Electronic Supporting Information (ESI)

A Highly Robust Tetraneclear Cobalt based 3D Framework for Efficient C_2H_2/CO_2 and C_2H_2/C_2H_4 Separations

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Characterization

The elemental analyses (C, N, H contents) were determined on a Vario EL III analyzer. Thermogravimetric analysis was performed on a NETZSCH TG 209 thermobalance in a nitrogen atmosphere, samples of **NbU-10** was placed in alumina containers and data were recorded at 10 °C/min between 30 and 800 °C. The diffraction data were collected on BL17B beamlines at National Facility for Protein Science Shanghai (NFPS) and Shanghai Synchrotron Radiation Facility, Shanghai, People's Republic of China. X-ray powder diffraction (XRPD) were collected on Panalytical X-Pert PRO diffractometer and Bruker D8 ADVANCE diffractometer using Cu $K\alpha$ (λ = 1.5418 Å) radiation. Gas sorption isotherms were performed on Micromeritics (3FLEX) aparatus. Prior to gas measurement, the methanol-exchanged samples were degassed at 150^{o}C under dynamic vacuum for 8h. The gas-separation properties of NbU-10 (588 mg) was examined by breakthrough experiments using 50:50 (v/v) and 1:99 (v/v)gas mixtures flowed through the activated samples packed into the same glass column (0.46 cm inner diameter, 5.0 cm in length). The gas mixture was dosed into the column at a flow rate of 1 mL min^{-1}. The relative amounts of the gases passing through the column were monitored using gas chromatography (Agilent 7890B) with a thermal conductivity detector (TCD) once every 30 seconds. The concentration of the outlet gas was normalized after calibration with the standard gases. After the breakthrough experiment, the sample was regenerated by heating at 80^{o}C under vacuum conditions for 5 hours.

Table S1 Crystal data and structure refinement for **NbU-10.**

NbU-10	
formula	$C_{27}H_{14.5}Co_2NO_9$
M_r / g mol^{-1}	614.76
cryst syst	hexagonal
space group	*P6₃/m*
a / Å	21.891(3)
b / Å	21.891(3)
c / Å	25.982(5)
α / deg	90
β / deg	90
γ / deg	120
V / Å^3	10783(4)
Z	12
D_c / g cm^{-3}	1.136
μ / mm^{-1}	0.963
reflns collected	34540
GOF	1.056
R_{int}	0.1014
R_1 ($I > 2\sigma(I)$) [a]	0.0385
wR_2 (all data)	0.1130

[a] $R_1 = ||F_o| - |F_c||/|F_o|$; $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma_2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$; and $Rw = [w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

Table S2. Selected bond lengths (Å) and angles (deg) associating with the bond cleavage.

NbU-10·S			
Co(1)-O(9)	1.946(2)	Co(2)-O(9a)	2.058(3)
Co(1)-O(1)	1.943(3)	Co(2)-O(9)	2.135(3)
Co(1)-O(5)	1.992(3)	Co(2)-O(4b)	2.069(3)
Co(1)-O(7)	1.965(3)	Co(2)-O(6)	2.087(3)
Co(1)-O(9)-Co(2a)	129.50(13)	Co(2)-O(8)	2.133(3)
Co(1)-O(9)-Co(2)	101.59(11)	Co(2)-N(1c)	2.124(3)
Co(2a)-O(9)-Co(2)	97.73(10)		

Symmetry codes: (a) *2-x,1-y,1-z;* (b) *2+y-x,2-x,+z;* (c) *1-y,+x-y,+z;*

Table S3 The calculation of bond valence sum for Co1 and Co2 atoms in **NbU-10**·S**.**

	Co(II) State	Co(III) State
Co(1)	1.93	1.97
Co(2)	2.14	2.18

Additional Figures

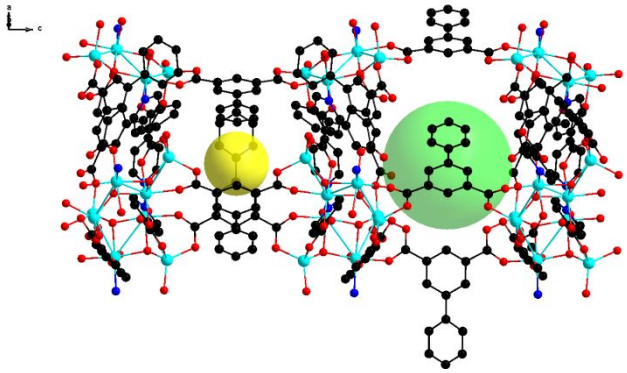

Fig. S1 Two kinds of cages divided by benzene rings of the H_2Pip linker in hexagonal channels.

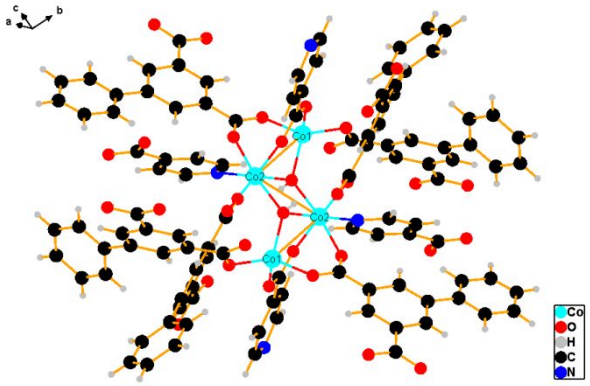

Fig. S2 The coordination environment of tetranuclear cobalt cluster of NbU-10·S.

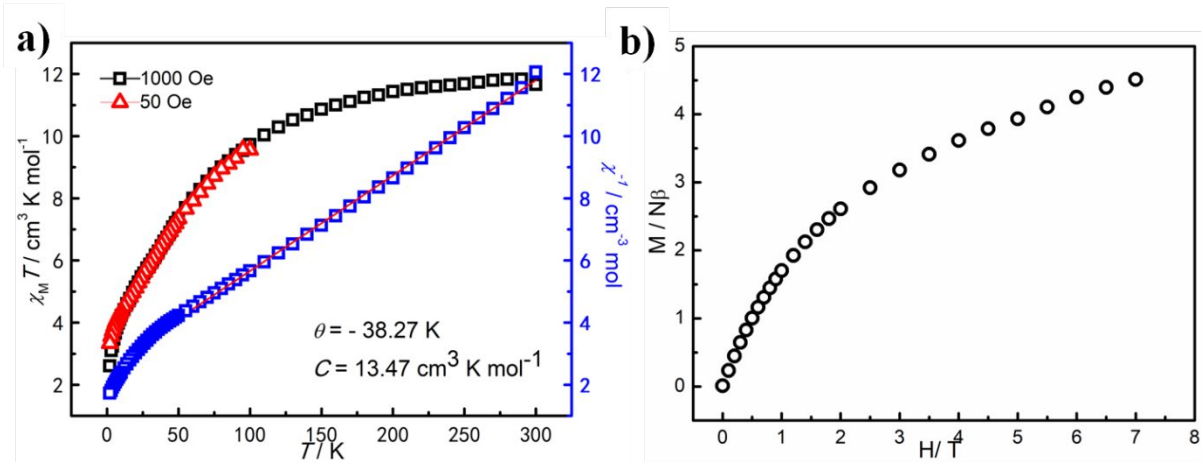

Fig. S3 $\chi_M T$ vs T plot (per Co^{II}_4) for **NbU-10**·S under applied field of 50 Oe and 1000 Oe (a); Field-dependent magnetization at 2 K (b).

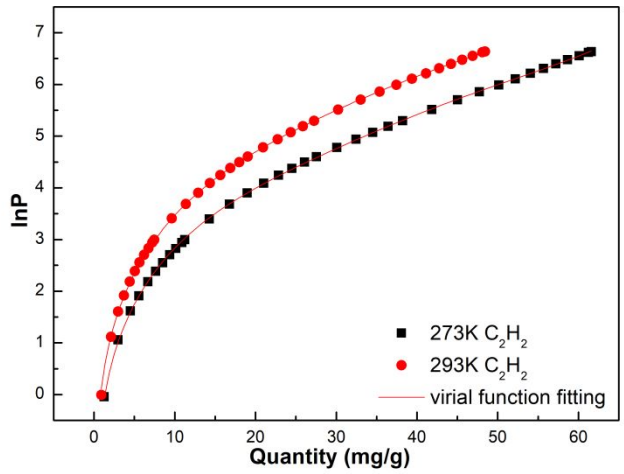

Fig. S4 The C_2H_2 fit isotherms of **NbU-10** at 273 K and 293 K by virial equation.

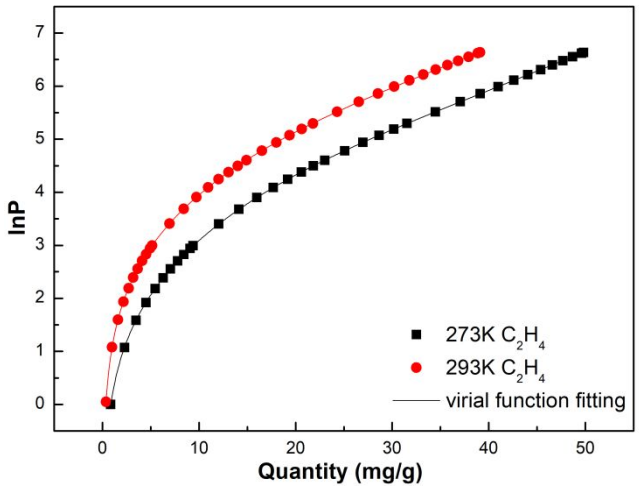

Fig. S5 The C_2H_4 fit isotherms of **NbU-10** at 273 K and 293 K by virial equation.

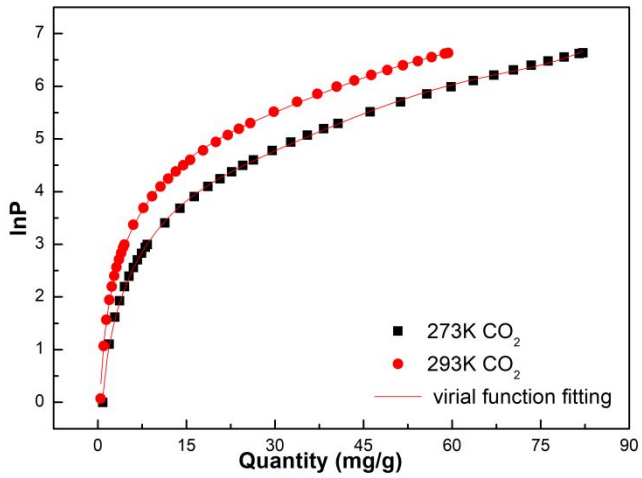

Fig. S6 The CO_2 fit isotherms of **NbU-10** at 273 K and 293 K by virial equation.

IAST adsorption selectivity calculation:[1,2]

The experimental isotherm data for pure C_2H_2, C_2H_4, C_2H_6, and CH_4 (measured at 273 K) were fitted using a Langmuir-Freundlich (L-F) model:

$$q = \frac{a * b * p^c}{1 + b * P^c}$$

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

Using the pure component isotherm fits, the adsorption selectivity is defined by

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

Where q_i is the amount of i adsorbed and p_i is the partial pressure of i in the mixture.

We used the following written codes to simulate the adsorption selectivity of C_2H_2/C_2H_4, and C_2H_4/CO_2 in Fig. 2:

28 # No. of Pressure Point

y1, y2 # Molar fraction of binary mixture (y1 and y2, y1 + y2 = 1)

1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109 #The unit is same parameter b, kPa

a1, a2 # fitting parameter Nsat (A1) for both component (Unit: mmol/g)

b1, b2 # fitting parameter b1 for both components (Unit: kPa^{-1})

c1, c2 # fitting parameter c1 for both components

0, 0 # fitting parameter Nsat2(A2) for both component(Unit: mmol/g)

0, 0 # fitting parameter b2 for both components (Unit: kPa^{-1})

1, 1 # fitting parameter c2 for both components

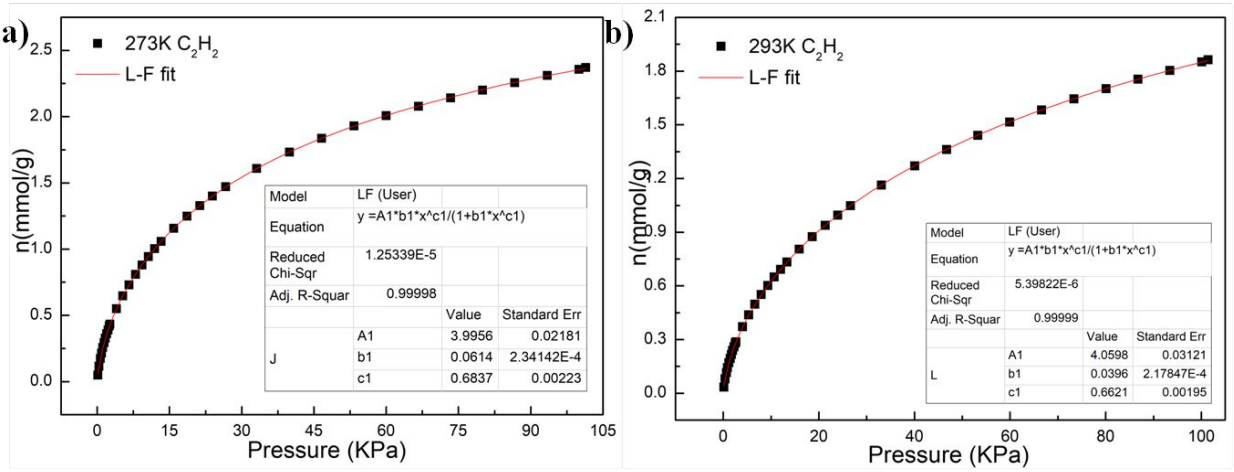

Fig. S7 C_2H_2 adsorption isotherm of **NbU-10** with fitting by L-F model.

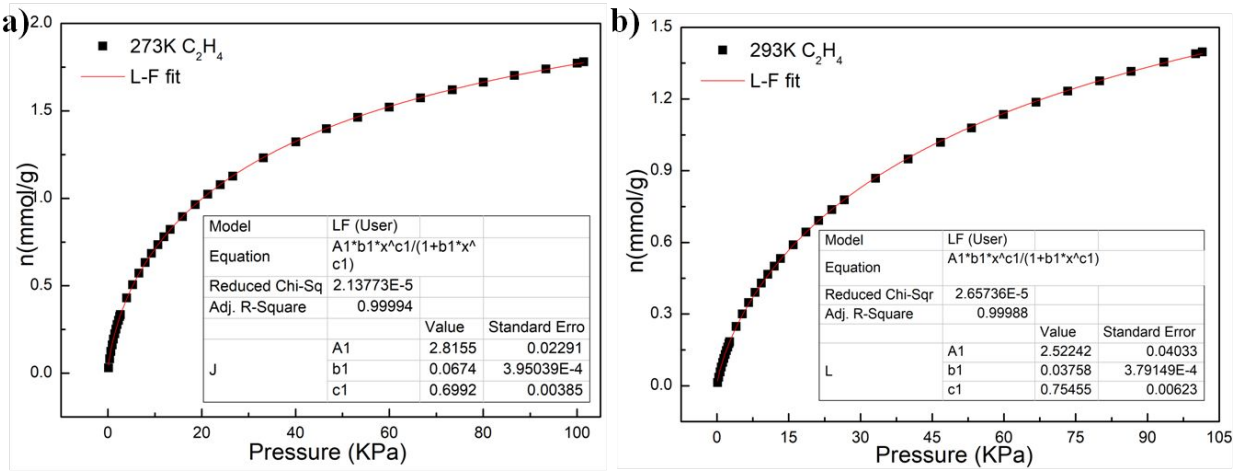

Fig. S8 C_2H_4 adsorption isotherm of **NbU-10** with fitting by L-F model.

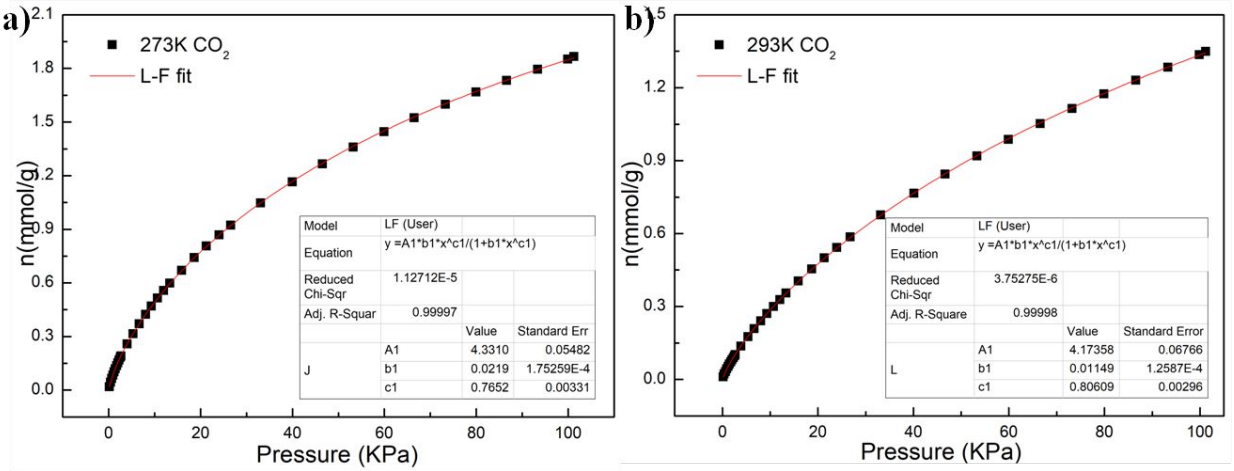

Fig. S9 CO_2 adsorption isotherm of **NbU-10** with fitting by L-F model.

References:

1. Daniels, F.; Alberty, R. A.; Williams, J. W.; Cornwell, C. D.; Bender P. and Harriman, J. E. *Experimental Physical Chemistry, 6th Ed, McGraw-Hill Book Co. Inc.*, New York, **1962**.

2. Dincă, M.; Long, J. R. *J. Am. Chem. Soc.,* 2005, **127**, 9376−9377.