Supporting Information

A Microporous Metal –Organic Framework with Rare lvt Topology for Highly Selective C_2H_2/C_2H_4 Separation at Room Temperature

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1. General Procedures and Materials. All reagents and solvents were commercially available and used without further purification. 1,2,4,5-tetraiodobenzene was prepared according to the literature procedure.[1] ^{1}H NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer using tetramethylsilane (TMS) as internal standards. The coupling constants reported in Hertz. FTIR spectra were performed on a Bruker Vector 22 spectrometer at room temperature. The elemental analyses were performed with Perkin–Elmer 240 CHN analyzers from Galbraith Laboratories, Knoxville. Thermogravimetric analyses (TGA) were carried out using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 5 $^{\circ}$C min^{-1}. Powder X–ray diffraction (PXRD) patterns were measured by a Rigaku Ultima IV diffractometer operated at 40 kV and 44 mA with a scan rate of 1.0 deg min^{-1}.

2. Gas sorption Measurements. A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption isotherms. To remove all the guest solvents in the framework, the fresh sample of **UTSA-60** was guest–exchanged with dry acetone at least 10 times, filtered and degassed at 273 K for two days, and then at 296 K for another 2 hours until the outgas rate was 5 μmHg min^{-1} prior to measurements. The sorption measurement was maintained at 77 K with liquid nitrogen. An ice-water bath (slush) and water bath were used for adsorption isotherms at 273 and 296 K, respectively.

3. Single-crystal X-ray crystallography. The crystal data were collected on an Agilent Supernova CCD diffractometer equipped with a graphite-monochromatic enhanced Cu Kα radiation (λ = 1.54184 Å) at 100 K. The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods and refined by full matrix least-squares methods with the SHELX-97 program package.[2] The solvent molecules in the compound are highly disordered. The SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules.[3] The resulting new files were used to further refine the structures. The H atoms on C atoms were generated

geometrically.

4. Fitting of pure component isotherms

Experimental data on pure component isotherms for C_2H_2, and C_2H_4 in **UTSA-60a** were measured at temperatures of 273 K and 296 K. The pure component isotherm data for C_2H_2, and C_2H_4 were fitted with the dual-Langmuir-Freundlich isotherm model

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

with T-dependent parameters b_A, and b_B

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

The fitted parameter values are presented in Table S1. The fits are excellent for both components over the entire pressure range.

5. Isosteric heat of adsorption

The isosteric heat of C_2H_2 adsorption, Q_{st}, defined as

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T}\right)_q \tag{3}$$

was determined using the Clausius-Clapeyron equation by fitting the adsorption isotherms taken at 273 and 296 K to a Langmuir expression. Figure 3c presents a comparison of the heats of adsorption of C_2H_2 in **UTSA-60a** with three other representative MOFs. The values of Q_{st} in **UTSA-60a** is lower than that for the other MOFs with coordinately unsaturated metal atoms **FeMOF-74**, **CoMOF-74**, and **MgMOF-74**.

6. IAST calculations of adsorption selectivities

The selectivity of preferential adsorption of component *1* over component *2* in a mixture containing *1* and *2*, can be formally defined as

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \qquad\qquad (4)$$

In equation (4), q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.[4]

Based on the IAST calculations for C_2H_2/C_2H_4 adsorption selectivities, at a total pressure of 100 kPa, the value of S_{ads} for **UTSA-60a** is in the range of 5.5 − 16, which is much higher than that for **MgMOF-74**, **FeMOF-74**, and **CoMOF-74** in the range of 1.6 to 2.2.

7. Transient breakthrough of C_2H_2/C_2H_4 mixtures in fixed bed adsorbers

The performance of industrial fixed bed adsorbers is dictated by a combination of adsorption selectivity and uptake capacity. For a proper comparison of various MOFs, we perform transient breakthrough simulations using the simulation methodology described in the literature.[5,6] For the breakthrough simulations, the following parameter values were used for **UTSA-60a**: framework density, $\rho = 763$ kg m^{-3}, length of packed bed, $L = 0.12$ m; voidage of packed bed, $\varepsilon = 0.75$; superficial gas velocity at inlet, $u = 0.00225$ m/s. The transient breakthrough simulation results are presented in terms of a *dimensionless* time, τ, defined by dividing the actual time, t, by the characteristic time, $\dfrac{L\varepsilon}{u}$.

The transient breakthrough simulations in Figure S9 show the concentrations of C_2H_2/C_2H_4 exiting the adsorber packed with **UTSA-60a** as a function of the dimensionless time, τ. Analogous breakthrough simulations were performed for **MgMOF-74**, **FeMOF-74**, and **CoMOF-74** using the isotherm fits parameters that are provided in our earlier work.[7] On the basis of the gas phase concentrations, we can calculate the impurity level of C_2H_2 in the gas mixture exiting the fixed bed packed with five different MOFs. Figure S10 shows the ppm C_2H_2 in the outlet gas mixture exiting an adsorber packed with **UTSA-60a**, **MgMOF-74**, **FeMOF-74**, **CoMOF-74**. At a certain time, τ_{break}, the impurity level will exceed the

desired purity level of 40 ppm (indicated by the dashed line), that corresponds to the purity requirement of the feed to the polymerization reactor. The adsorption cycle needs to be terminated at that time τ_{break} and the regeneration process needs to be initiated. From a material balance on the adsorber, the amount of C_2H_4 (of the required purity < 40 ppm C_2H_2) produced during the time interval 0 - τ_{break} can be determined. Table S3 provides a summary of the breakthrough times, τ_{break} for various MOFs and the amount of C_2H_4 produced, expressed in mol per L adsorbent in fixed bed.

Notation

b_A dual-Langmuir-Freundlich constant for species i at adsorption site A, Pa^{-v_i}

b_B dual-Langmuir-Freundlich constant for species i at adsorption site B, Pa^{-v_i}

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_t total molar loading in mixture, mol kg^{-1}

q_{sat} saturation loading, mol kg^{-1}

Q_{st} isosteric heat of adsorption, J $kmol^{-1}$

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

v exponent in dual-Langmuir-Freundlich isotherm, dimensionless

ρ framework density, kg m^{-3}

τ time, dimensionless

Subscripts

i   referring to component i

t   referring to total mixture

Scheme S1. Synthetic routes to the organic linker H_4BTAA.
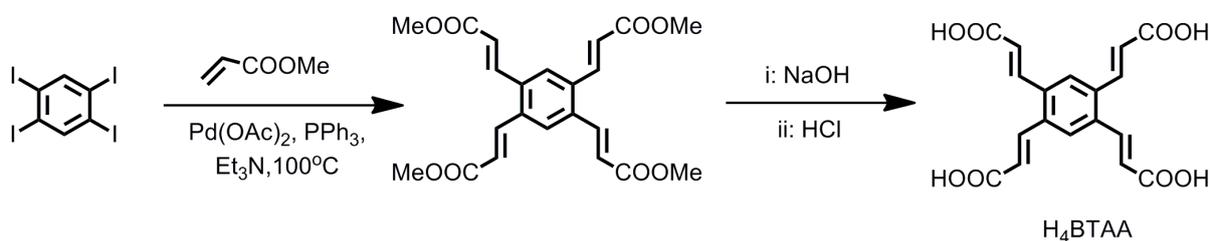
1,2,4,5-tetrakis[(methoxycarbonyl)ethenyl]benzene. In a 15 mL thick-walled Pyrex tube is placed 1,2,4,5-tetraiodobenzene (582 mg, 1 mmol), $Pd(OAc)_2$ (89.8 mg, 0.4 mmol), triphenylphosphine (210 mg, 0.8 mmol), and methyl acrylate (2 mL, 10.7 mmol), and 10 mL of triethylamine. The tube is capped and then heated at 100 ^{o}C for 24 h. After cooling the reactions mixtures, the precipitate was collected by filtration, washed quickly with CH_2Cl_2 for several times, and dried to afford white powder. Yield: 15% (62.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.98 (d, J = 13.25 Hz, 4H), 7.73 (s, 2H), 6.41 (d, J = 13.25 Hz, 4H), 3.84 (s, 12H).

Benzene-1,2,4,5-tetraacrytic acid (H$_4$BTAA). 1,2,4,5-tetrakis[(methoxycarbonyl)ethenyl]benzene (496 mg, 1.2 mmol) was suspended in 30 mL THF, and then a 2M KOH aqueous solution (40 mL) was added. The mixture was stirred under reflux overnight until it became clear. After that THF was removed under reduced pressure and dilute HCl was then added to the remaining aqueous solution to acidify PH = 2. The precipitate was collected by filtration, washed with water for several times, and dried to afford white solid. Yield: 408 mg (95%). ^{1}H NMR (500 MHz, d6-DMSO, ppm): δ = 13.11

(s, 4H), 9.31 (s, 2H), 9.13 (s, 2H), 8.54 (s, 1H), 8.50 (s, 2H), 8.50 (s, 1H). ^{13}C NMR (d^6-DMSO, ppm): δ = 166.69, 166.65, 161.42, 156.24, 137.96, 135.20, 132.79, 132.57, 132.36, 131.95, 130.80, 130.45.

Synthesis of UTSA-60. A mixture of the organic linker H$_4$BTAA (5.0 mg, 0.014 mmol) and Cu(NO$_3$)$_2$·2.5H$_2$O (12.0 mg, 0.052 mmol) was dissolved into a 1.25 mL mixed solvent (DMF/H$_2$O, 1 mL/0.25 mL) in a screw-capped vial (20 mL), to which one drop of HBF$_4$ was added. The vial was capped and heated in an oven at 60 ºC for 24 h. Green block crystals were obtained by filtration and washed with DMF several times to afford UTSA-60 in 65% yield. **UTSA-60** has a best formula as [Cu$_2$BTAA(H$_2$O)$_2$]·2DMF·2H$_2$O, which was obtained based on the basis of single-crystal X-ray structure determination, elemental analysis and TGA. Anal. Calcd for C$_{24}$H$_{32}$N$_2$O$_{14}$Cu$_2$: C, 41.20; H, 4.61; N, 4.00; found: C, 41.09; H, 4.68; N, 4.05. TGA data for loss of 2DMF and 4H$_2$O: calcd: 31.16%, found: 31.25%. IR (neat, cm^{-1}): 1640, 1573, 1478, 1391, 1284, 1188, 1098, 967, 864, 701.
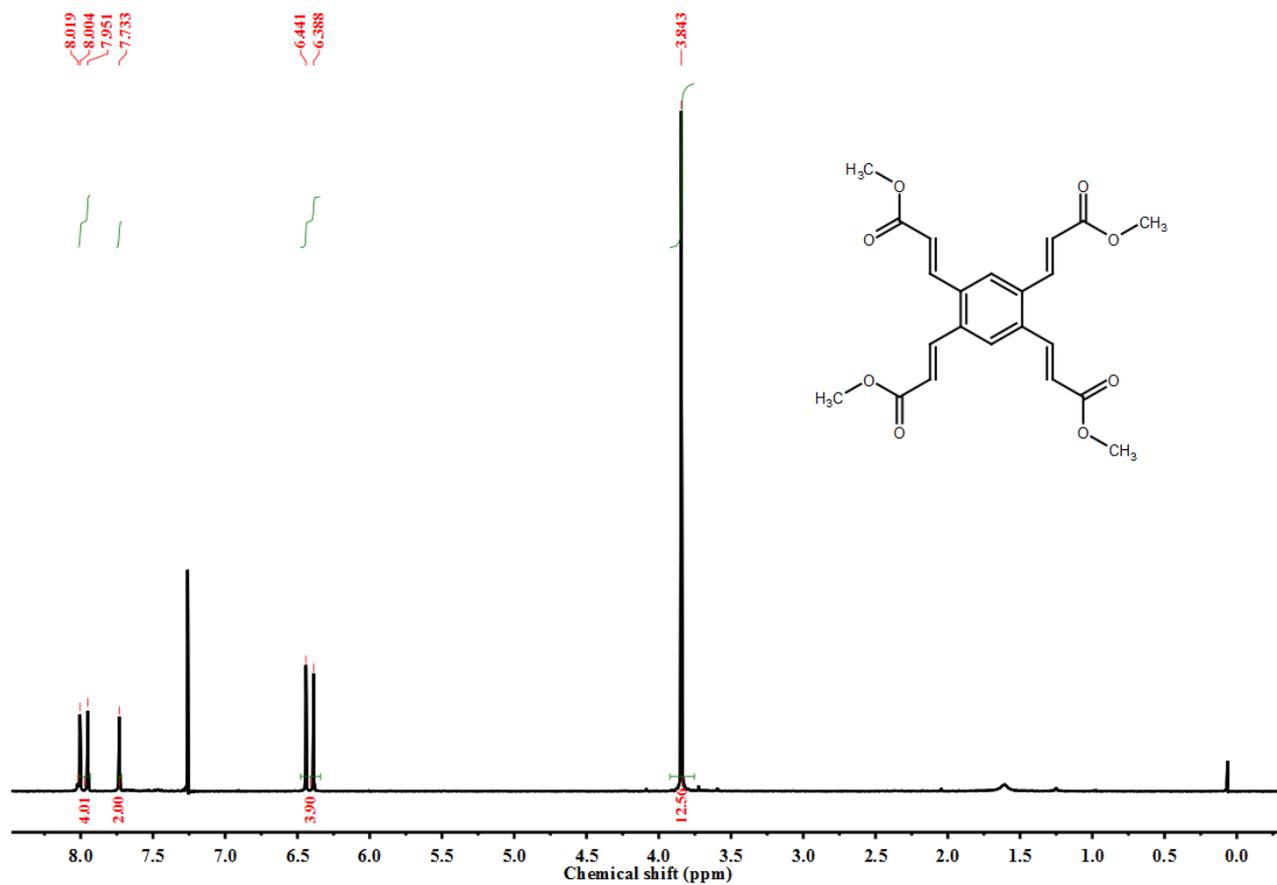
Figure S1. ^1H (CDCl$_3$, 500MHz) spectra of 1,2,4,5-tetrakis[(methoxycarbonyl)ethenyl] - benzene.
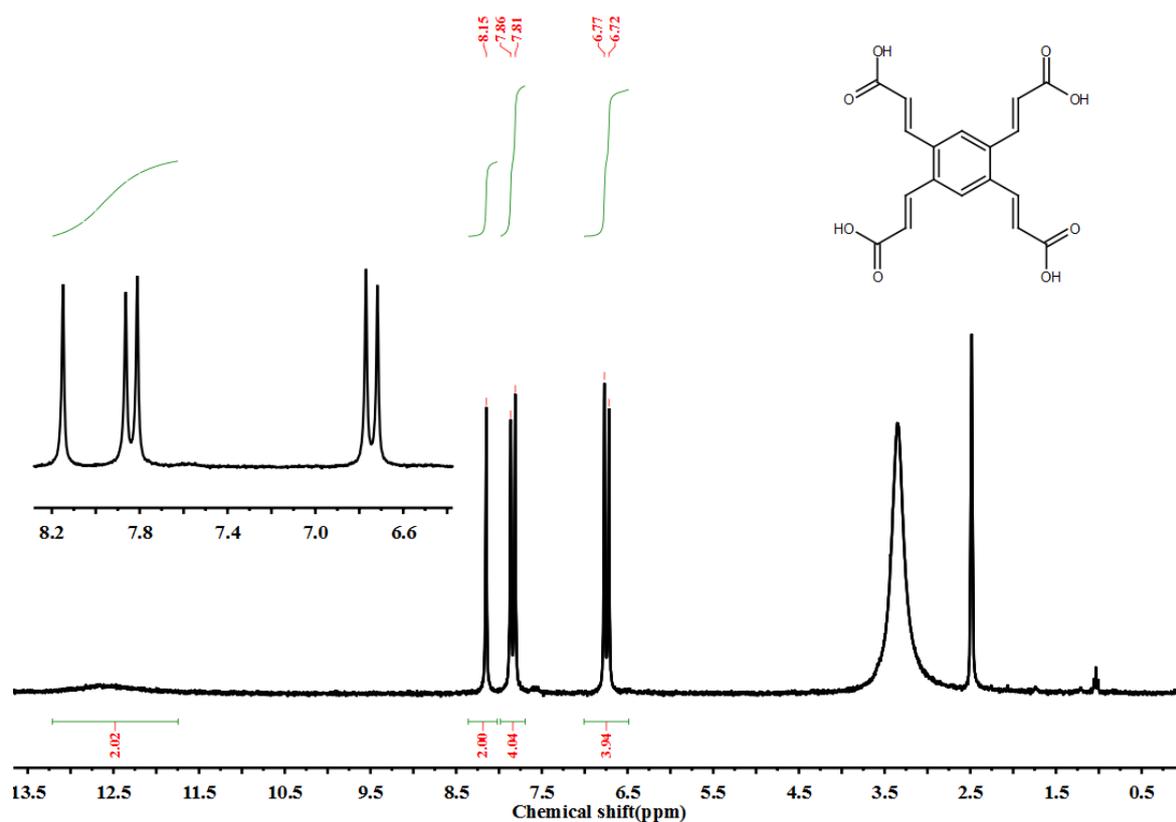
Figure S2. ^{1}H (DMSO-d$_6$, 500MHz) spectra of the ligand H$_4$BTAA.
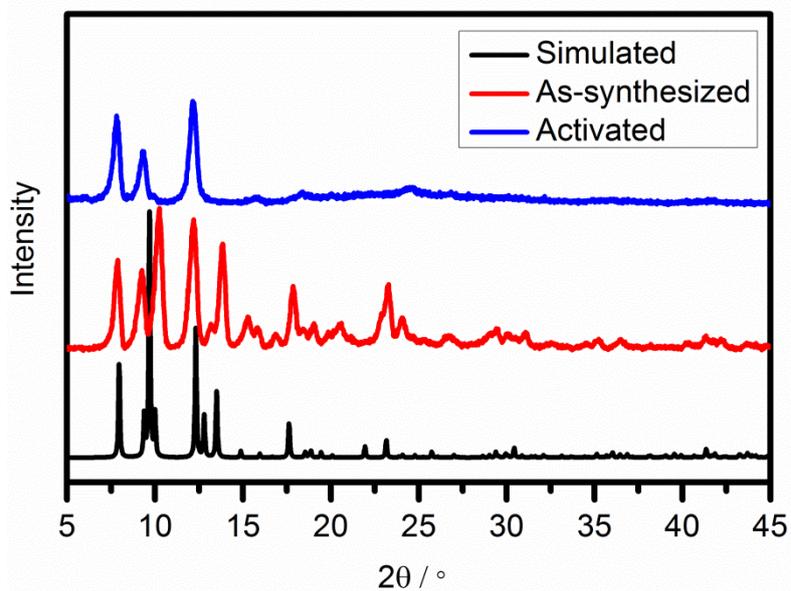
Figure S3. PXRD patterns of as-synthesized **UTSA-60** (red) and activated **UTSA-60a** (blue) along with the simulated XRD pattern from the single-crystal X-ray structure (black).
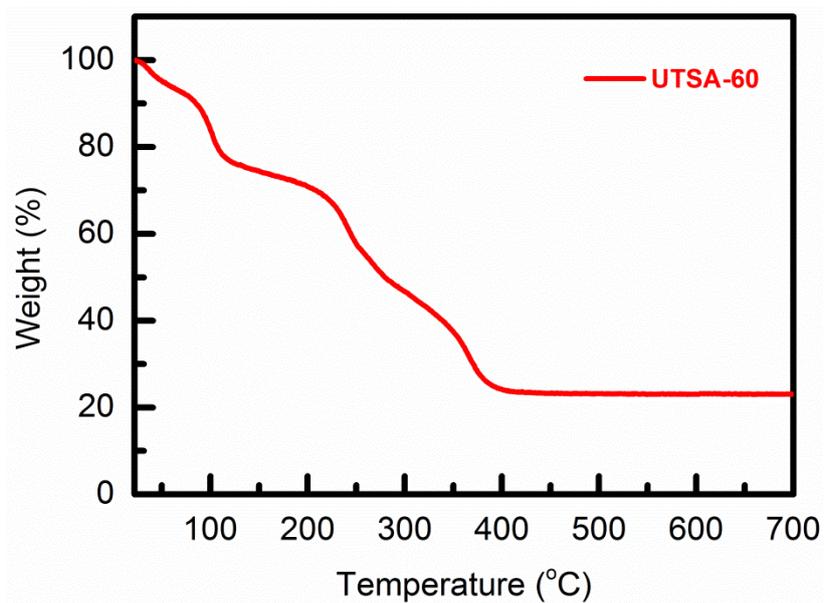
Figure S4. TGA curves of as–synthesized **UTSA-60**.
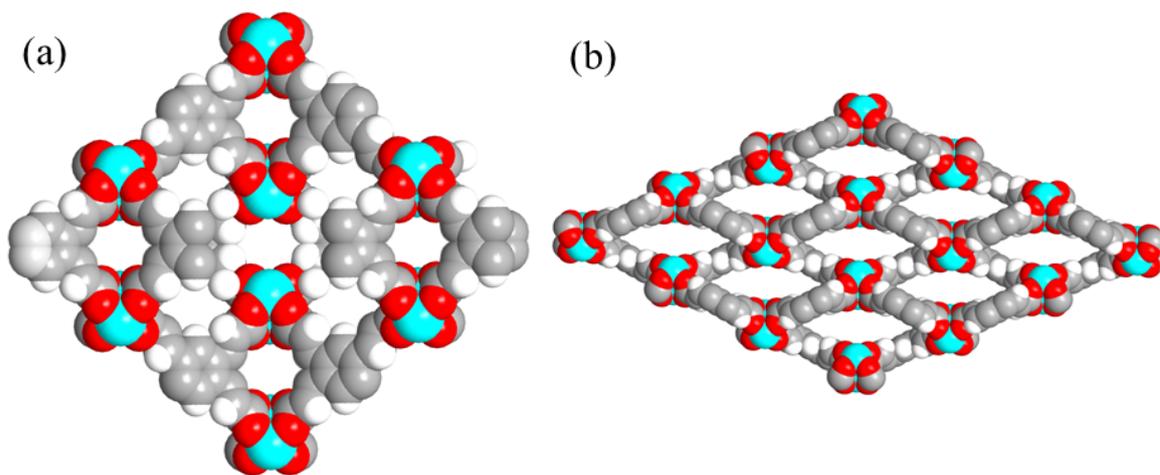
Figure S5. X-ray single crystal structure of **UTSA-60**: (a) the pore channels viewed along the *a* axes; (b) viewed along the *c* axes. Blue, red, gray, and white spheres represent Cu, O, C, and H atoms, respectively.
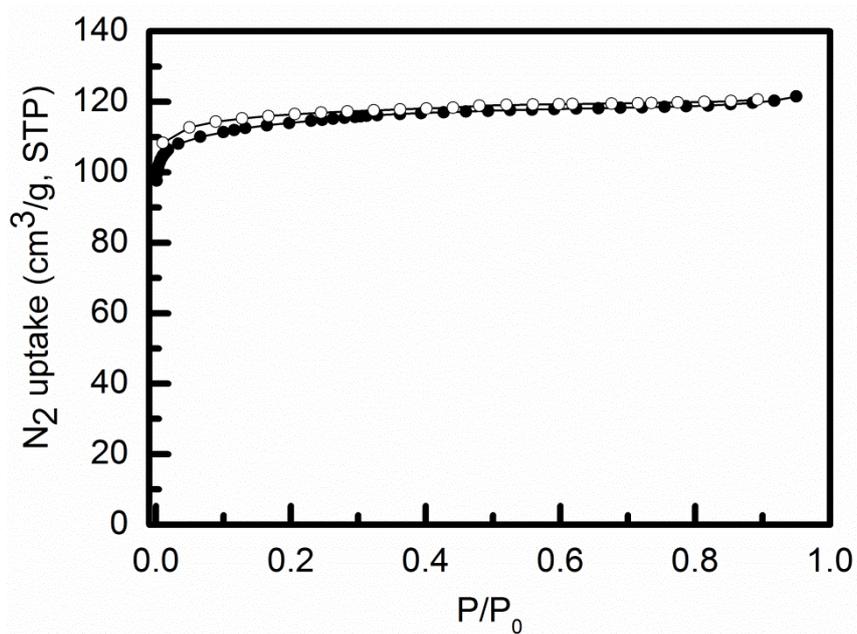
Figure S6. N$_2$ sorption isotherms of **UTSA-60a** at 77 K. Closed symbols, adsorption; open symbols, desorption.
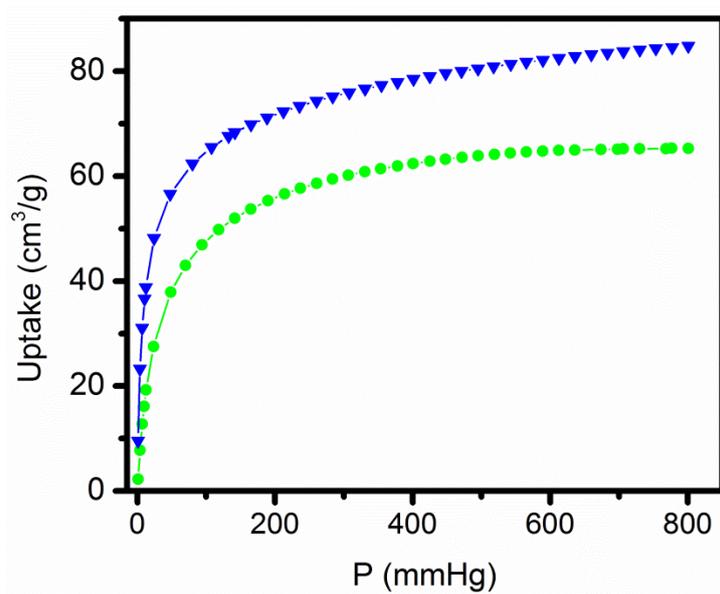
Figure S7. Single-component adsorption isotherms for C$_2$H$_2$ (blue) and C$_2$H$_4$ (green) of **UTSA-60a** at 273 K.
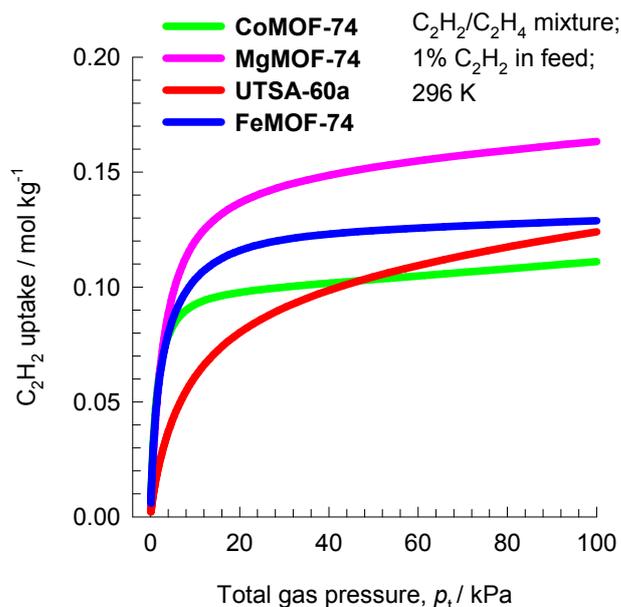
Figure S8. IAST calculations of the uptake capacity of C_2H_2 for adsorption in **UTSA-60a, MgMOF-74**, **FeMOF-74**, and **CoMOF-74** from C_2H_2/C_2H_4 mixtures containing 1% C_2H_2. The partial pressures of C_2H_2, and C_2H_4 are, respectively, $p_1 = 1$ kPa, $p_2 = 99$ kPa at T = 296 K. The data for **FeMOF-74** is at a temperature of 318 K; this is the lowest temperature used in the isotherm measurements of Bloch et al.[8]
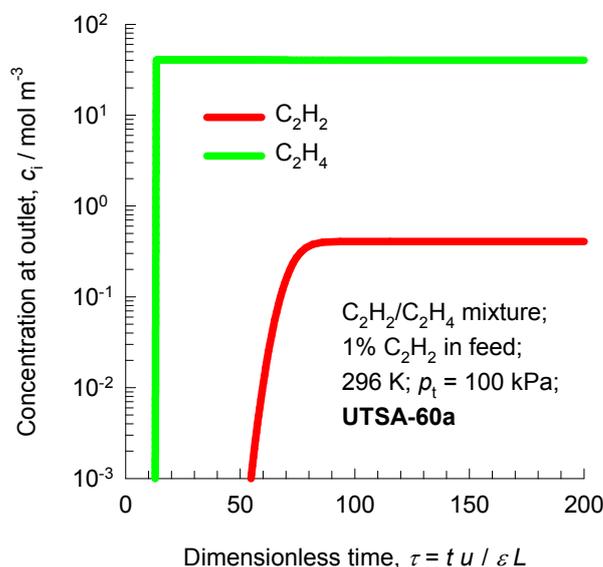
Figure S9. Transient breakthrough of C_2H_2/C_2H_4 mixture containing 1% C_2H_2 mixture in an adsorber bed packed with **UTSA-60a**. The total bulk gas phase is at 296 K and 100 kPa. The partial pressures of C_2H_2, and C_2H_4 in the inlet feed gas mixture are, respectively, $p_1 = 1$ kPa, $p_2 = 99$ kPa. For the breakthrough simulations, the following parameter values were used, as before, $L = 0.12$ m; $\varepsilon = 0.75$; $u = 0.00225$ m/s.
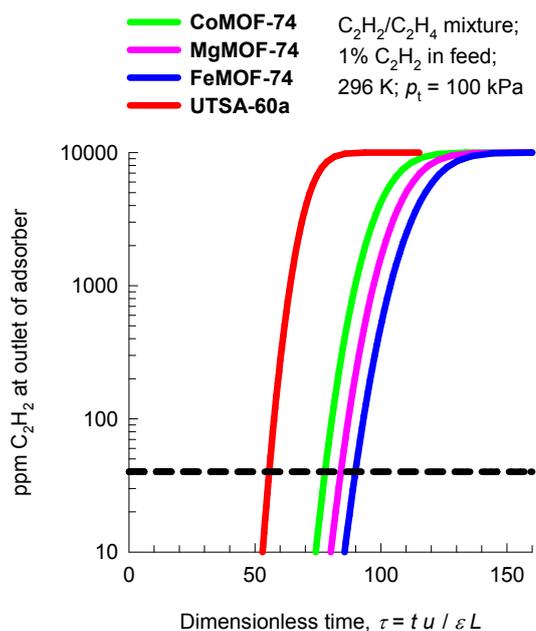
Figure S10. Ppm C_2H_2 in the outlet gas of an adsorber bed packed with **MgMOF-74**, **CoMOF-74**, **FeMOF-74**, and **UTSA-60a**. The total bulk gas phase is 100 kPa; the partial pressures of C_2H_2, and C_2H_4 in the inlet feed gas mixture are, respectively, $p_1 = 1$ kPa, $p_2 = 99$ kPa. The temperature is 296 K for all MOFs except **FeMOF-74** for which the chosen temperature is 318 K.

Table S1. Crystallographic data and structure refinement results for **UTSA-60** (from single-crystal X-ray diffraction analysis on the as-synthesized sample).

	UTSA-60
Formula	$C_{18}H_{14}Cu_2O_{10}$
Formula weight	517.37
Temperature/K	100.00(19)
Crystal system	orthorhombic
Space group	Imma
a (Å)	18.6261(10)
b (Å)	22.1934(9)
c (Å)	10.0062(8)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	4180.7(4)
Z	4
D_{calcd} (g cm^{-3})	0.822
μ (mm^{-1})	1.493
$F(000)$	1040.0
Crystal size/mm^3	$0.40 \times 0.32 \times 0.20$
GOF	0.948
R_{int}	0.0338
R_1, wR_2 [I>=2σ (I)]	0.0639, 0.1574
R_1, wR_2 [all data]	0.0806, 0.1700
Largest diff. peak and hole (e Å^{-3})	0.568, -1.958

Table S2. Dual-Langmuir-Freundlich parameter fits for **UTSA-60a**.

	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	3.3	2.35×10^{-9}	31	0.86	3.1	2.12×10^{-19}	68	1
C_2H_4	2.3	2.82×10^{-13}	46	1.1	0.75	3.17×10^{-36}	146	1.7

Table 3. Breakthrough calculations for separation of C_2H_2/C_2H_4 mixture containing 1 mol% C_2H_2 at 296 K. The data for FeMOF-74 is at a temperature of 318 K; this is the lowest temperature used in the isotherm measurements of Bloch et al.[8] The product gas stream contains less than 40 ppm C_2H_2.

	Dimensionless breakthrough time τ_{break}	C_2H_4 produced during 0 - τ_{break} mol L^{-1}
CoMOF-74	77.4	1.97
MgMOF-74	84	3.93
FeMOF-74	89.6	3.57
UTSA-60a	55	5.1

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