Supporting Information For

A pyridyl-decorated Zr-organic framework for enhanced gas separation and CO_2 transformation

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Experimental section

Py-UiO-66 was prepared by adding $ZrCl_4$ (47 mg), 3-(2′,5′-dicarboxylphenyl)pyridine acid (49 mg), and acetic acid (1.8 mL) successively into 5 mL of N,N-dimethylformamide (DMF) in a 10 mL screw-capped glass vial. The mixture was sonicated sufficiently and capped tightly. The glass vial was heated at 120 °C for 48 h and then slowly cooled to room temperature. The resulting white power were filtered, washed with a small amount of DMF and methanol and air-dried with ~67% yield.

Sorption Measurements.

All the gas sorption isotherms were measured by using a ASAP 2020M adsorption equipment. The activated samples were prepared by soaking the as-synthesized samples

in methanol for 3 days and subsequently drying the material overnight at 140 °C under vacuum to remove the solvent molecules prior to measurements.

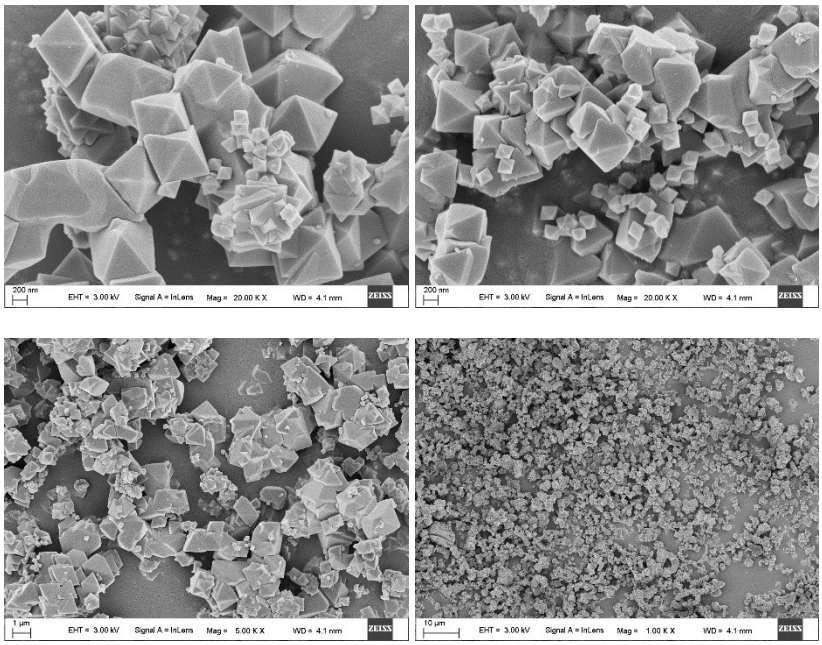

Figure S1. The SEM images of as-synthesized Py-UiO-66.

IAST adsorption selectivity calculation:

The experimental isotherm data for pure C_2H_2, CO_2, and CH_4 (measured at 298) were fitted using a dual Langmuir-Freundlich (L-F) model:

$$q = \frac{a_1 * b_1 * P^{1/c1}}{1 + b_1 * P^{1/c1}} + \frac{a_2 * b_2 * P^{1/c2}}{1 + b_1 * P^{1/c1}}$$

Where q and p are adsorbed amounts and pressures of component i, respectively.

The adsorption selectivities for binary mixtures of C_2H_2/CH_4 and CO_2/CH_4, defined by

$$S_{i/j} = \frac{x_i * y_j}{x_j * y_i}$$

were calculated using the Ideal Adsorption Solution Theory (IAST) of Myers and Prausnitz.

Where x_i is the mole fraction of component i in the adsorbed phase and y_i is the mole fraction of component i in the bulk.

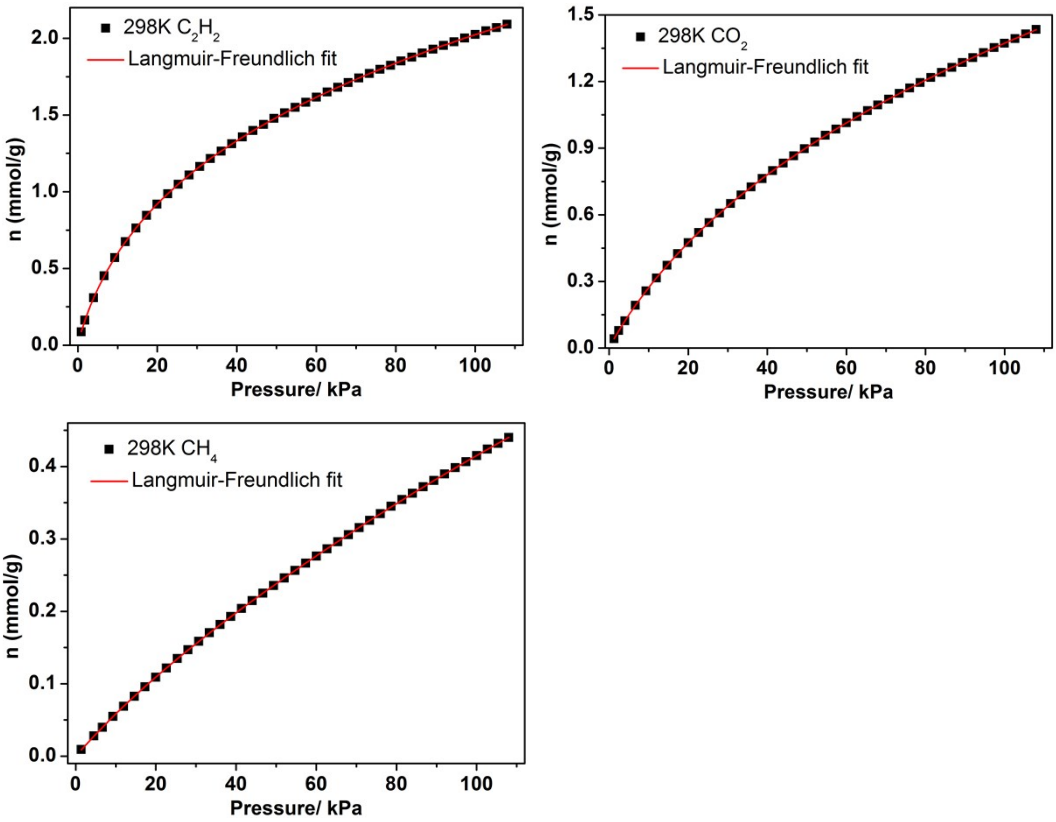

Figure S2. C_2H_2 adsorption isotherms of Py-UiO-66 with fitting by L-F model: a1 = 2.04275, b1 = 6.8237×10^{-4}, c1 = 1.34667, a2 = 2.02034, b2 = 0.05177, c2 = 0.87805, Chi^2 = 1.33524×10^{-6}, R^2 = 1; CO_2 adsorption isotherms of Py-UiO-66 with fitting by L-F model: a1 = 1.37277, b1 = 0.0209, c1 = 0.9475, a2 = 7.31808, b2 = 8.27011×10^{-4}, c2 = 0.98282, Chi^2 = 2.71916×10^{-7}, R^2 = 1; CH_4 adsorption isotherms of Py-UiO-66 with fitting by L-F model: a1 = 0.30952, b1 = 0.01955, c1 = 1.00146, a2 = 0.90831, b2 = 0.00024, c2 = 1.54606, Chi^2 = 1.7122×10^{-7}, R^2 = 0.99999.

Calculation of sorption heat for C_2H_2, CO_2 and CH_4 uptakes using Virial 2 model

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} aiN^i + \sum_{i=0}^{n} biN^i \qquad Q_{st} = -R\sum_{i=0}^{m} aiN^i$$

The above equation was applied to fit the combined C_2H_2, CO_2 and CH_4 and isotherm data for Py-UiO-66 at 273 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, ai and bi are virial coefficients, and m and n are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.

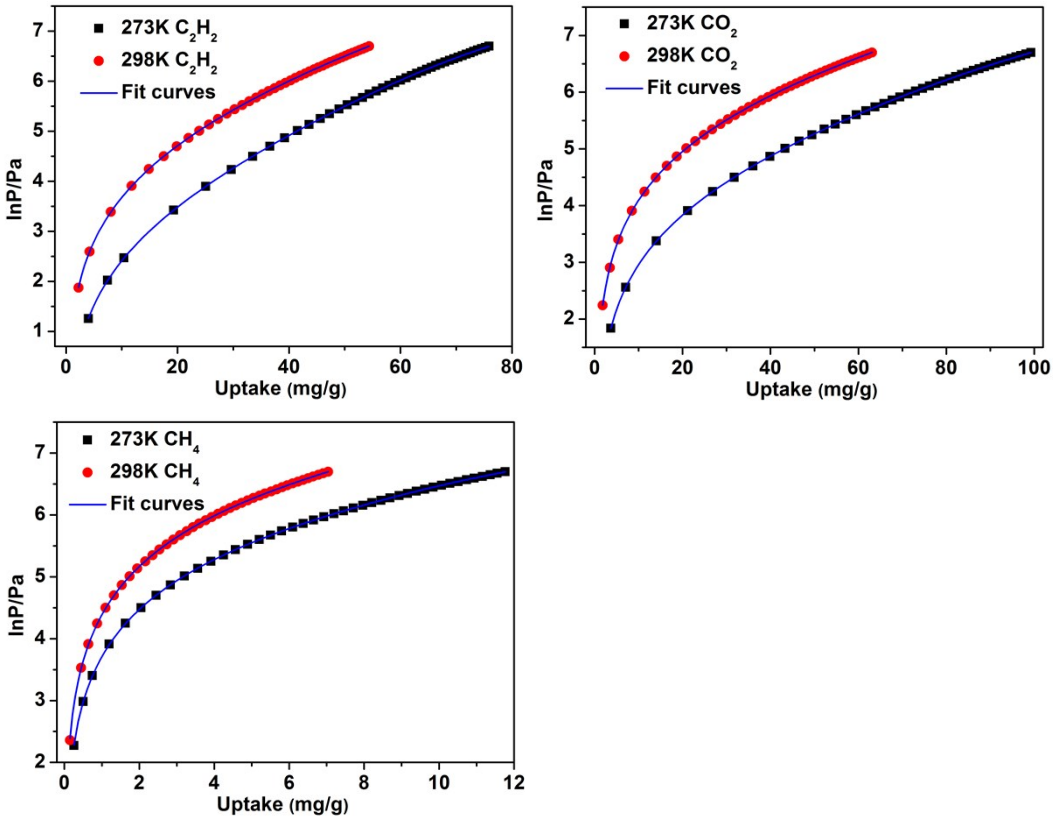

Figure S3. C_2H_2 adsorption isotherms for Py-UiO-66 with fitting by Virial 2 model. Fitting results: a0 = -4141.31876, a1 = -3.71155, a2 = 0.63667, a3 = -0.00377, a4 = -9.409×10^{-6}, b0 = 14.87678, b1 = 0.05536, b2 = -0.00254, b3 = 1.79743×10^{-5}, Chi^2 = 8.22299×10^{-6}, R^2 = 0.99999; CO_2 adsorption isotherms for Py-UiO-66 with fitting by Virial 2 model. Fitting results: a0 = -3697.89527, a1 = -2.50709, a2 = 0.28829, a3 = -0.00193, a4 = -1.25008×10^{-6}, b0 = 14.01509, b1 = 0.02854, b2 = -0.00112, b3 = 7.83869 ×10^{-6}, Chi^2 = 7.29667×10^{-6}, R^2 = 0.99999.