Supporting Information

Multiple Functions of Gas Separation and Vapor Adsorption in a New MOF with Open Tubular Channels

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X-Ray Crystallography

Single crystal X-ray diffraction data of compound **1** was collected at 158(2) K on a Bruker SMART APEX II CCD detector using Mo radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures with SHELXL-2014 program package. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms added to their geometrically ideal positions and were refined isotropically. The crystallographic data are listed in Tables S1 and S2.

GCMC Simulation

All the 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 gases were geometry optimized during the simulation. Partial charges for atoms of guest-free framework were derived from Qeq method and QEq_neutral1.0 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 2×10^6 maximum loading steps, 2×10^6 production steps were employed.

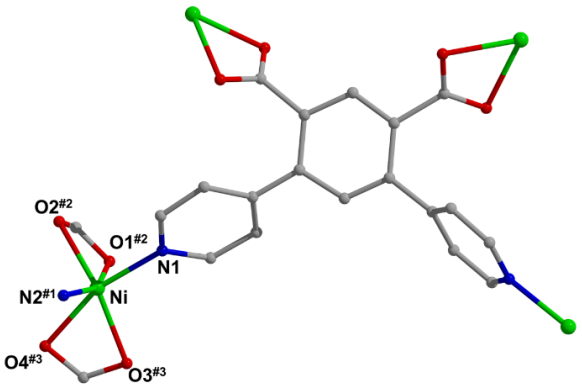

Figure S1. Coordination environment of Ni^{2+} ion in **1** (Symmetry codes: #1= y+1/2, -x+1/2, -z+3/2, #2 = -y+1, -x+1, -z+3/2, #3 = -x+1, y, z+1/2).

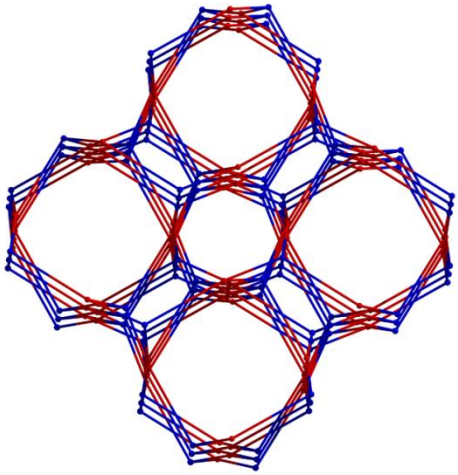

Figure S2. 3D (4,4)-c sqc net with the point symbol of $(4^2 8^3 10)(4^2 8^4)$.

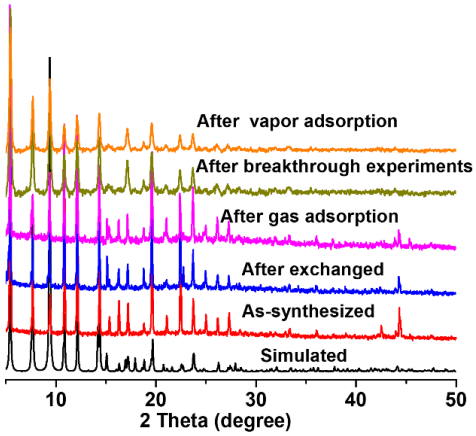

Figure S3. Simulated and experimental PXRD of **1**.

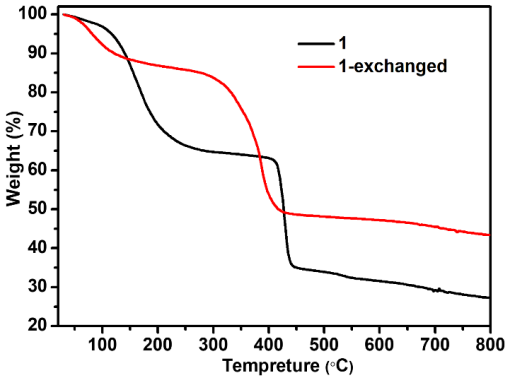

Figure S4. TGA curves of as-synthesized and exchanged samples of **1**.

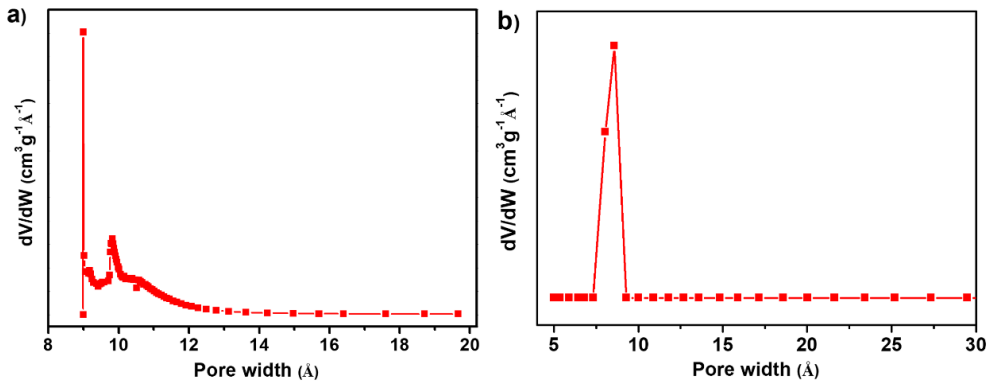

Figure S5. Porous distributions of **1a** calculated from N_2 adsorption isotherm at 77 K by the Horvath-Kawazoe model (a) and b) non-local density functional theory (NLDFT) model (b).

Calculation of sorption heat for gas using Virial 2 model

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

The above virial expression was used to fit the combined isotherm data for **1a** at 273.15 and 298 K (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.

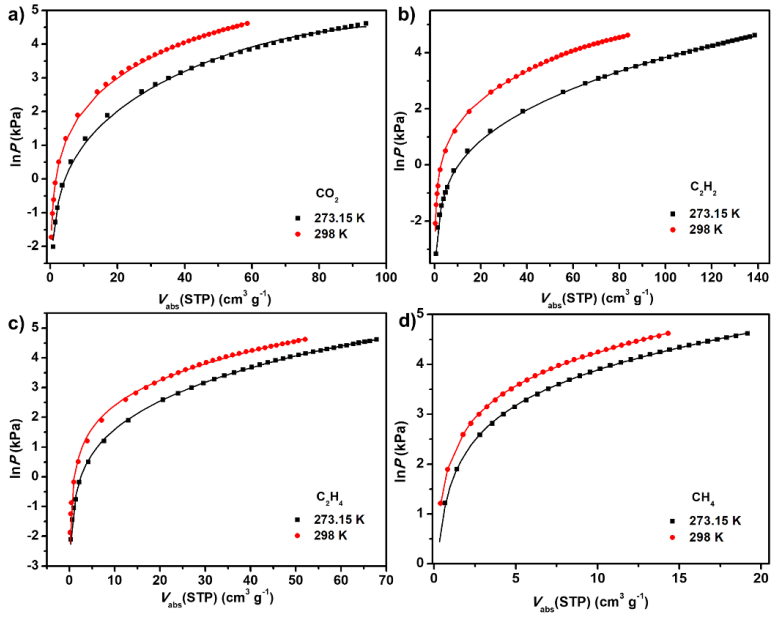

Figure S6. a-d) Fitted CO_2, C_2H_2, C_2H_4 and CH_4 adsorption isotherms for **1a**. Fitted parameters, for C_2H_2: a0 = -5016.59958, a1 = 12.93475, a2 =-0.01412, b0 = 15.7983, b1 =

-0.02425, Chi^2 = 0.00249, R^2 = 0.99949; for C_2H_4: a0 = -3031.98597, a1 = 42.47688, a2 = -0.30682, b0 = 10.11803, b1 =-0.12636, b2 = 0.00099,Chi^2 = 0.0046, R^2 = 0.99877; for CH_4: a0 = -1711.48531, a1 = 106.4792, a2 = -4.80572, b0 = 7.83856, b1 = -0.39312, b2 = 0.01805, Chi^2 = 0.0003, R^2 = 0.99959; for CO_2: a0 = -3651.93584, a1 = 23.25684, a2 = -0.05705, b0 = 11.7393, b1 = -0.04838, Chi^2 = 0.00417, R^2 = 0.99876.

Selectivity prediction via IAST

The experimental isotherm data for pure gas A, and gas B were fitted at 298 K using a dual Langmuir-Freundlich (L-F) model (Figure S4):

$$q = \frac{a_1 * b_1 * P^{c_1}}{1 + b_1 * P^{c_1}} + \frac{a_2 * b_2 * P^{c_2}}{1 + b_2 * P^{c_2}}$$

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

The adsorption selectivities for binary mixtures of gas A/gas B, defined by

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

were respectively calculated using the Ideal Adsorption Solution Theory (IAST) of Myers and Prausnitz. Where xi is the mole fraction of component i in the adsorbed phase and yi is the mole fraction of component i in the bulk.

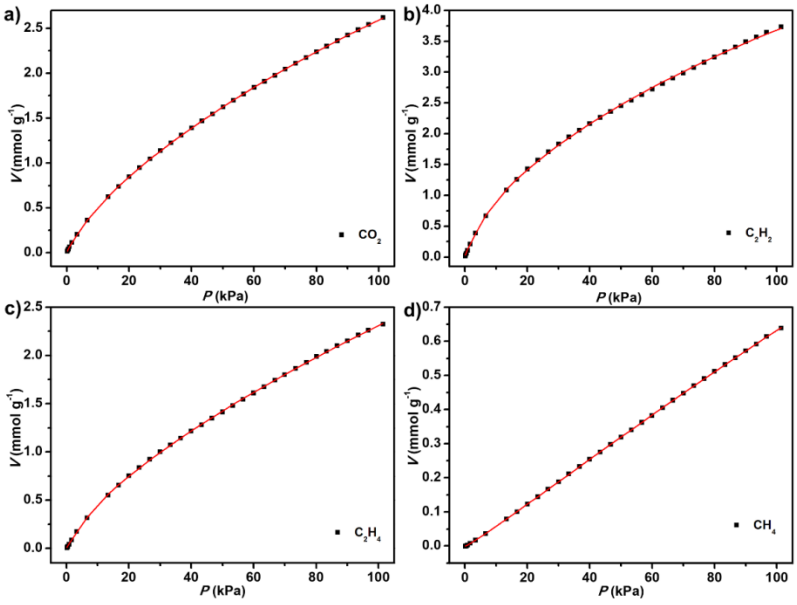

Figure S7. a-d) Fitted CO_2, C_2H_2, C_2H_4 and CH_4 adsorption isotherms for **1a**. Fitted parameters, for CO_2: a1 = 14.51495, b1 = 0.00511, c1 = 0.80842, a2 = 0.06285, b2 = 0.01147,

c2 = 2.30043, Chi^2 = 7.8454E-6, R^2 = 0.99999; for C_2H_2: a1 = 15.3714, b1 = 0.00891, c1 = 0.75877, a2 = 0.19682, b2 = 0.01256, c2 = 2.53725, Chi^2 = 0.00033, R^2 = 0.99981; for C_2H_4: a1 = 16.77069, b1 = 0.00324, c1 = 0.83294, a2 = 0.12197, b2 = 0.01304, c2 = 2.28949, Chi^2 = 0.00004, R^2 = 0.99993; for CH_4: a1 = 3.32963, b1 = 0.00081, c1 = 1.21262, a2 = 0.04822, b2 = 0.02783, c2 = 1.18866, Chi^2 = 7.032E-7, R^2 = 0.99999.

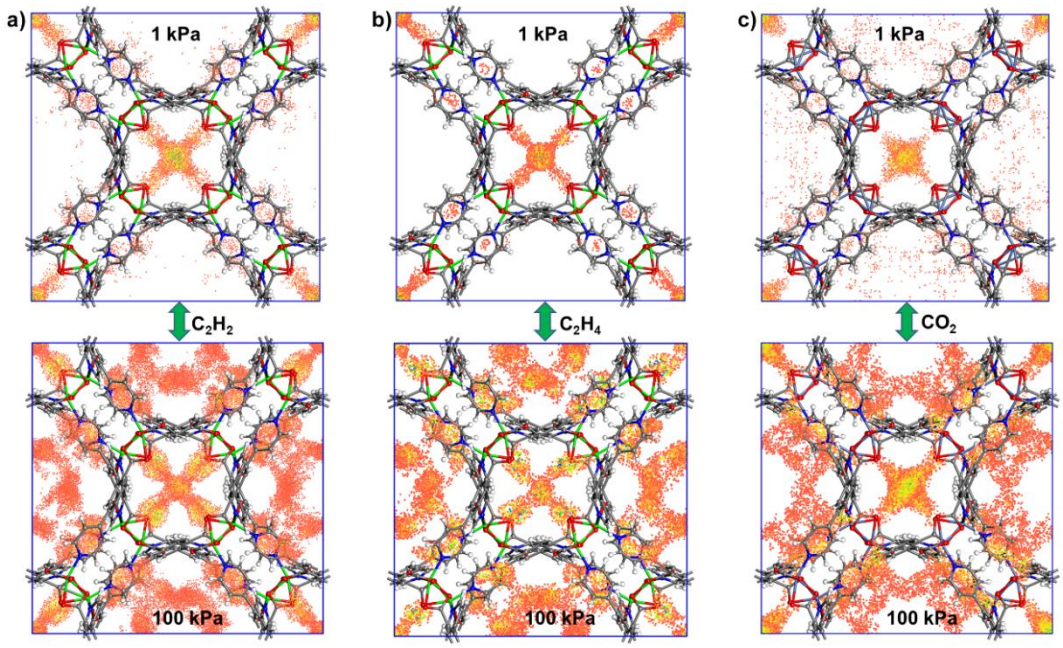

Figure S8. Density contours of C_2H_2 (a), C_2H_4 (b) and CO_2 (c) adsorption in **1a** obtained from GCMC simulations at 298 K under 1 kPa and 100 kPa, respectively.

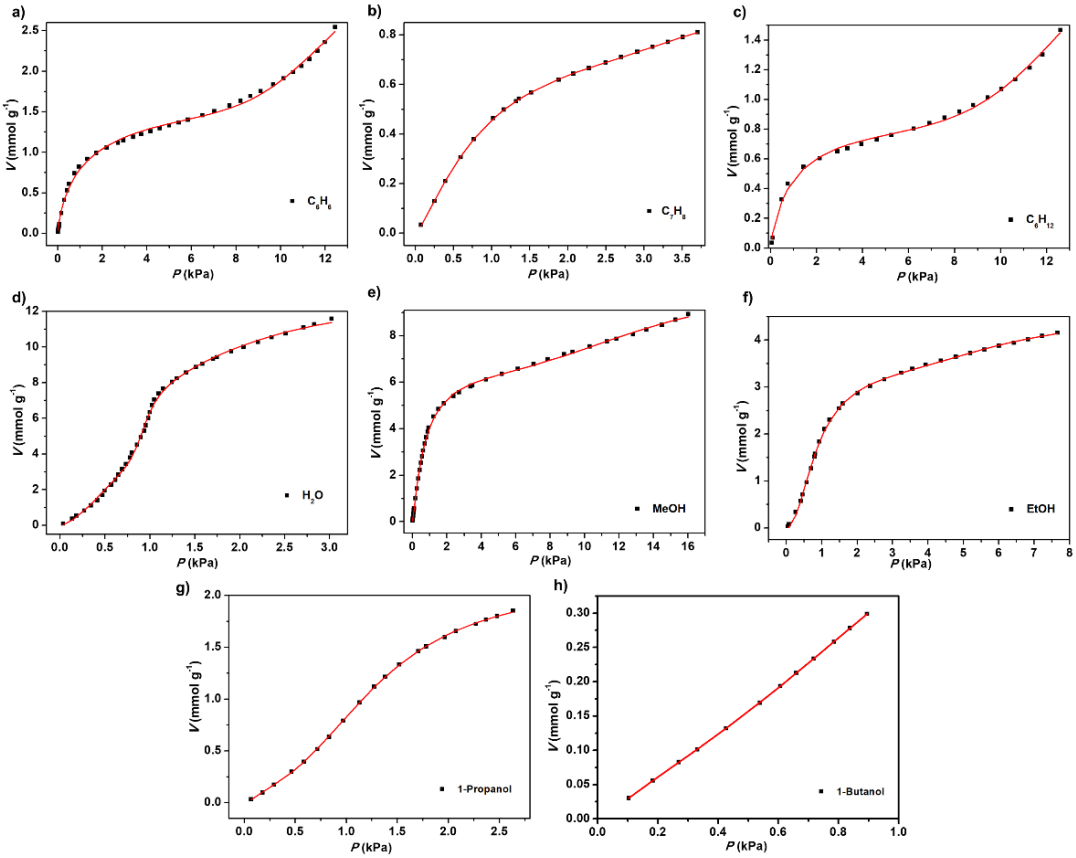

Figure S9. (a-h) VOCs adsorption isotherms of **1a** with fitted by dual L-F model, for benzene: a1 = 1.86677, b1 = 0.73767, c1 = 0.78161, a2 = 1.90415, b2 = 8.4021E-8, c2 = 6.43656, Chi^2 = 0.00119, R^2 = 0.99794; for toluene: a1 = 0.85524, b1 = 1.13759, c1 = 1.33393, a2 = 0.11925, b2 = 0.00016, c2 = 6.88569, Chi^2 = 6.204E-6, R^2 = 0.99991; for cyclohexane: a1 = 0.94933, b1 = 0.93693, c1 = 0.88068, a2 = 1.53884, b2 = 5.1542E-7, c2 = 5.53546, Chi^2 = 0.00047, R^2 = 0.99731; for water: a1 = 2.7382, b1 = 2.44623, c1 = 12.80286, a2 = 10.77821, b2 = 0.69176, c2 = 1.59655, Chi^2 = 0.01448, R^2 = 0.99903; for MeOH: a1 = 6.89317, b1 = 1.41766, c1 = 1.16138, a2 = 3.26423, b2 = 0.00013, c2 = 3.45521, Chi^2 = 0.00462, R^2 = 0.99956; for EtOH: a1 = 3.4174, b1 = 1.31428, c1 = 2.04758, a2 = 1.06477, b2 = 0.00133, c2 = 3.69954, Chi^2 = 0.00103, R^2 = 0.99953; for 1-Propanol: a1 = 1.89003, b1 = 0.48556, c1 = 2.55188, a2 = 0.23619, b2 = 8.43597, c2 = 1.49221, Chi^2 = 0.00005, R^2 = 0.9999; for 1-Butanol: a1 = 0.9002, b1 = 0.37251, c1 = 1.95485, a2 = 0.10891, b2 = 6.04309, c2 = 1.2868, Chi^2 = 7.9334E-8, R^2 = 0.99999

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

Chemical formula	$C_{18}H_{10}N_2NiO_4$
Formula weight	376.99
T (K)	158(2)
Crystal system	Tetragonal
Space group	*I-4c2*
a, b, c (Å)	22.9846(9), 22.9846(9), 23.4908(12)
α , β, γ (°)	90, 90, 90
V (Å^3)	12410.0(12)
Z	16
$D_{calcd.}$ (g cm^{-3})	0.807
μ (mm^{-1})	0.639
Reflns collected/unique/R_{int}	31579/ 5600/0.1073
Goof	1.036
R_1[a], wR_2[b] ($I > 2\sigma$)	0.0653, 0.1718
R_1[a], wR_2[b] (all data)	0.0892, 0.1952

[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**.

Ni(1)-N(2)$^{\#1}$	2.041(6)	N(2)$^{\#1}$-Ni(1)-O(3)$^{\#3}$	98.3(2)
Ni(1)-N(1)	2.047(7)	N(1)-Ni(1)-O(3)$^{\#3}$	99.8(2)
Ni(1)-O(2)$^{\#2}$	2.058(6)	O(2)$^{\#2}$-Ni(1)-O(3)$^{\#3}$	156.3(2)
Ni(1)-O(3)$^{\#3}$	2.086(5)	N(2)$^{\#1}$-Ni(1)-O(4)$^{\#3}$	89.4(2)
Ni(1)-O(4)$^{\#3}$	2.146(5)	N(1)-Ni(1)-O(4)$^{\#3}$	162.9(2)
Ni(1)-O(1)$^{\#2}$	2.155(6)	O(2)$^{\#2}$-Ni(1)-O(4)$^{\#3}$	100.0(2)
O(3)$^{\#3}$-Ni(1)-O(1)$^{\#2}$	99.3(3)	O(3)$^{\#3}$-Ni(1)-O(4)$^{\#3}$	63.2(2)
O(4)$^{\#3}$-Ni(1)-O(1)$^{\#2}$	88.7(3)	N(2)$^{\#1}$-Ni(1)-O(1)$^{\#2}$	159.2(3)
N(2)$^{\#1}$-Ni(1)-N(1)	94.7(3)	N(1)-Ni(1)-O(1)$^{\#2}$	93.1(3)
N(2)$^{\#1}$-Ni(1)-O(2)$^{\#2}$	98.2(2)	O(2)$^{\#2}$-Ni(1)-O(1)$^{\#2}$	61.9(3)
N(1)-Ni(1)-O(2)$^{\#2}$	95.8(3)		

Symmetry codes: #1= y+1/2, -x+1/2, -z+3/2, #2 = -y+1, -x+1, -z+3/2, #3 = -x+1, y, z+1/2.