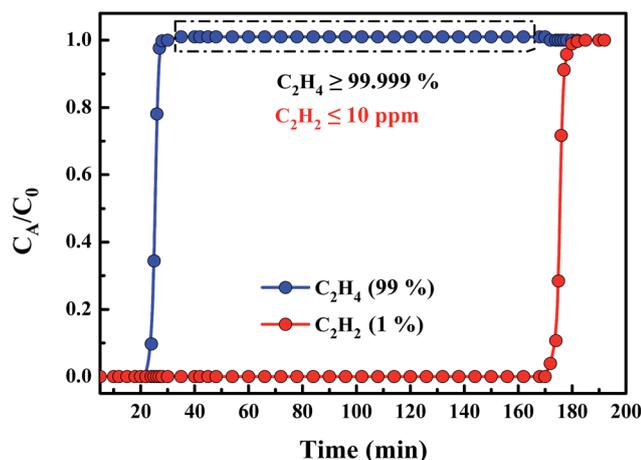


Fig. 3 Experimental column breakthrough curves of ELM-12 material for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99 mixture) separation at 298 K and 1 bar.

## Conclusions

We have identified a flexible-robust porous MOF (ELM-12) for the highly efficient removal of C<sub>2</sub>H<sub>2</sub> from C<sub>2</sub>H<sub>4</sub> mixtures. By using high-resolution neutron powder diffraction with Rietveld

structural refinements, we revealed the two primary C<sub>2</sub>H<sub>2</sub> binding sites in ELM-12. The separation potential of ELM-12 has been established by IAST calculations and transient breakthrough experiments. Based on a fixed-bed adsorber, C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures can be purified to higher than 99.999%. The high efficiency of ELM-12 in removing trace C<sub>2</sub>H<sub>2</sub> from important raw C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures under ambient conditions to produce high-purity C<sub>2</sub>H<sub>4</sub> indicates that this MOF might be potentially useful for this industrially important separation. It is expected that extensive research on porous MOFs will eventually lead to some practically useful materials at a reasonable cost in the near future for important hydrocarbon separation and purification processes.

## Acknowledgements

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## *Supporting Information*

### **Efficient separation of ethylene from acetylene/ethylene mixtures by a flexible-robust metal-organic framework**

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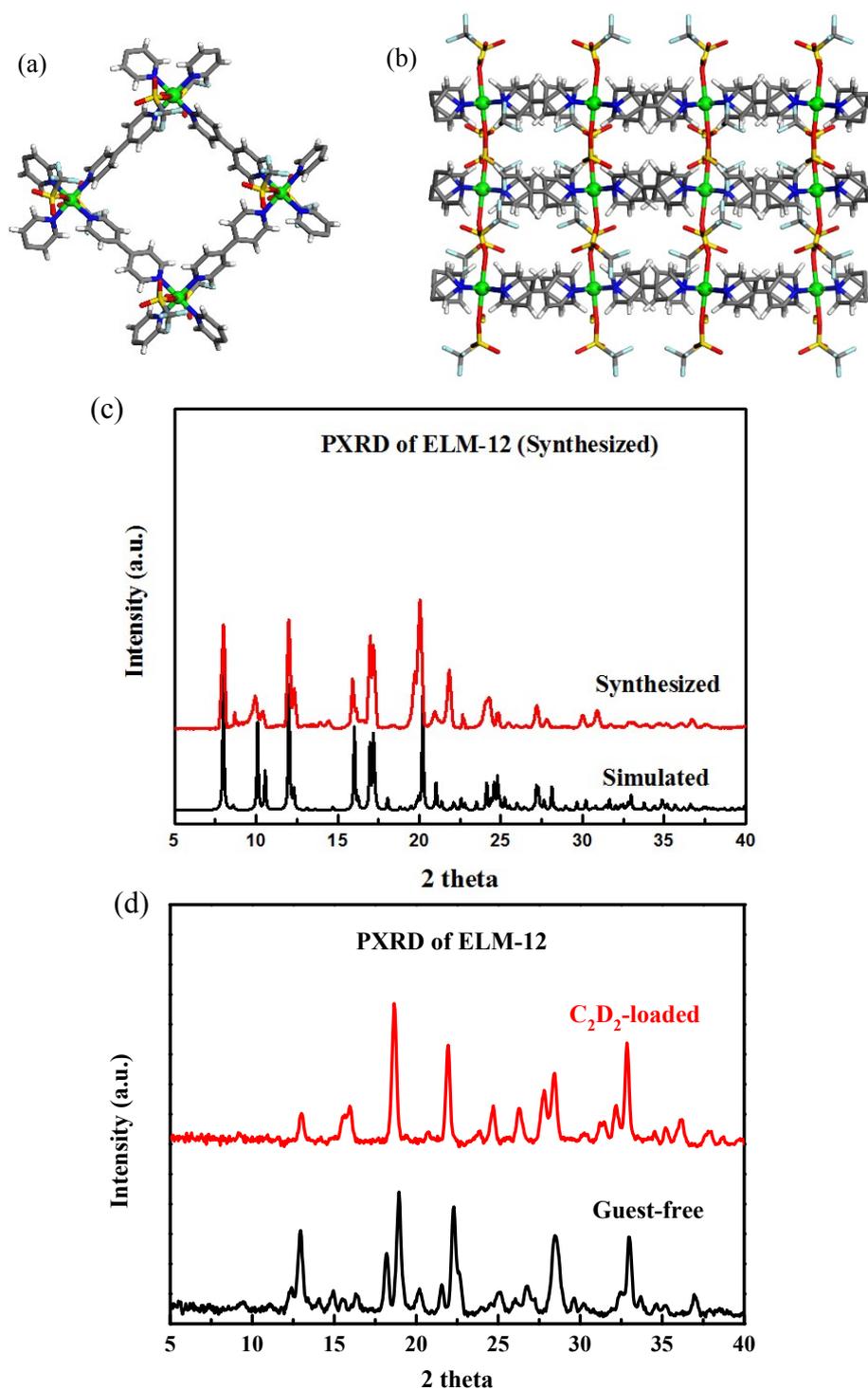
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### Table of Contents

1. Experimental section .....	2
1.1 Synthesis and characterization of ELM-12 .....	2
1.2 Breakthrough experiments .....	3
2. Calculation of the separation potential of ELM-12.....	4
2.1 Fitting of pure component isotherms .....	4
2.2 IAST calculations of adsorption selectivities.....	5
3. Breakthrough curves for C <sub>2</sub> H <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> separation.....	7
4. Adsorption cycling experiments for ELM-12 .....	8
5. Separation cycling experiments for ELM-12 .....	9
6. Structural stability experiments for ELM-12 .....	10

# 1. Experimental section

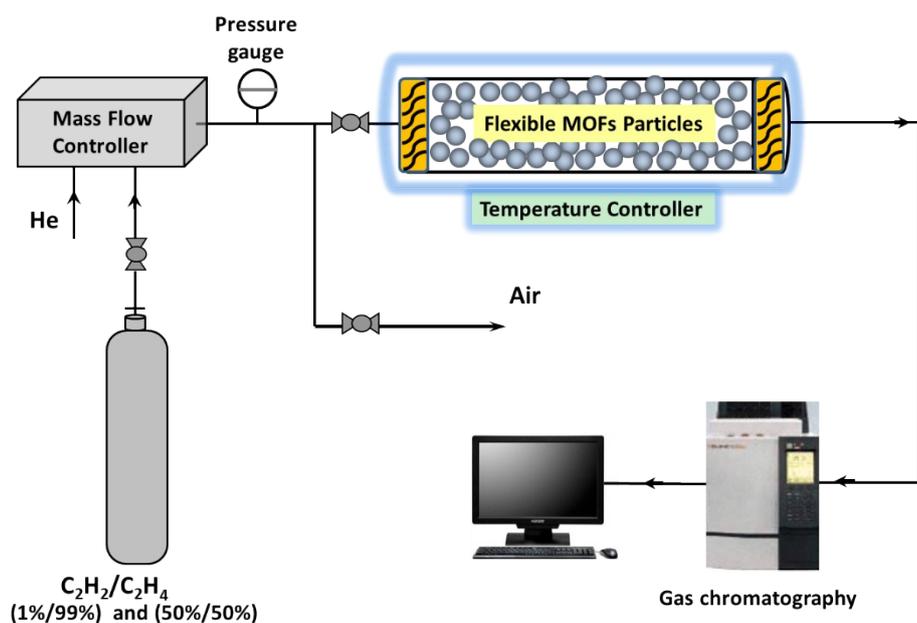
## 1.1 Synthesis and characterization of ELM-12



**Fig S1.** (a, b) Schematic diagram of the structure of ELM-12. (c) Powder X-ray diffraction (PXRD) patterns of synthesized ELM-12 sample. (d) PXRD patterns of guest-free and  $C_2D_2$ -loaded ELM-12 samples. (Cu, green; C, gray; O, red; H, white; S, yellow; F, blue).

## 1.2 Breakthrough experiments

The breakthrough curves were measured on a homemade apparatus for gases mixtures  $C_2H_2/C_2H_4$  (1/99 and 50/50) at 298 K and 1 bar. The gas flows were controlled at the inlet by a mass flow meter as 2 mL/min, and a gas chromatograph (TCD-Thermal Conductivity Detector) continuously monitored the effluent gas from the adsorption bed. Prior to every breakthrough experiment, we activated the sample by flushing the adsorption bed with helium gas for 2 hours at 373 K. Subsequently, the column was allowed to equilibrate at the measurement rate before we switched the gas flow.



**Fig. S2** Breakthrough experiment apparatus.

## 2. Calculation of the separation potential of ELM-12

### 2.1 Fitting of pure component isotherms

The experimentally measured excess loadings for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> at temperatures of 273 and 298 K for ELM-12 were fitted with the dual-Langmuir-Freundlich isotherm model

$$q = q_{A,sat} \frac{b_A p^{v_A}}{1 + b_A p^{v_A}} + q_{B,sat} \frac{b_B p^{v_B}}{1 + b_B p^{v_B}} \quad (1)$$

with  $T$ -dependent parameters  $b_A$ , and  $b_B$

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right); \quad b_B = b_{B0} \exp\left(\frac{E_B}{RT}\right) \quad (2)$$

The parameters are provided in table S1.

For all other MOFs, the isotherm data are taken from Cui et al.<sup>1</sup>

	Site A				Site B			
	$q_{A,sat}$	$b_{A0}$	$E_A$	$v_A$	$q_{B,sat}$	$b_{B0}$	$E_B$	$v_B$
	mol kg <sup>-1</sup>	Pa <sup>-<math>v_i</math></sup>	kJ mol <sup>-1</sup>	dimensionless	mol kg <sup>-1</sup>	Pa <sup>-<math>v_i</math></sup>	kJ mol <sup>-1</sup>	dimensionless
C <sub>2</sub> H <sub>2</sub>	0.65	8.7×10 <sup>-6</sup>	4.5	1.36	2.5	1.87×10 <sup>-9</sup>	24.6	1
C <sub>2</sub> H <sub>4</sub>	1.45	1.54×10 <sup>-8</sup>	18	1				

**Table S1.** Dual-Langmuir-Freundlich fitting parameters for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> isotherms.

### Reference

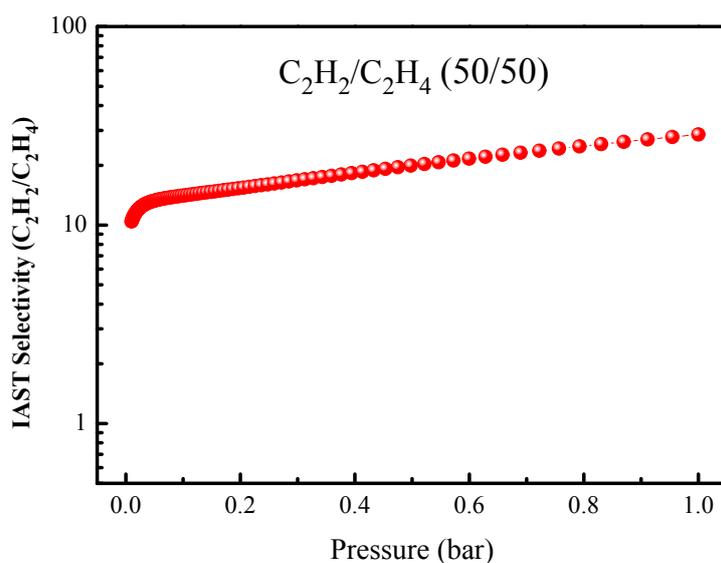
[1] X. Cui, K. Chen, H. Xing, Q. Yang, R. Krishna, Z. Bao, H. Wu, W. Zhou, X. Dong, Y. Han, B. Li, Q. Ren, M. J. Zaworotko, B. Chen, *Science*, **2016**, 353, 141-144.

## 2.2 IAST calculations of adsorption selectivities

We consider the separation of binary  $C_2H_2/C_2H_4$  mixtures. The adsorption selectivity for  $C_2H_2/C_2H_4$  separation is defined by

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \quad (3)$$

$q_1$ , and  $q_2$  are the molar loadings in the adsorbed phase in equilibrium with the bulk gas phase with partial pressures  $p_1$ , and  $p_2$ .



**Fig. S3** IAST calculations of the adsorption selectivity of  $C_2H_2/C_2H_4$  (50/50) mixtures on ELM-12.

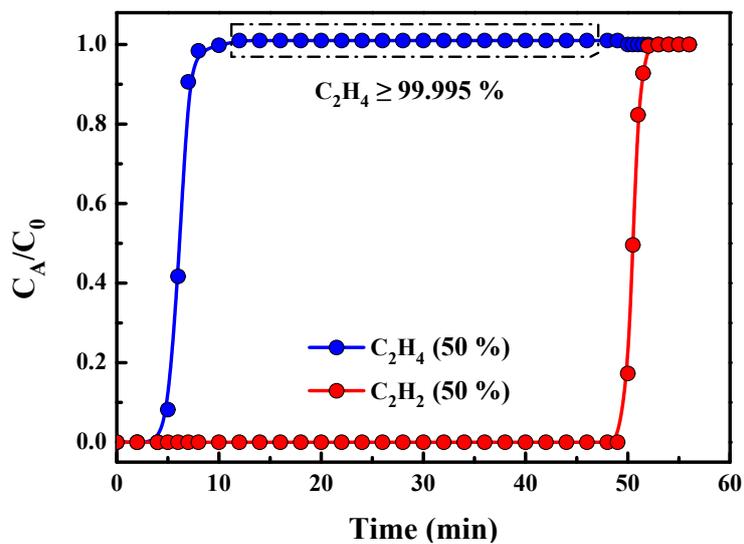
## Notation

$b_A$	Langmuir-Freundlich constant for species $i$ at adsorption site A, $\text{Pa}^{-V_{iA}}$
$b_B$	Langmuir-Freundlich constant for species $i$ at adsorption site B, $\text{Pa}^{-V_{iB}}$
$c_i$	molar concentration of species $i$ in gas mixture, $\text{mol m}^{-3}$
$c_{i0}$	molar concentration of species $i$ in gas mixture at inlet to adsorber, $\text{mol m}^{-3}$
$E$	energy parameter, $\text{J mol}^{-1}$
$L$	length of packed bed adsorber, m
$p_i$	partial pressure of species $i$ in mixture, Pa
$p_t$	total system pressure, Pa
$q_i$	component molar loading of species $i$ , $\text{mol kg}^{-1}$
$Q_{\text{st}}$	isosteric heat of adsorption, $\text{J mol}^{-1}$
$t$	time, s
$T$	absolute temperature, K
$u$	superficial gas velocity in packed bed, $\text{m s}^{-1}$

### *Greek letters*

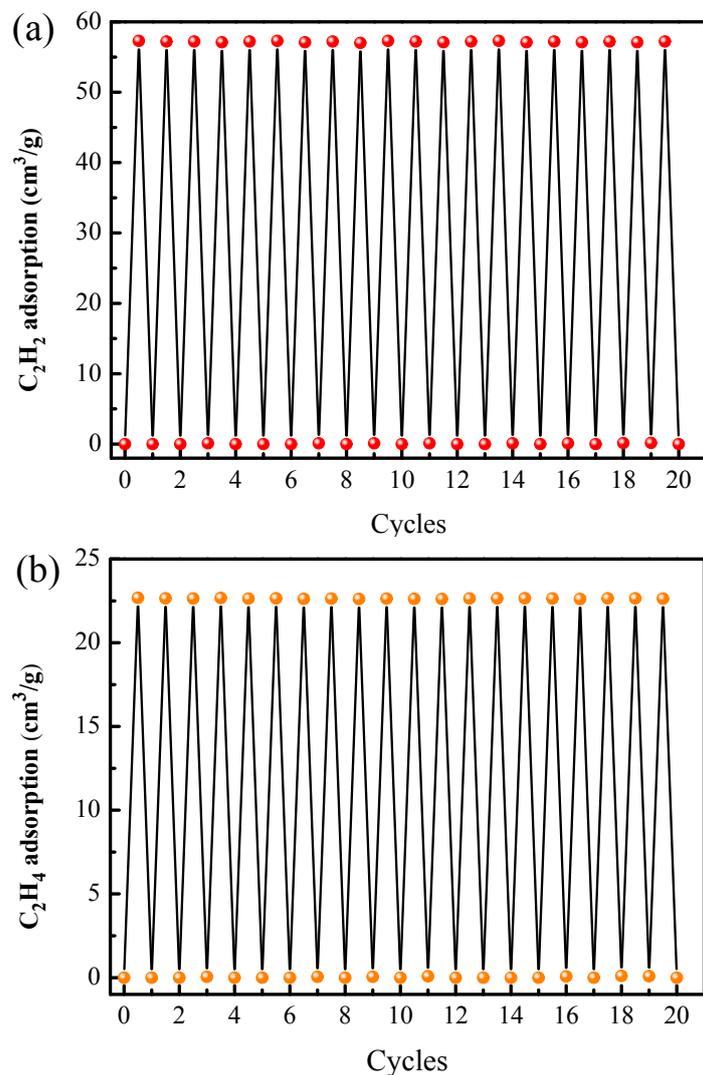
$\varepsilon$	voidage of packed bed, dimensionless
$\nu$	Freundlich exponent, dimensionless
$\rho$	framework density, $\text{kg m}^{-3}$
$\tau$	time, dimensionless

### 3. Breakthrough curves for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation



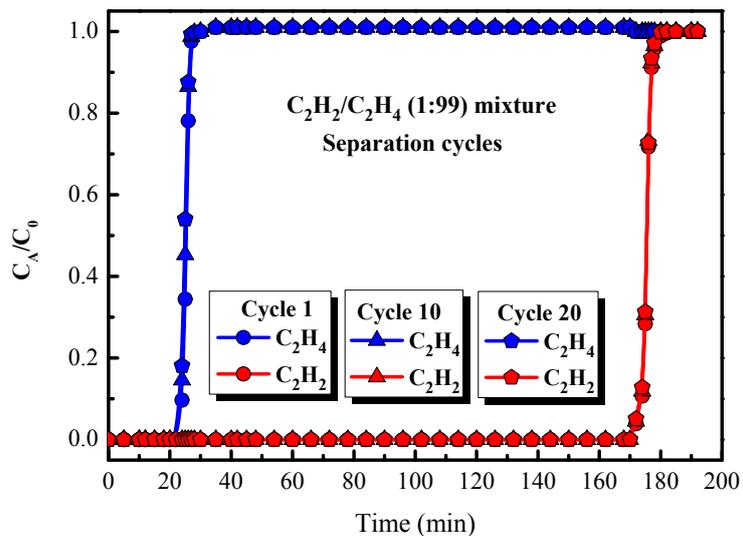
**Fig. S4** Experimental breakthrough curves of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (50/50) mixtures separation for ELM-12 materials at 298 K and 1 bar.

#### 4. Adsorption cycling experiments for ELM-12



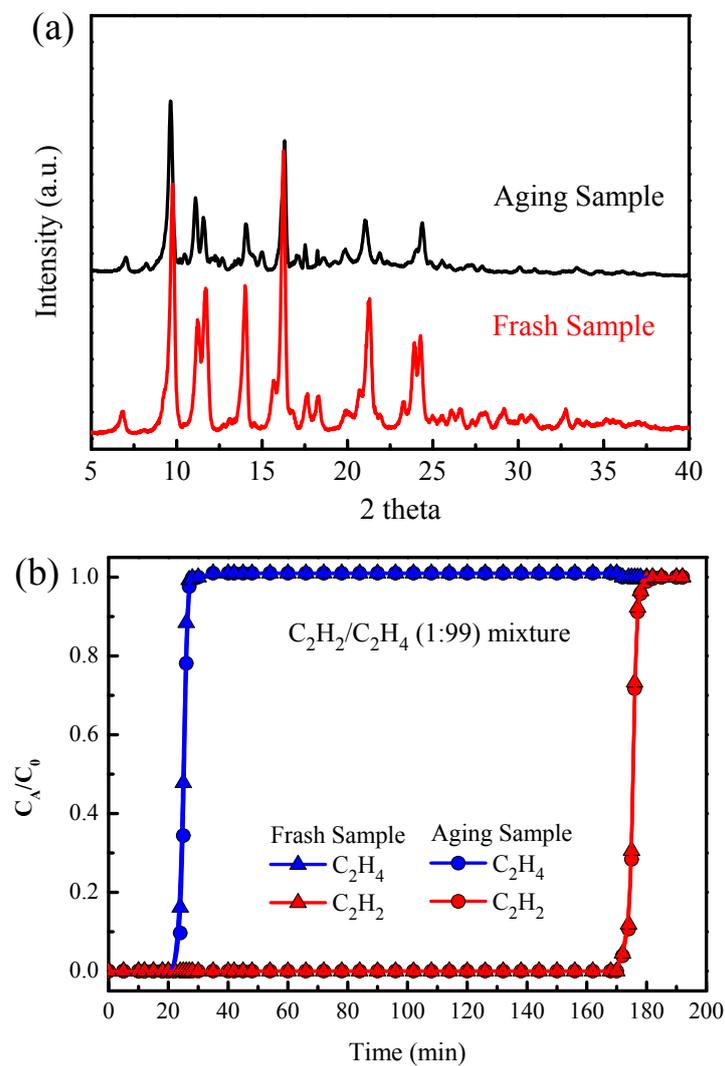
**Fig. S5**  $\text{C}_2\text{H}_2$  (a) and  $\text{C}_2\text{H}_4$  (b) adsorption cycles for ELM-12. After each adsorption process, sample was evacuated under  $10^{-6}$  bar for 30 minutes.

## 5. Separation cycling experiments for ELM-12



**Fig. S6 (a)** Cycling column breakthrough curves of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation (1/99) for ELM-12 at 298 K and 1 bar. The breakthrough experiments were carried out at a flow rate of 2 mL/min. Regeneration with He flow (100 mL/min) for 30 minutes at 373 K.

## 6. Structural stability experiments for ELM-12



**Fig. S7** (a) PXR D and (b) breakthrough experiment of  $C_2H_2/C_2H_4$  (1/99) mixture for ELM-12 samples (fresh sample and two-years aging sample), respectively.

Crystal data	ELM-12 (Guest-free) <sup>#</sup>	ELM-12 (C <sub>2</sub> D <sub>2</sub> )
system	monoclinic	monoclinic
space group	C2/c	C2/c
MF	C <sub>22</sub> H <sub>16</sub> CuF <sub>6</sub> N <sub>4</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>24.43</sub> H <sub>16</sub> CuD <sub>2.43</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6</sub> S <sub>2</sub>
FW	674.05	708.19
a/Å	27.080	27.315
b/Å	15.096	14.930
c/Å	16.136	16.516
α/°	90.00	90.00
β/°	111.344	110.786
γ/°	90.00	90.00
volume/Å <sup>3</sup>	6144	6296.8
Z	8	8
density/g/cm <sup>3</sup>	1.457	1.422
theoretical pore volume/cm <sup>3</sup> /g	0.138 <sup>a</sup>	0.141 <sup>a</sup>
refinement parameters	R <sub>1</sub> = 0.1415, wR <sub>2</sub> = 0.3556	R <sub>p</sub> = 0.0112, R <sub>wp</sub> = 0.0135

<sup>a</sup> Calculated on the basis of the MOF crystal structures using PLATON software.

**Table S2.** Comparison of the Crystallographic and Refinement Parameters for Guest-free ELM-12<sup>#</sup> and C<sub>2</sub>D<sub>2</sub>-loaded ELM-12.

<sup>#</sup> Kondo, A. et al. *J. Am. Chem. Soc.*, **2007**, 129, 12362.

†