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Supporting Information

A Dy_6-Clusters Based *fcu*-MOF with Efficient Separation of C_2H_2/C_2H_4 and Seelective Adsorption of Benzene

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Contents

1. IR spectrum, TGA and PXRD

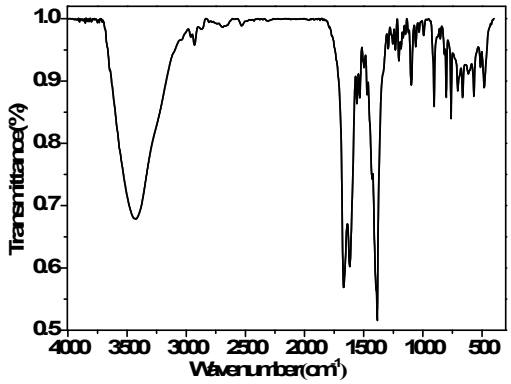

Fig. S1 IR spectrum of as synthesized sample of complex **1**.

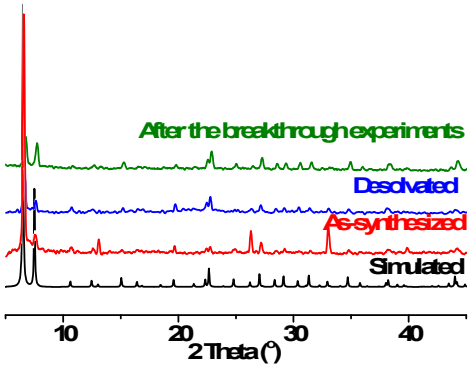

Fig. S2 PXRD patterns of complex **1**.

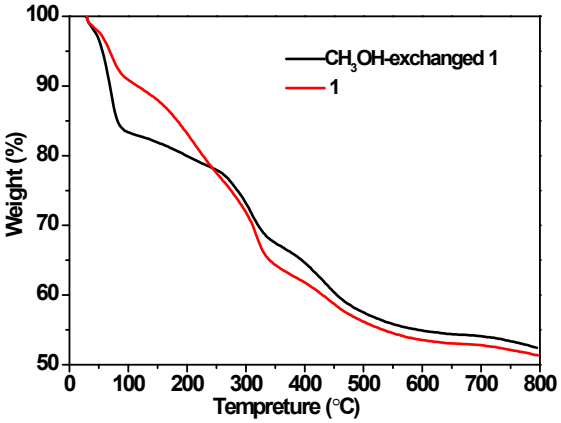

Fig. S3 TGA curves of as-synthesized and CH_3OH-exchanged samples of complex **1**.

2. Gas adsorption isotherms

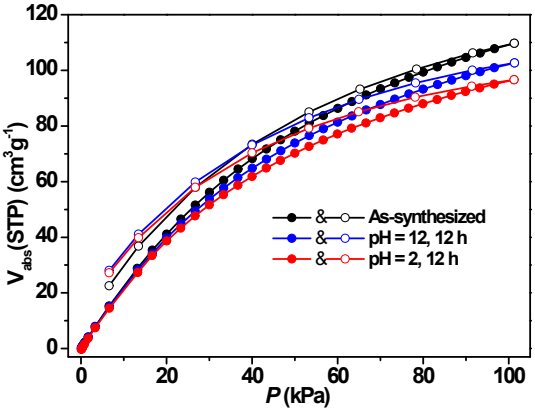

Fig. S4 Sorption isotherms of **1a** and the treated samples soaked in acidic (pH = 2) and basic (pH = 12) aqueous solutions for 12 hours.

3. Pore size distribution

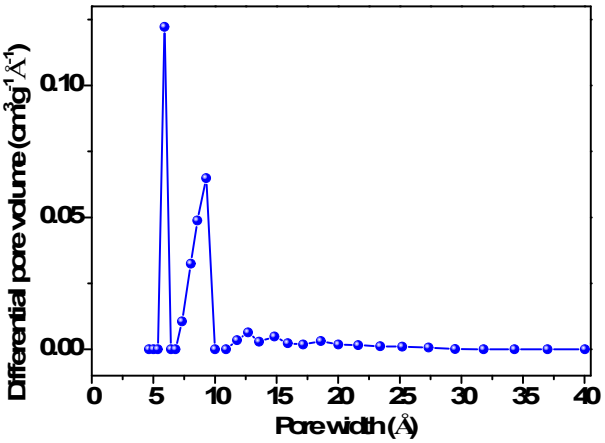

Fig. S5 Differential pore volume as a function of pore width calculated from the N_2 adsorption isotherm at 77 K for **1a** using the Horvath-Kawazoe model.

4. Calculation of sorption heat

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

The above virial expression was used to fit the combined isotherm data for **1a** at 273.15 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, a_i and b_i

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.

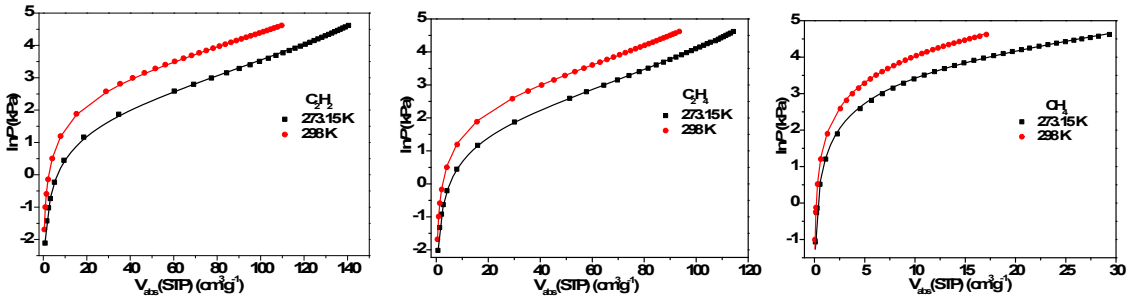

Fig. S6 Fitted adsorption isotherms of C_2H_2, C_2H_4 and CH_4. Fitting results: for C_2H_2, a0 = -3215.24962, a1 = 2.35543, a2 = 0.01674, b0 = 9.88605, b1 = -0.00647, b2 = 0.00057, Chi^2 = 0.00067, R^2 = 0.99981; for C_2H_4, a0 = -2544.83477, a1 = -0.0516, a2 = 0.03193, b0 = 7.67194, Chi^2 = 0.00025, R^2 = 0.99993; for CH_4, a0 = -1960.72484, a1 = -1.3773, a2 = 0.08892, b0 = 8.31443, Chi^2 = 0.00237, R^2 = 0.99903.

5. Selectivity prediction

The experimental isotherm data for pure C_2, CH_4, C_6H_6, C_7H_8 and C_6H_{12} were fitted using a dual Langmuir-Freundlich (L-F) model:

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

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

The adsorption selectivities for binary mixtures of C_2/CH_4, C_2H_2/C_2H_4, C_6H_6/C_7H_8 and C_6H_6/C_6H_{12} defined by

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

were respectively calculated using the Ideal Adsorption Solution Theory (IAST). 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.

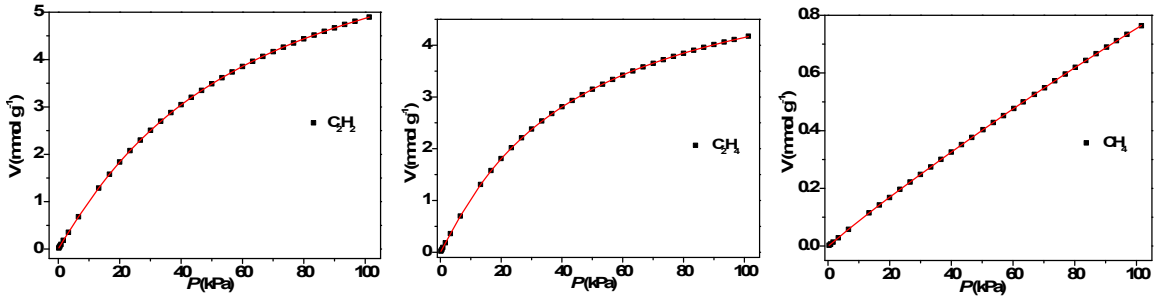

Fig. S7 Fitted adsorption isotherms of C_2H_2, C_2H_4 and CH_4. Fitting results: for C_2H_2, a1 = 6.63211, b1 = 0.01184, c1 = 1.1078, a2 = 2.64638, b2 = 0.01265, c2 = 0.62804, Chi^2 = 4.6442E-6, R^2 = 1; for C_2H_4, a1 = 5.82518, b1 = 0.01823, c1 = 1.04157, a2 = 0.14196, b2 = 0.00672, c2 = 1.98292, Chi^2 = 0.00002, R^2 = 0.99999; for CH_4, a1 = 4.92093, b1 = 0.00132, c1 = 1.06129, a2 = 0.02295, b2 = 0.05033, c2 = 1.45173, Chi^2 = 2.1002E-7, R^2 = 1.

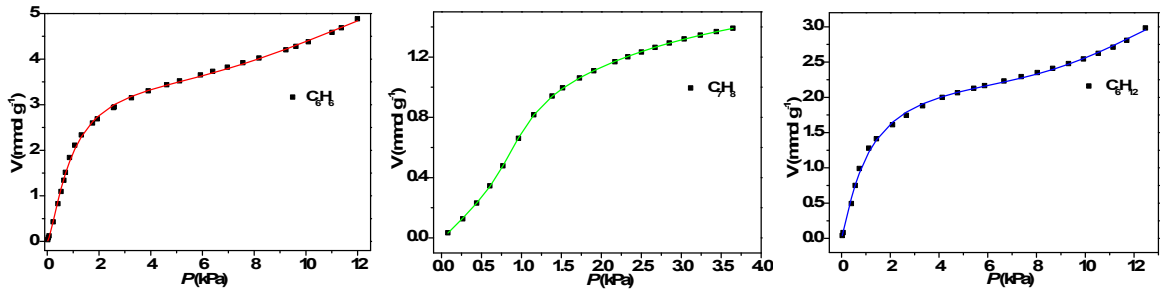

Fig. S8 Fitted adsorption isotherms of C_6H_6, C_7H_8 and C_6H_{12}. Fitting results: for C_6H_6, a1 = 3.68273, b1 = 1.11744, c1 = 1.41879, a2 = 3.49345, b2 = 0.00018, c2 = 3.23897, Chi^2 = 0.00208, R^2 = 0.99923; for C_7H_8, a1 = 1.48163, b1 = 0.49475, c1 = 1.22674, a2 = 0.34264, b2 = 1.53047, c2 = 5.66832, Chi^2 = 8.3382E-6, R^2 = 0.99997; for C_6H_{12}, a1 = 2.44472, b1 = 0.87441, c1 = 1.16341, a2 = 1.72177, b2 = 2.3751E-6, c2 = 4.9358, Chi^2 = 0.00119, R^2 = 0.99868.

6. Theoretic simulations

Grand canonical Monte Carlo (GCMC) simulations were performed for the gas adsorption in the framework by the Sorption module of Material Studio (Accelrys. Materials Studio Getting Started, release 5.0). The framework was considered to be rigid, and the optimized gas and epoxide molecules were used. The partial charges for atoms of the framework were derived from QEq method and QEq_neutral 1.0 parameter. One unit cell was used during the simulations. The interaction energies between the gas molecules and framework were

computed through the Coulomb and Lennard-Jones 6-12 (LJ) potentials. All parameters for the atoms were modeled with the universal force field (UFF) embedded in the MS modeling package. A cutoff distance of 12.5 Å was used for LJ interactions, and the Coulombic interactions were calculated by using Ewald summation. For each run, the 3×10^6 maximum loading steps, 3×10^6 production steps were employed.

The binding energy was calculated by DFT method using the Dmol^3 software. The exchange-correlation functional used in calculations was in the framework of the generalized gradient approximation (GGA) proposed by Perdew and Wang (PBE). DND basis set was used to describe the atomic orbital. The SCF convergence was set to 10^{-5}. The binding energy of is evaluated by the following equation: $E_{bind} = E_{framework+gas} - E_{framework} - E_{gas}$, in which $E_{framework+gas}$ is the total energy of the framework and the adsorbed gas molecule, $E_{framework}$ and E_{CO2} are the energies of the framework and gas molecule.

7. Table of crystallographic data

Table S1. Crystallographic data for **1**.

Chemical formula	$C_{48}H_{38}Dy_6F_6N_{24}O_{26}$
Formula weight	2456.02
T (K)	296(2)
Space group	Fm-3m
a,b,c (Å)	23.625(5), 23.625(5), 23.625(5)
α, β, γ (°)	90, 90, 90
V (Å^3)	13186(9)
Z, $D_{calcd.}$ (g·cm^{-3})	4, 1.237
μ (mm^{-1})	3.416
Reflns collected/unique/R_{int}	17839/710/0.0504
Goof	1.152
R_1[a], wR_2[b] ($I > 2\sigma$)	$R_1 = 0.0494$, $wR_2 = 0.1297$
R_1[a], wR_2[b] (all data)	$R_1 = 0.0542$, $wR_2 = 0.1356$

[a] $R_1 = \Sigma||F_o| - |F_c||)/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond lengths [Å] and angles [°] for **1**.

Dy(1)-O(1)	2.336(17)	O(2)#4-Dy(1)-O(2)#5	65.0(3)	O(2)#3-Dy(1)-N(1)	69.3(4)
Dy(1)-O(1)#1	2.336(17)	O(1)#1-Dy(1)-O(2)	139.3(3)	O(2)#4-Dy(1)-N(1)	133.3(3)

Dy(1)-O(2)#3	2.339(3)	O(1)#2-Dy(1)-O(2)	77.2(4)	O(2)#5-Dy(1)-N(1)	69.3(4)
Dy(1)-O(2)#4	2.339(3)	O(1)#3-Dy(1)-O(2)	77.2(4)	O(2)-Dy(1)-N(1)	133.3(3)
Dy(1)-O(2)#5	2.339(3)	O(1)-Dy(1)-O(2)	139.3(3)	O(3)-Dy(1)-N(1)	75.2(4)
Dy(1)-O(2)	2.339(3)	O(2)#3-Dy(1)-O(2)	65.0(3)	O(1)#2-Dy(1)-N(1)#1	140.8(6)
Dy(1)-O(3)	2.458(15)	O(2)#4-Dy(1)-O(2)	65.0(3)	O(1)#3-Dy(1)-N(1)#1	83.9(2)
Dy(1)-N(1)#1	2.58(2)	O(2)#5-Dy(1)-O(2)	98.9(6)	O(1)-Dy(1)-N(1)#1	83.9(2)
Dy(1)-N(1)#2	2.58(2)	O(1)#1-Dy(1)-O(3)	65.6(4)	O(2)#3-Dy(1)-N(1)#1	133.3(3)
O(1)#1-Dy(1)-O(1)#2	131.3(9)	O(1)#2-Dy(1)-O(3)	65.6(4)	O(2)#4-Dy(1)-N(1)#1	69.3(4)
O(1)#1-Dy(1)-O(1)#3	80.2(3)	O(1)#3-Dy(1)-O(3)	65.6(4)	O(2)#5-Dy(1)-N(1)#1	69.3(4)
O(1)#2-Dy(1)-O(1)#3	80.2(3)	O(1)-Dy(1)-O(3)	65.6(4)	O(2)-Dy(1)-N(1)#1	133.3(3)
O(1)#1-Dy(1)-O(1)	80.2(3)	O(2)#3-Dy(1)-O(3)	130.6(3)	O(3)-Dy(1)-N(1)#1	75.2(4)
O(1)#2-Dy(1)-O(1)	80.2(3)	O(2)#4-Dy(1)-O(3)	130.6(3)	N(1)-Dy(1)-N(1)#1	86.3(2)
O(1)#3-Dy(1)-O(1)	131.3(9)	O(1)#1-Dy(1)-O(2)#5	77.2(4)	O(1)#1-Dy(1)-N(1)#2	140.8(6)
O(1)#1-Dy(1)-O(2)#3	139.3(3)	O(1)#2-Dy(1)-O(2)#5	139.3(3)	O(1)#3-Dy(1)-N(1)#2	83.9(2)
O(1)#2-Dy(1)-O(2)#3	77.2(4)	O(1)#3-Dy(1)-O(2)#5	139.3(3)	O(1)-Dy(1)-N(1)#2	83.9(2)
O(1)#3-Dy(1)-O(2)#3	139.3(3)	O(1)-Dy(1)-O(2)#5	77.2(4)	O(2)#3-Dy(1)-N(1)#2	69.3(4)
O(1)-Dy(1)-O(2)#3	77.2(4)	O(2)#3-Dy(1)-O(2)#5	65.0(3)	O(2)#4-Dy(1)-N(1)#2	133.3(3)
O(1)#1-Dy(1)-O(2)#4	77.2(4)	O(2)#5-Dy(1)-O(3)	130.6(3)	O(2)#5-Dy(1)-N(1)#2	133.3(3)
O(1)#2-Dy(1)-O(2)#4	139.3(3)	O(2)-Dy(1)-O(3)	130.6(3)	O(2)-Dy(1)-N(1)#2	69.3(4)
O(1)#3-Dy(1)-O(2)#4	77.2(4)	O(1)#1-Dy(1)-N(1)	83.9(2)	O(3)-Dy(1)-N(1)#2	75.2(4)
O(1)-Dy(1)-O(2)#4	139.3(3)	O(1)#2-Dy(1)-N(1)	83.9(2)	N(1)-Dy(1)-N(1)#2	86.3(2)
O(2)#3-Dy(1)-O(2)#4	98.9(6)	O(1)#3-Dy(1)-N(1)	140.8(6)	N(1)#1-Dy(1)-N(1)#2	150.4(9)

Symmetry codes: #1 x, z+1/2, -y+1/2; #2 x, -z+1/2, -y+1/2; #3 x, y, -z; #4 x, -y+1, z; #5 x, -y+1, -z.