Electronic Supporting Information

Highly selective C_2H_2 and CO_2 capture and magnetic properties of robust Co-chain based metal–organic framework

Tao Ding[a,b], Sheng Zhang[c], Weiqiang Zhang[a], Guofang Zhang[a], Zi-Wei Gao*[a]

[a]*Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P. R China. E-mail: zwgao@snnu.edu.cn*

[b]*College of Environment and Chemistry Engineering, Xi'an Polytechnic University, Xi'an 710048, P. R China.*

[c]*College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721013, P. R China.*

**Scheme S1 The scheme for the synthesis of H₄L.**

(1) 2,6-di(2',5'-dicarboxylphenyl)pyridine (H₄L)

2,6-dibromopyridine (2.37 g, 10.00 mmol), (2,5-bis(methoxycarbonyl)phenyl)boronic acid (5.24 g, 22.00 mmol), $Pd(PPh_3)_4$ (0.58 g, 0.50 mmol) and K_2CO_3 (6.64 g, 48.00 mmol) were mixed in a 250 mL Schlenk flask. After vacuumized and refilled with N_2 for three times, toluene-ethanol-water (60 ml, 30 ml, 30 ml) was added. The mixture was stirred at 75℃ for 18h and then cooled to room temperature. After removing the organic phase under vacuum, dichloromethane (150 mL) and H_2O (75 mL) were added. The organic phase was separated and then the aqueous phase was extracted three times with dichloromethane (100×3 mL). The combined organic phases were washed with saturated brine, dried over anhydrous $MgSO_4$. After removing the organic solvent by rotary evaporation, the residue was purified by column chromatography with dichloromethane/ethyl acetate (3/1, v/v) as eluent to obtain white solid product (3.84 g, 83.0% yield). 3.84 g (8.30 mmol) of dimethyl tetramethyl 2,2'-(pyridine-2,6-diyl)diterephthal ate was dissolved in THF (100 mL), and then 160 mL 2 M NaOH aqueous solution was added. The solut was stirred at 60℃ for 6h and the THF was removed in vacuum. Concentrated hydrochloric acid was added to the remaining aqueous solution until the solution became acidic (pH = 2~3). The solid was collected by filtration, washed several   times   with distilled water, and dried under vacuum to give white solid product (3.09 g, 91% yield).^{1}H and ^{13}C NMR spectra were recorded on 500 MHz spectrometer. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.00 or to the signal of the residual protonated solvent: $(CD_3)_2SO$ δ 2.50. ^{13}C NMR chemical shifts

were determined relative to internal TMS at δ 0.0.

^{1}H NMR (500 MHz, CDCl₃) δ 13.21 (s, 4H), 8.17 (d, $J = 1.5$ Hz, 2H), 8.06 (dd, $J = 1.5$,

8.0 Hz, 2H), 7.96 (t, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H);

^{13}C NMR (125 MHz, CDCl$_3$) δ 169.4, 166.9, 157.0, 140.4, 137.6, 137.2, 133.2, 131.1, 129.8, 129.5, 122.3.
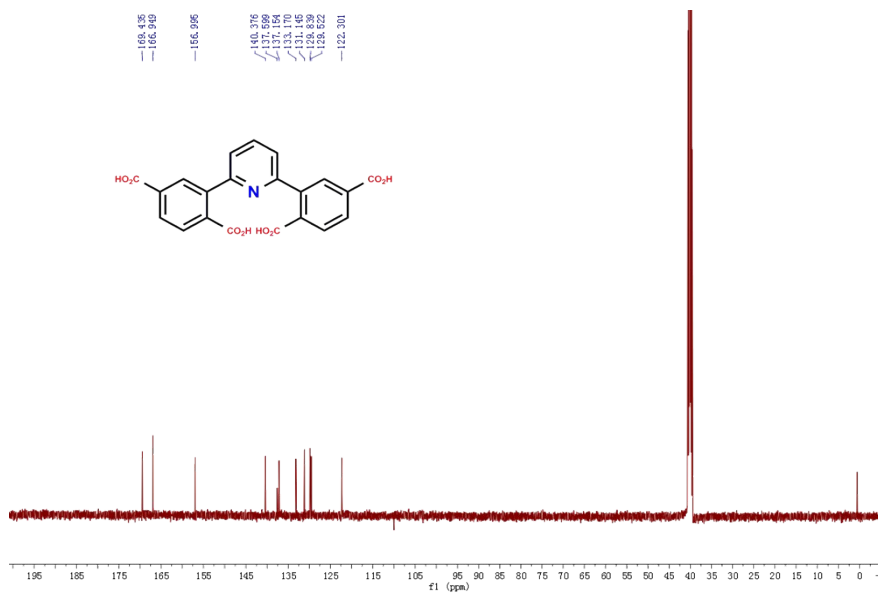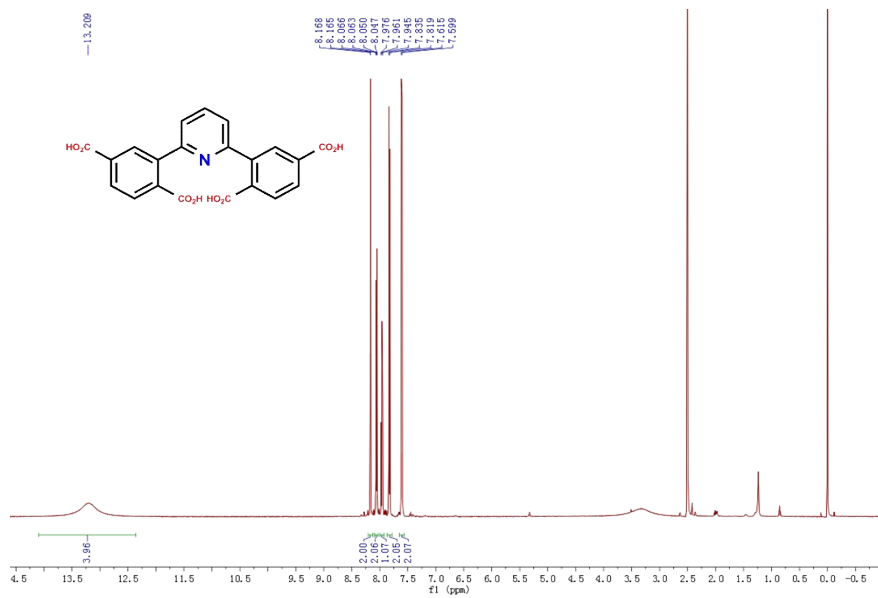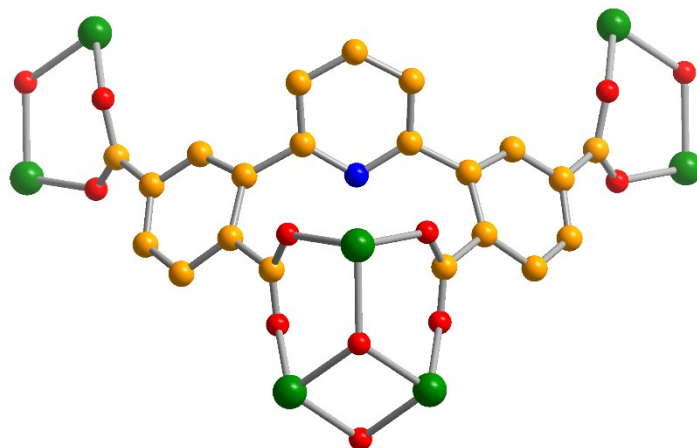
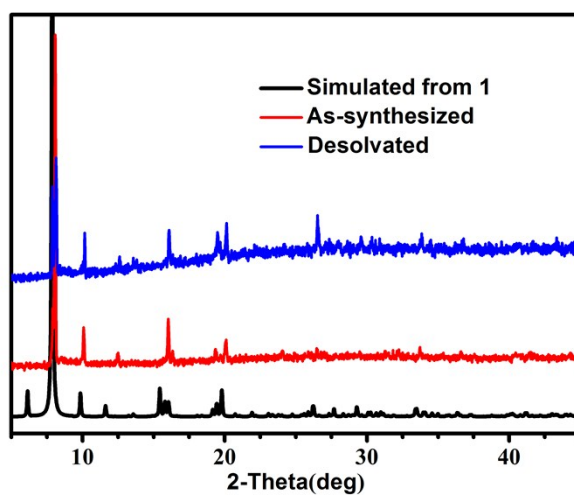**Fig. S1** The bridging mode of L^{4-} in **1**.

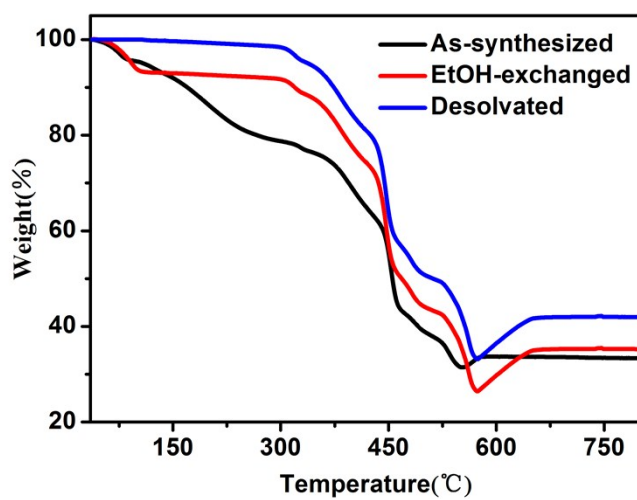**Fig. S2** PXRD patterns for **1**: simulated, as-synthesized, and desolved samples.

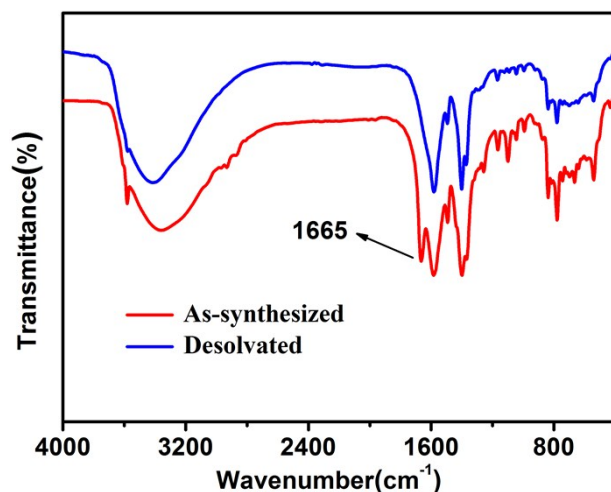**Fig. S3** TGA for **1**: as-synthesized, EtOH-exchanged, and desolved samples.

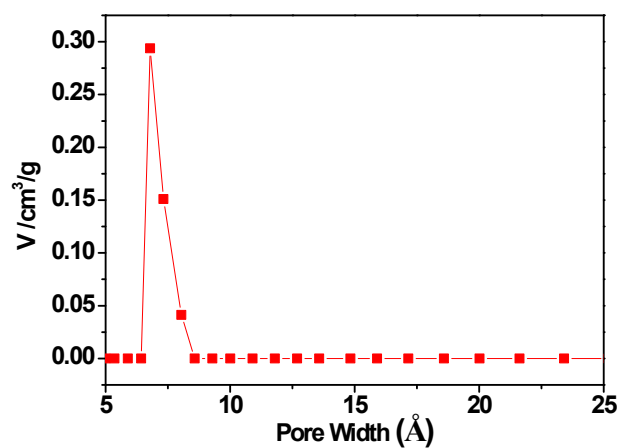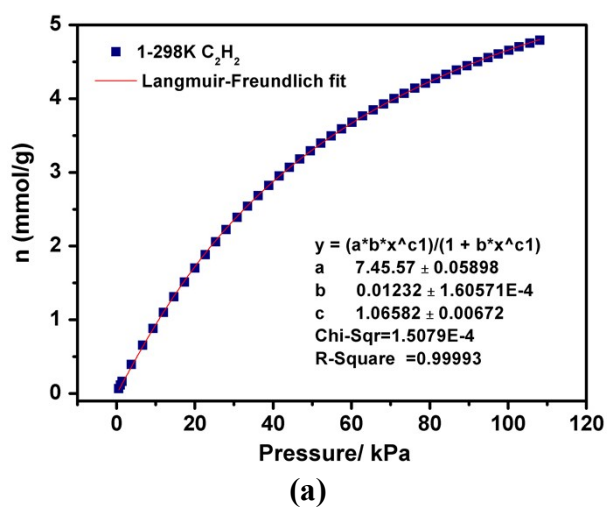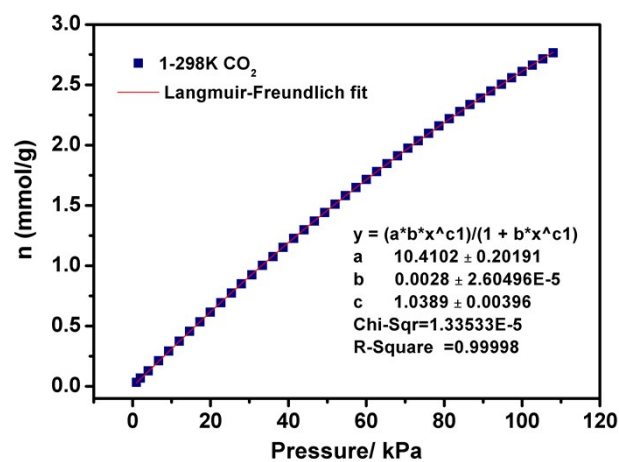**Fig. S4** IR for **1**: as-synthesized and desolved samples.

Fig. S5 The pore size distribution incremental pore volume vs. pore width

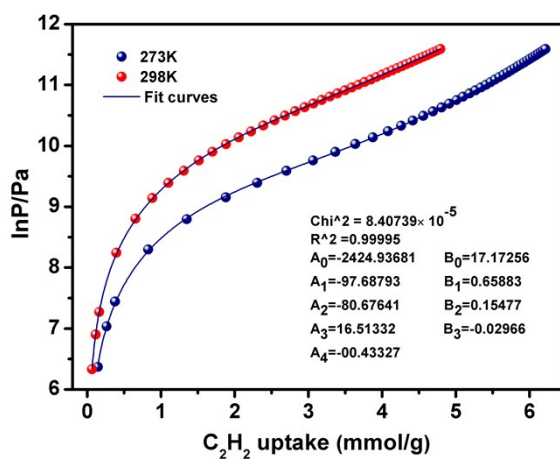$y = (a*b*x^c1)/(1 + b*x^c1)$
a 7.45.57 ± 0.05898
b 0.01232 ± 1.60571E-4
c 1.06582 ± 0.00672
Chi-Sqr=1.5079E-4
R-Square =0.99993

(a)

(b)
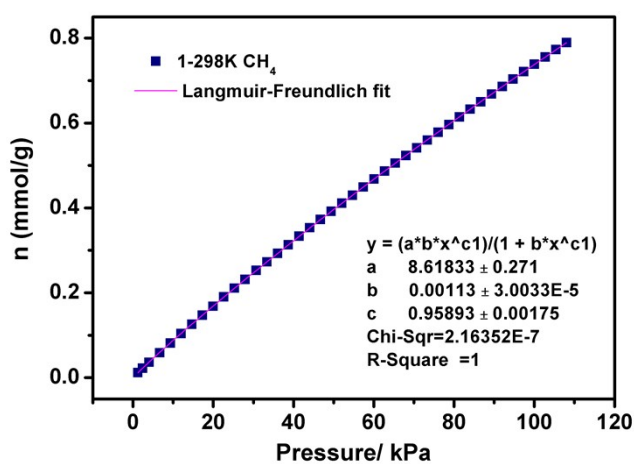
(c)

Fig. S6 C_2H_2 (a), CO_2 (b), and CH_4 (c) adsorption isotherms of **1a** with fitting by L-F model.

(a)
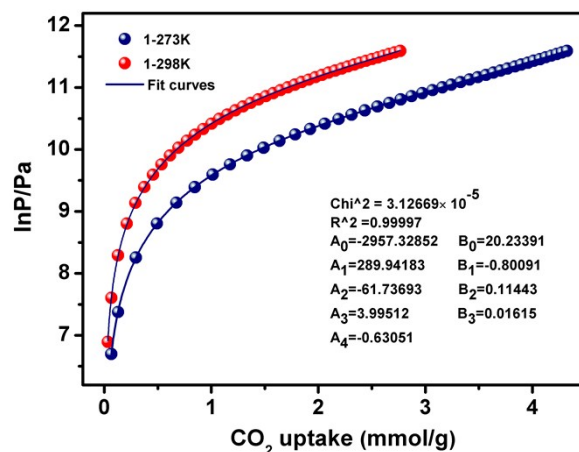
(b)

Fig. S7 C_2H_2 (a) and CO_2 (b) adsorption isotherms for **1a** with fitting by Virial 2 model.
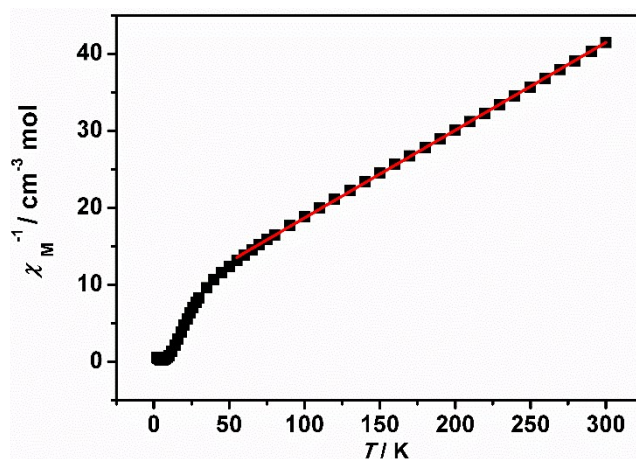

Fig. S8 χ_M^{-1} versus T plots fit by the Curie−Weiss law.
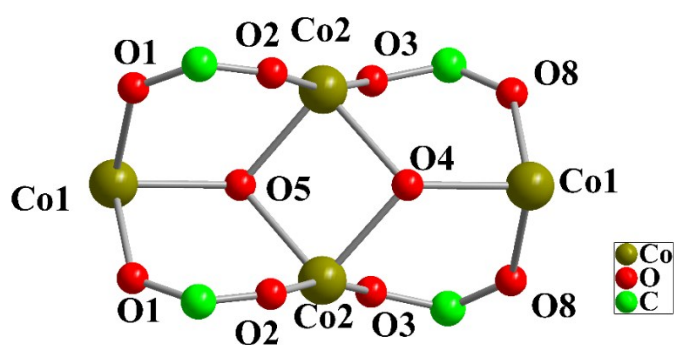

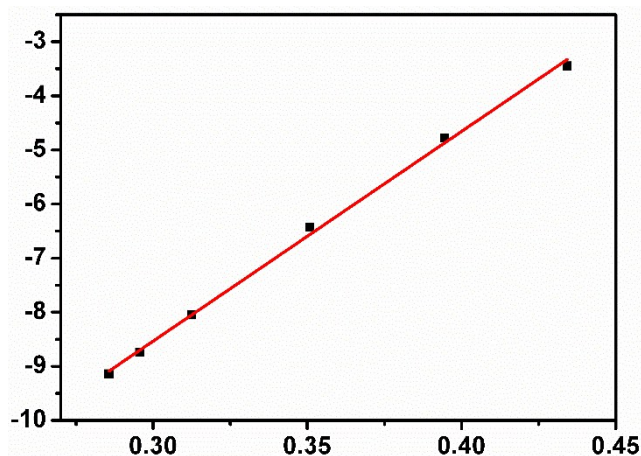**Fig. S9** Coordination polyhedra of Co1 and Co2 cations, and details of tetrameric cluster.

Fig. S10 Linear fit by Arrhenius law for **1**.

Table. S1 Selected bond lengths (Å) and bond angles (deg) for **1**.

Co(1)-O(1)	2.168(6)
Co(1)-O(4)#2	2.069(8)
Co(1)-O(5)#3	2.147(8)
Co(1)-O(8)#2	2.124(6)
Co(2)-O(2)#5	2.100(7)
Co(2)-O(3)	2.079(7)
Co(2)-O(4)	2.108(5)
Co(2)-O(5)	2.095(6)
Co(2)-O(6)	2.201(8)
Co(2)-O(7)	2.164(8)
O(1)#1-Co(1)-O(1)	89.1(3)
O(4)#2-Co(1)-O(1)	84.8(2)
O(4)#2-Co(1)-O(5)#3	179.3(4)
O(4)#2-Co(1)-O(8)#4	95.4(2)
O(5)#3-Co(1)-O(1)	95.6(3)
O(8)#2-Co(1)-O(1)	179.7(4)
O(8)#4-Co(1)-O(1)	90.73(18)
O(8)#4-Co(1)-O(1)#1	179.7(4)
O(8)#4-Co(1)-O(5)#3	84.1(3)
O(8)#4-Co(1)-O(8)#2	89.4(4)
O(2)#5-Co(2)-O(4)	96.0(3)
O(2)#5-Co(2)-O(6)	89.6(4)

O(2)#5-Co(2)-O(7)	84.4(4)
O(3)-Co(2)-O(2)#5	169.0(2)
O(3)-Co(2)-O(4)	92.6(3)
O(3)-Co(2)-O(5)	92.5(3)
O(3)-Co(2)-O(6)	82.0(3)
O(3)-Co(2)-O(7)	88.6(3)
O(4)-Co(2)-O(6)	174.2(3)
O(4)-Co(2)-O(7)	91.0(3)
O(5)-Co(2)-O(2)#5	94.8(3)
O(5)-Co(2)-O(4)	86.91(16)
O(5)-Co(2)-O(6)	91.1(3)
O(5)-Co(2)-O(7)	177.7(3)
O(7)-Co(2)-O(6)	91.0(2)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1,z   #2 x-1/2,y+1/2,z   #3 x-1/2,y+1/2,z-1

#4 x-1/2,-y+1/2,z   #5 x+1/2,-y+1/2,z+1