Supporting Information

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

Libo Li,[a,b,e] Rui-Biao Lin,[b] Rajamani Krishna,[c] Xiaoqing Wang,[a,e] Bin Li,[b] Hui Wu,[d] Jinping Li,[a,e,*] Wei Zhou,[d,*] and Banglin Chen[b,*]

[a]College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, Shanxi, P. R. China

[b]Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249-0698, United States

[c]Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

[d]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102, United States

[e]Shanxi Key Laboratory of Gas Energy Efficient and Clean Utilization, Taiyuan 030024, Shanxi, P. R. China

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1. Experimental section

1.1 Synthesis and characterization of ELM-12

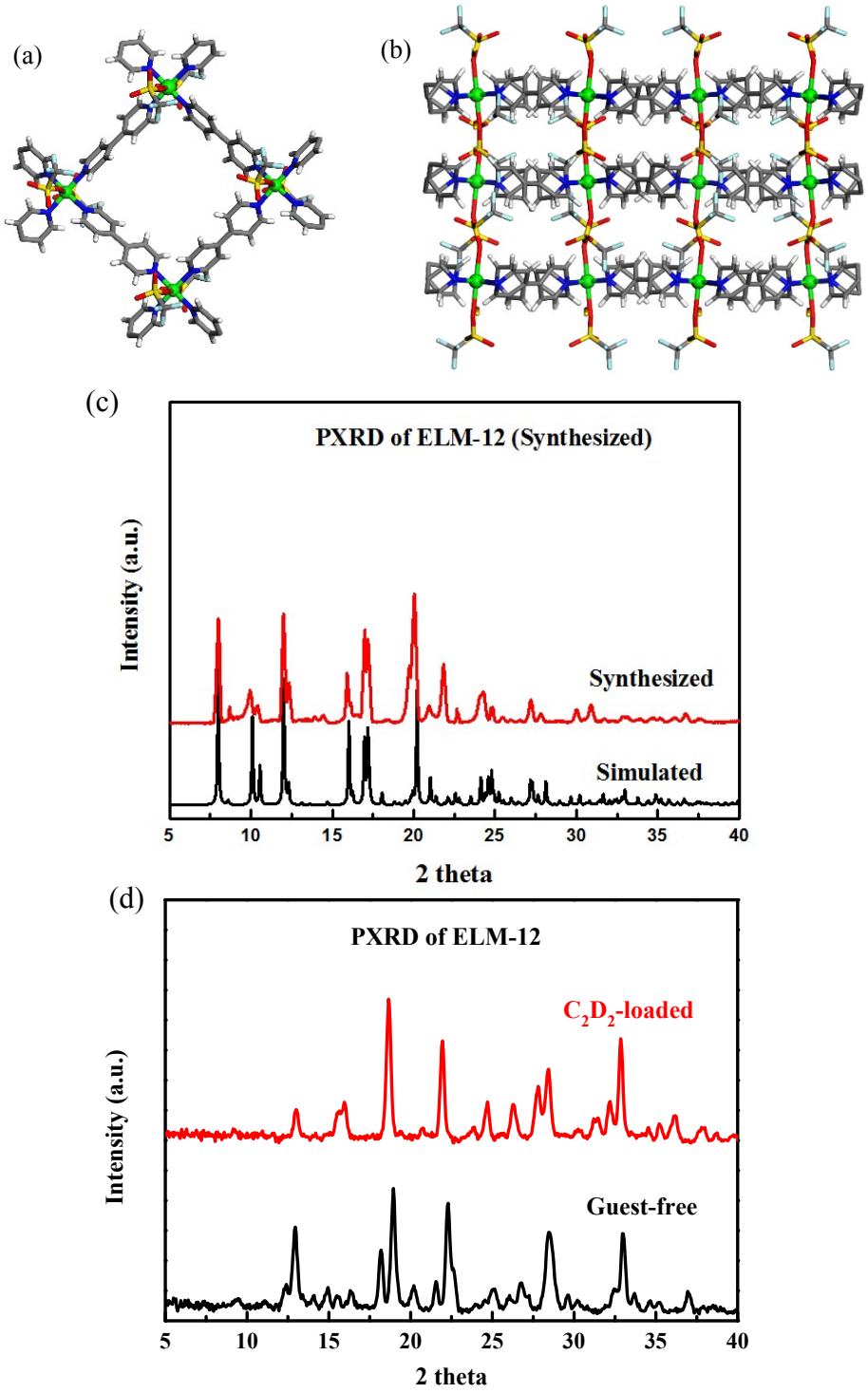

Fig S1. (a, b) Schematic diagram of the structure of ELM-12. (c) Powder X-ray diffraction (PXRD) patterns of synthesized ELM-12 sample. (d) PXRD patterns of guest-free and C_2D_2-loaded ELM-12 samples. (Cu, green; C, gray; O, red; H, white; S, yellow; F, blue).

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.

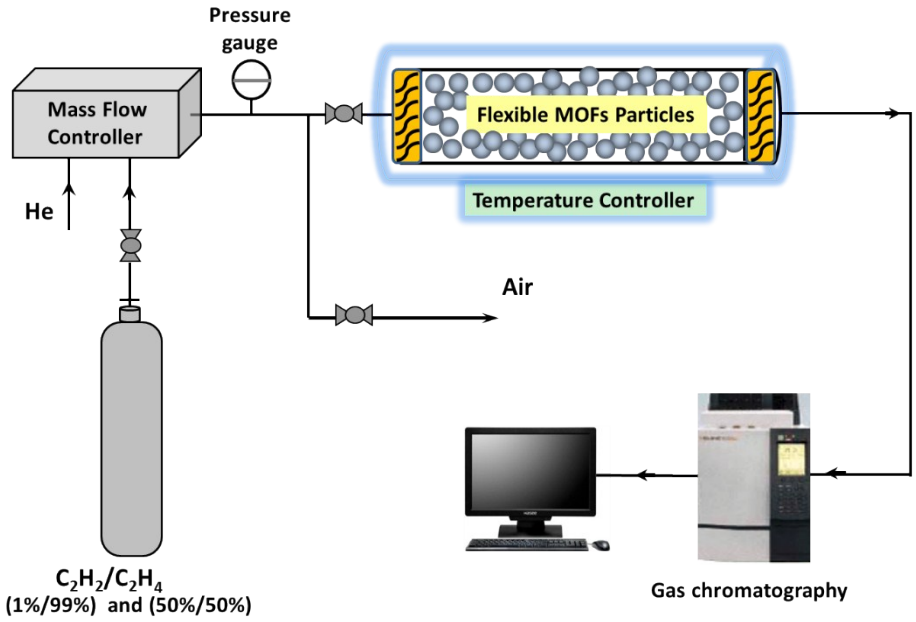

Fig. S2 Breakthrough experiment apparatus.

2. Calculation of the separation potential of ELM-12

2.1 Fitting of pure component isotherms

The experimentally measured excess loadings for C_2H_2 and C_2H_4 at temperatures of 273 and 298 K for ELM-12 were fitted with the dual-Langmuir-Freundlich isotherm model

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

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.[1]

	Site A				Site B			
	$q_{A,sat}$ mol kg^{-1}	b_{A0} Pa$^{-\nu_i}$	E_A kJ mol^{-1}	ν_A dimensionless	$q_{B,sat}$ mol kg^{-1}	b_{B0} Pa$^{-\nu_i}$	E_B kJ mol^{-1}	ν_B dimensionless
C_2H_2	0.65	8.7×10^{-6}	4.5	1.36	2.5	1.87×10^{-9}	24.6	1
C_2H_4	1.45	1.54×10^{-8}	18	1				

Table S1. Dual-Langmuir-Freundlich fitting parameters for C_2H_2 and C_2H_4 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

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \tag{3}$$

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.

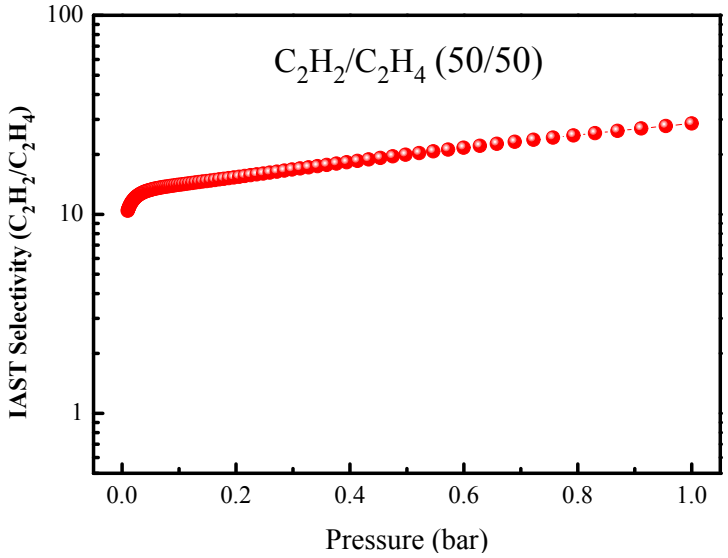

Fig. S3 IAST calculations of the adsorption selectivity of C_2H_2/C_2H_4 (50/50) mixtures on ELM-12.

Notation

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

Greek letters

ε	voidage of packed bed, dimensionless
ν	Freundlich exponent, dimensionless
ρ	framework density, kg m^{-3}
τ	time, dimensionless

3. Breakthrough curves for C_2H_2/C_2H_4 separation

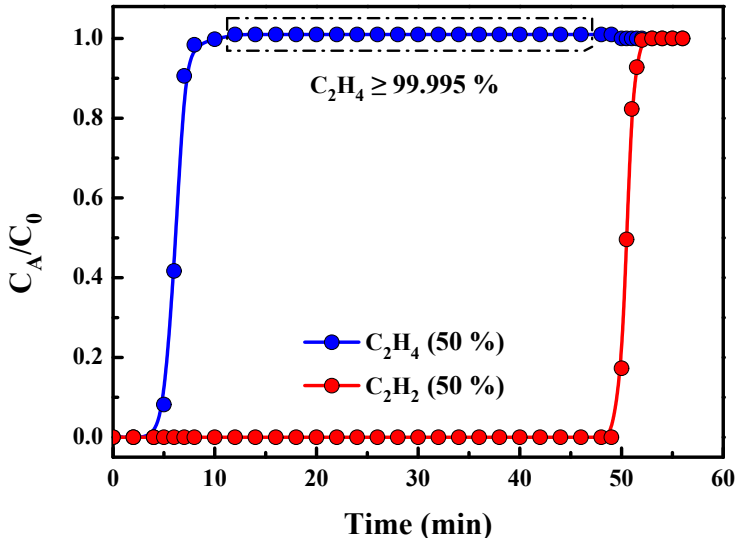

Fig. S4 Experimental breakthrough curves of C_2H_2/C_2H_4 (50/50) mixtures separation for ELM-12 materials at 298 K and 1 bar.

4. Adsorption cycling experiments for ELM-12

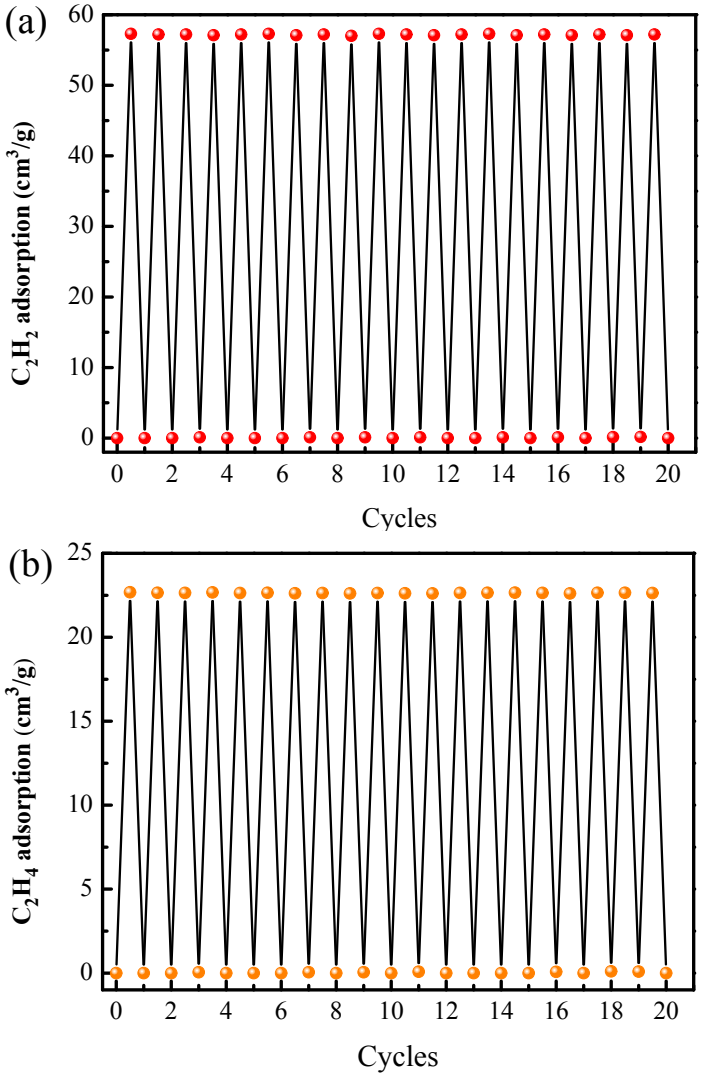

Fig. S5 C_2H_2 (a) and C_2H_4 (b) adsorption cycles for ELM-12. After each adsorption process, sample was evacuated under 10^{-6} bar for 30 minutes.

5. Separation cycling experiments for ELM-12

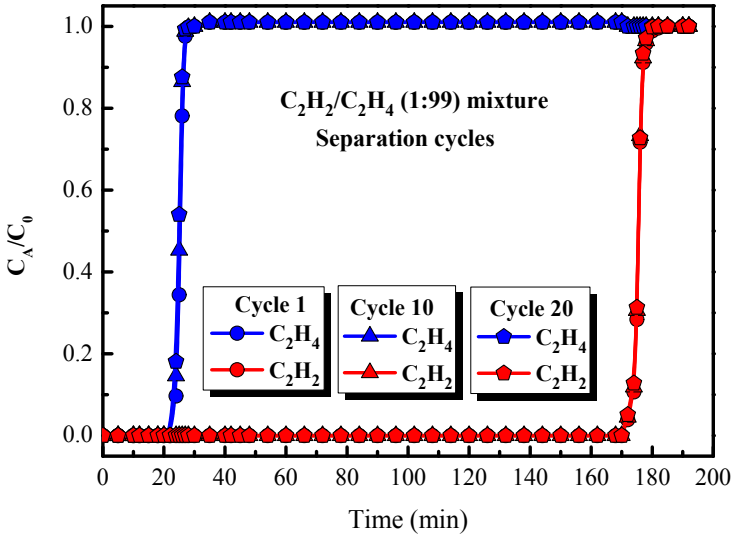

Fig. S6 (a) Cycling column breakthrough curves of C_2H_2/C_2H_4 separation (1/99) for ELM-12 at 298 K and 1 bar. The breakthrough experiments were carried out at a flow rate of 2 mL/min. Regeneration with He flow (100 mL/min) for 30 minutes at 373 K.

6. Structural stability experiments for ELM-12

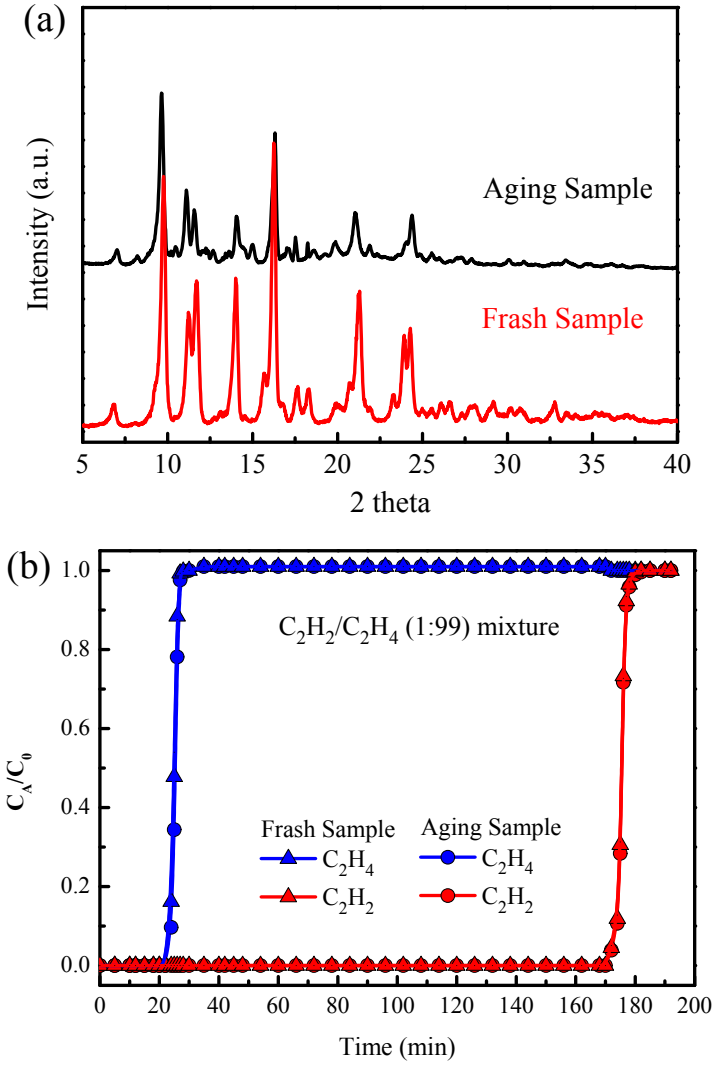

Fig. S7 (a) PXRD and (b) breakthrough experiment of C_2H_2/C_2H_4 (1/99) mixture for ELM-12 samples (fresh sample and two-years aging sample), respectively.

Crystal data	ELM-12 (Guest-free)[#]	ELM-12 (C_2D_2)
system	monoclinic	monoclinic
space group	C2/c	C2/c
MF	$C_{22}H_{16}CuF_6N_4O_6S_2$	$C_{24.43}H_{16}CuD_{2.43}F_6N_4O_6S_2$
FW	674.05	708.19
a/Å	27.080	27.315
b/Å	15.096	14.930
c/Å	16.136	16.516
α/^{o}	90.00	90.00
β/^{o}	111.344	110.786
γ/^{o}	90.00	90.00
volume/Å^3	6144	6296.8
Z	8	8
density/g/cm^3	1.457	1.422
theoretical pore volume/cm^3/g	0.138[a]	0.141[a]
refinement parameters	R_1 = 0. 1415, wR_2 = 0.3556	R_p = 0.0112, R_{wp} = 0.0135

a 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[#] and C_2D_2-loaded ELM-12.

[#] Kondo, A. et al. *J. Am. Chem. Soc.*, **2007**, 129, 12362.

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