Supporting Information for the manuscript

A Cationic MicroporousMetal-Organic Framework for Highly Selective Separation of Small Hydrocarbons at Room Temperature

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1. Fitting of pure component isotherms

The measured experimental data on pure component isotherms for **ZJU-48a**, were first converted to absolute loading using the Peng-Robinson equation of state for estimation of the fluid densities. The pure component isotherm data for CH_4, C_2H_2, C_2H_4, and C_2H_6, expressed in terms of *absolute* loadings, were fitted with the Langmuir isotherm model

$$q = q_{A,sat} \frac{b_A p}{1 + b_A p} \tag{1}$$

with T-dependent parameter b_A

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right) \tag{2}$$

The fitted parameter values are presented in Table S1. Figure S4 presents IAST calculations of the component molar loadings in equilibrium with an *equimolar* $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture as a function of the total bulk gas phase pressure at 296K.

2. Adsorption selectivity

Let us first consider the separation of CH_4 from a mixture containing C_2 hydrocarbons. Rather than restrict our investigations to just binary CH_4/C_2H_6 mixtures, we consider the selective adsorption of C_2 hydrocarbons from an equimolar 4-component $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture. The choice of such a mixture is dictated by the fact that such mixture separations are encountered in the process oxidative coupling of methane for producing ethene.

We define the *adsorption selectivity*, defined by

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

Here p_1 and p_2 are taken to be the partial pressures of C_2H_6 and CH_4, respectively. The q_1 and q_2 are the molar loadings in the adsorbed phase, C_2H_6 and CH_4, respectively, expressed in mol per kg of adsorbent material.

3. Isosteric heat of adsorption

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

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \tag{4}$$

were determined using the pure component isotherm fits.

4. Breakthrough in fixed bed adsorber unit

In demonstrate the separation performance of a pressure swing adsorption (PSA) unit, we performed breakthrough calculations with step-input of an equimolar $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture. The x-axis in Figure 5 is a dimensionless time, τ, defined by dividing the actual time, t, by the characteristic time, $\frac{L\varepsilon}{u}$.

Table S1. Langmuir isotherm parameter fits for **ZJU-48a**

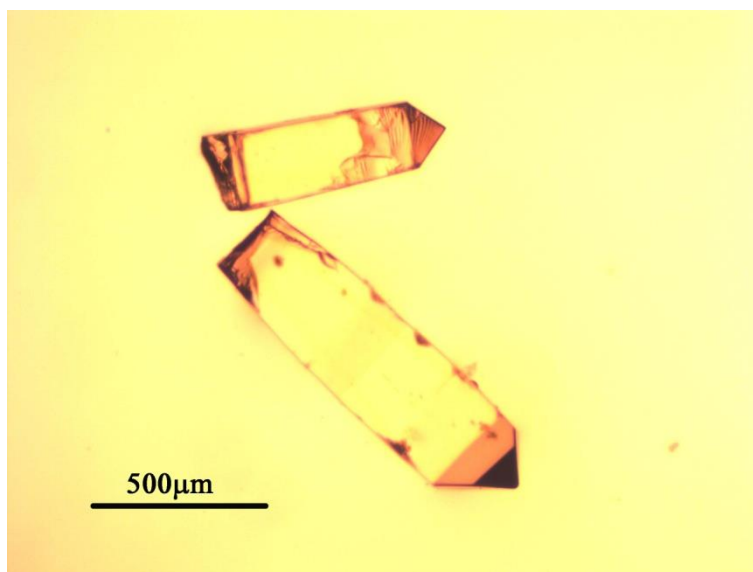|	$q_{A,sat}$ mol kg^{-1}	b_{A0} Pa^{-1}	E_A kJ mol^{-1}
C_2H_2	6.9	9.6×10^{-9}	15.6
C_2H_4	6.9	4.87×10^{-10}	21.7
C_2H_6	9	2.91×10^{-11}	28
CH_4	3.2	4.06×10^{-9}	14

Figure S1 Fluorescent microscope images of **ZJU-48** crystals illuminated with visible light.
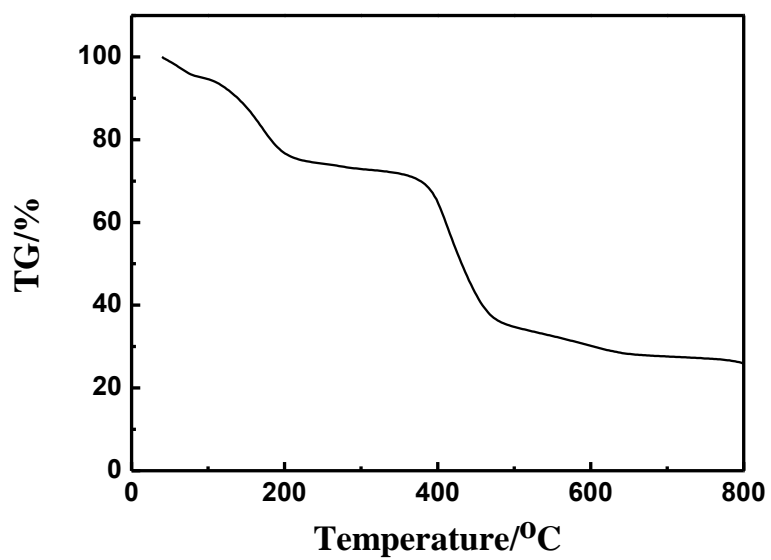

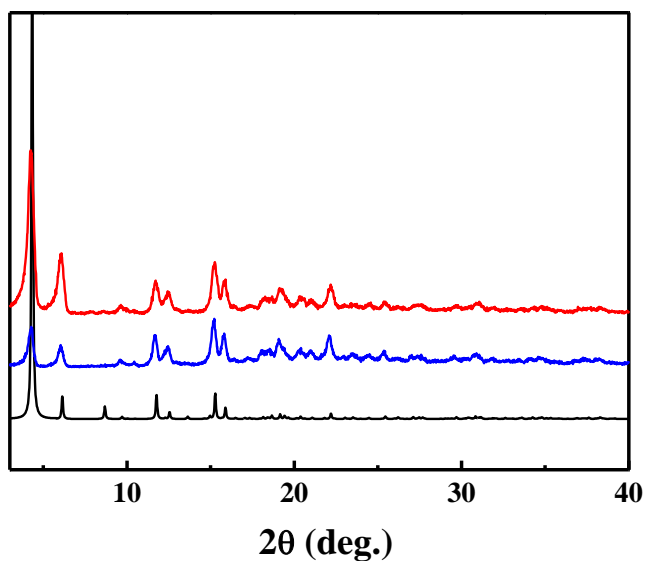**Figure S2**. TG of **ZJU-48**

Figure S3. PXRD patterns of **ZJU-48** (simulated: black; as-synthesized: blue; activated at 0 °C in vacuum for 12h: red).
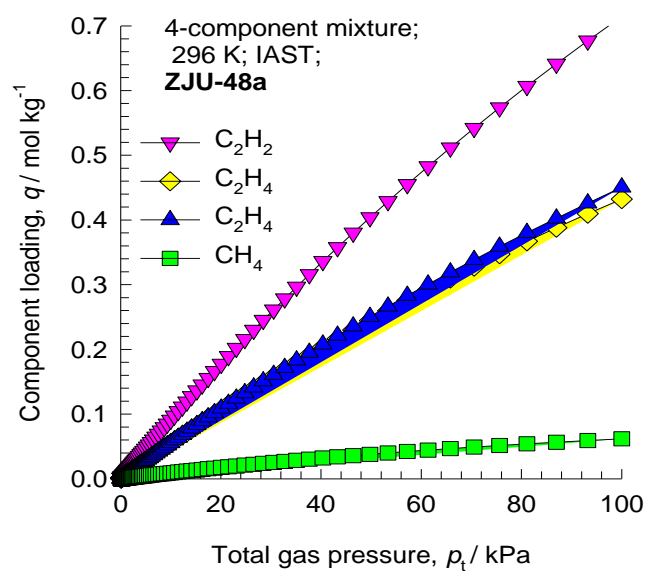

Figure S4. IAST calculations of the component molar loadings in equilibrium with an *equimolar* $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture at total bulk gas phase at 296 K.
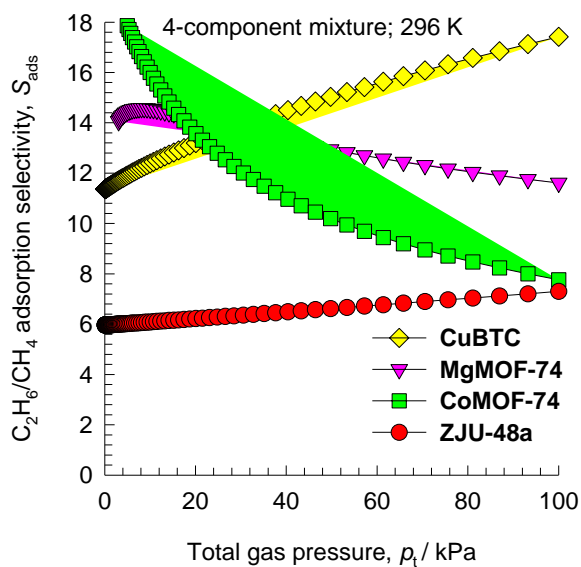
Figure S5. IAST calculations of the C_2H_6/CH_4 adsorption selectivity of four MOFs for adsorption from an equimolar $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture at total bulk gas phase at 296 K.
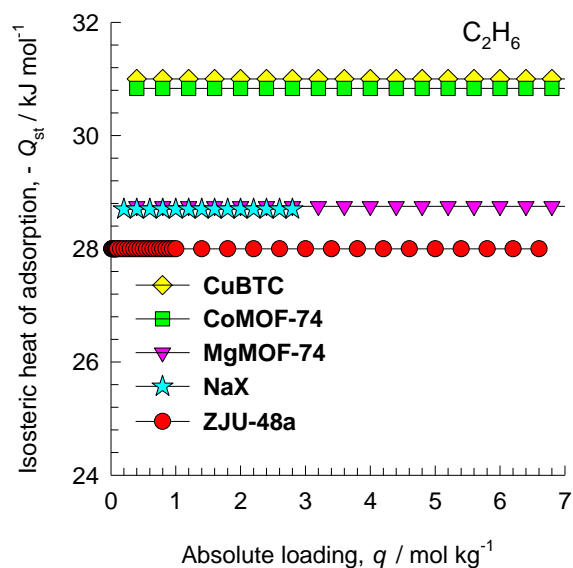
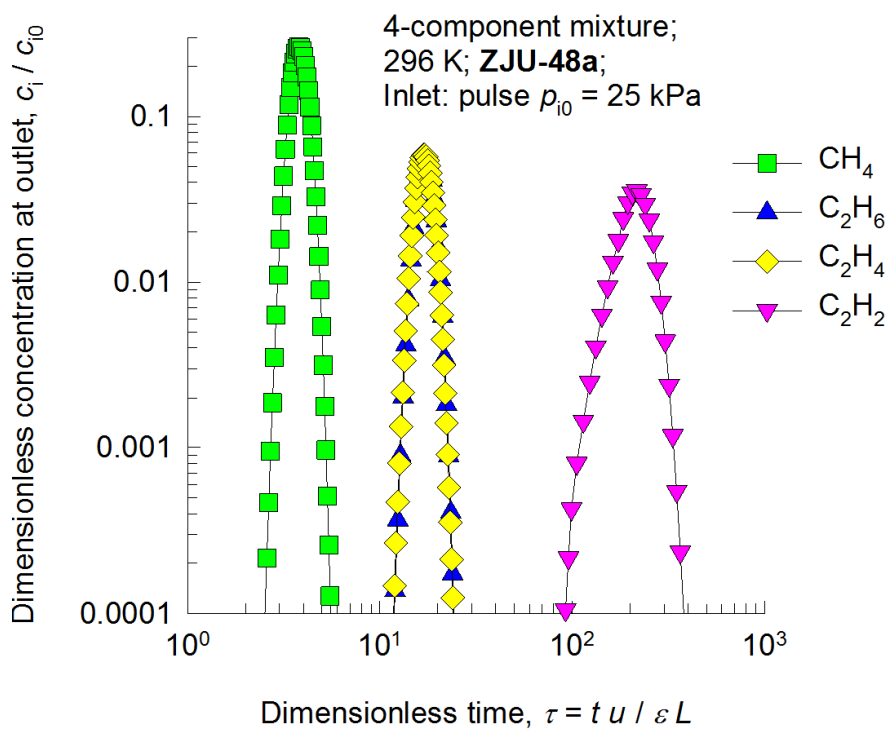**Figure S6** The isoteric heats of adsorption of different porous materials for C_2H_6.

Figure S7. Pulse chromatographic simulations for separation of an *equimolar* 4-component $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture with **ZJU-48a** as adsorbent material. A pulse of the equimolar mixture is injected for 10 s at the start of the process, and subsequently the adsorbed components are desorbed by use of purge inert gas.

5.   References

(1) Myers, A. L.; Prausnitz, J. M. Thermodynamics of mixed gas adsorption, *A.I.Ch.E.J.* **1965**, *11*, 121-130.