Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Pore Partition Effect on Gas Sorption Properties of an anionic Metal-Organic Framework with Exposed Cu^{2+} Coordination Sites

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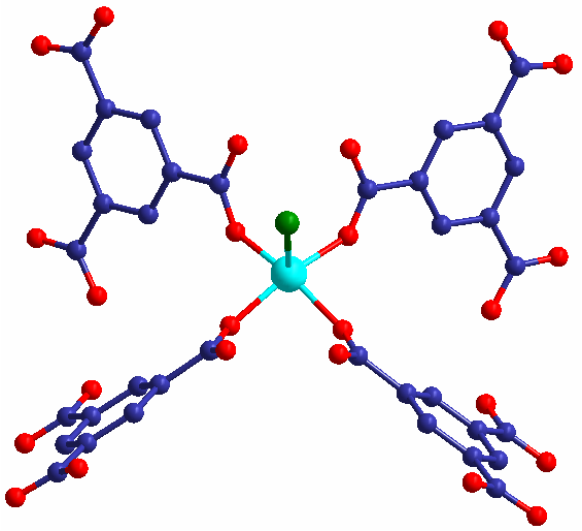

Figure S1. The coordination environment of Cu atom in **1** (some equivalent atoms have been generated to complete the Cu(II) coordination, H atom omitted for clarity).

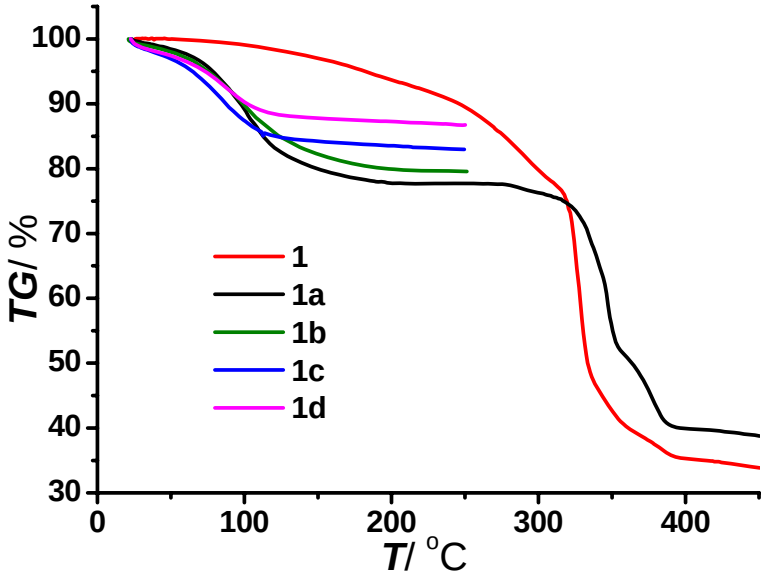

Figure S2. The TG plots of **1**-**1d**.

To examine the thermal stability the sodalite-type nanoporous framework, thermal gravimetric (TG) analyses and X-ray powder diffraction pattern (XRPD) measurements were carried out. The phase purity of the bulk product was independently confirmed by powder X-ray diffraction (XRD)

through comparing the powder X-ray diffraction patterns of **1** with the simulated one. The TG curve of **1** shows that the trapped solvent DMA molecules can be slowly removed at 300 ^{o}C to gain a vacant nanoporous MOF **1-ht** with a weight loss of 21.5%, corresponding to the expectant weight loss of 22.5%. To attain a complete evacuation and protect the structural integrality, DMA was exchanged with methanol by soaking crystals of **1** in methanol for one week. As indicated by TG analysis, the resulting material is DMA free, with formula $[(Cu_4Cl)_3(BTC)_8]\cdot 3NH_2(CH_3)_2\cdot 18MeOH$ (**1a**). TG analysis of **1a** showed a weight loss step below 150 °C, corresponding to methanol loss, followed by a plateau between 150 and 320 °C, beyond which framework decomposition occurred. While other organic solvents can be exchanged inside the framework, methanol was chosen for its relatively low boiling point and ease of potential removal via evacuation. With the weight loss of methanol guest is lower.

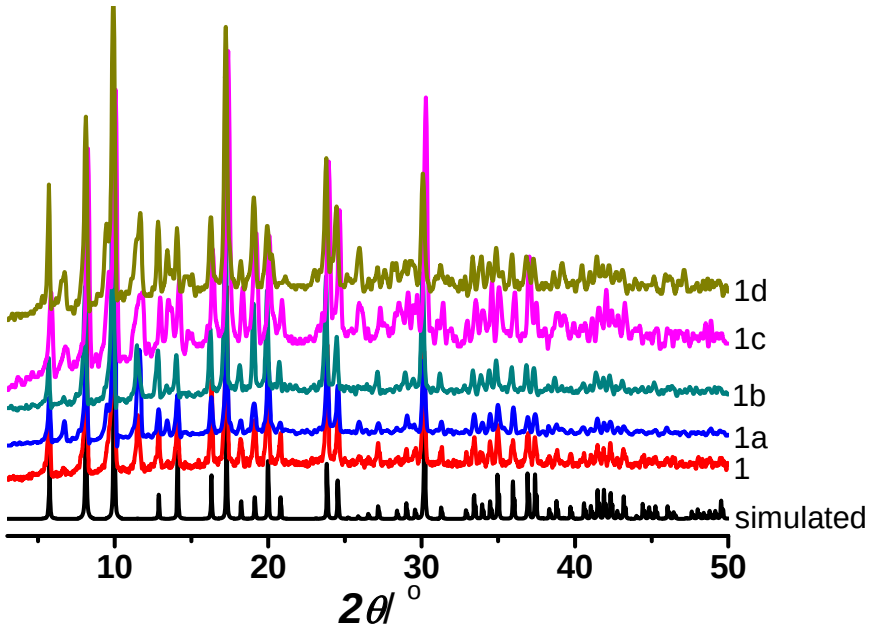

Figure S3. The Powder XRD patterns of simulated one and compounds **1-1d**

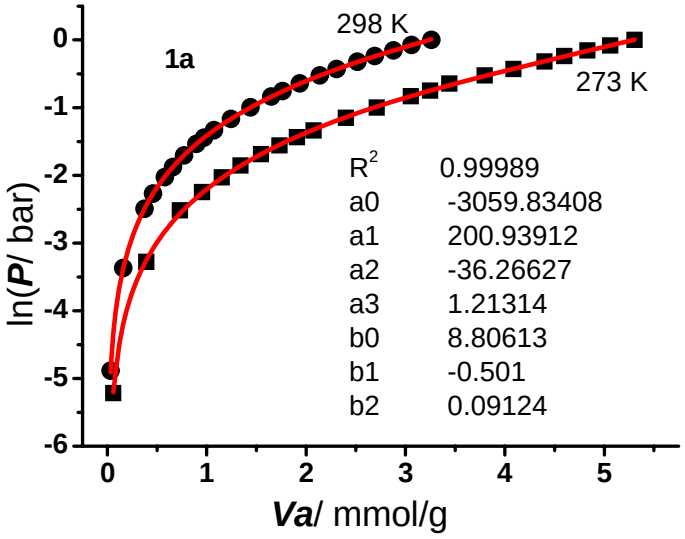

Figure S4 CO_2 adsorption isotherms for **1a** fitting by virial method.

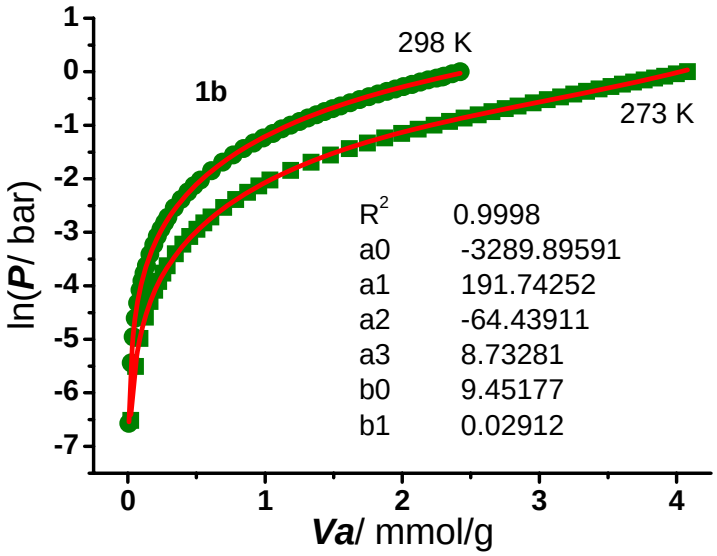

Figure S5 CO_2 adsorption isotherms for **1b** fitting by virial method.

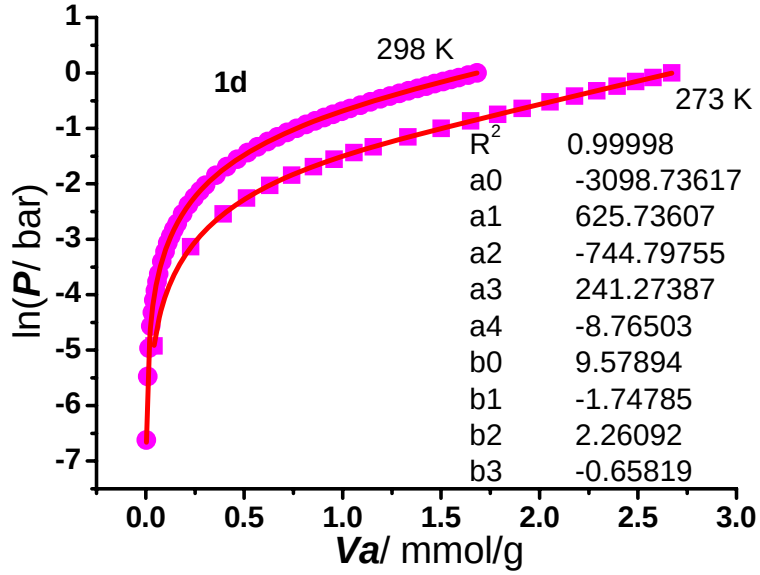

Figure S6 CO_2 adsorption isotherms for **1d** fitting by virial method.

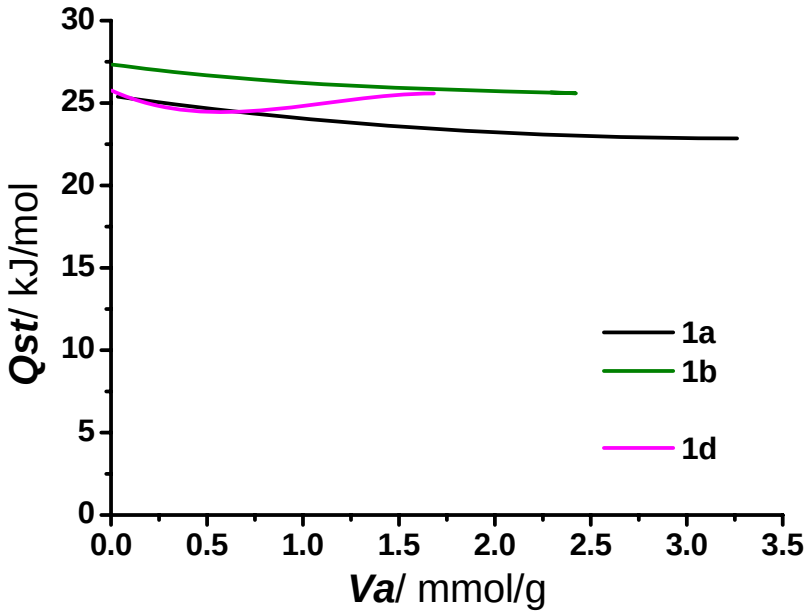

Figure S7 The isosteric heat of CO_2 adsorption for **1a-d** estimated by the virial equation.

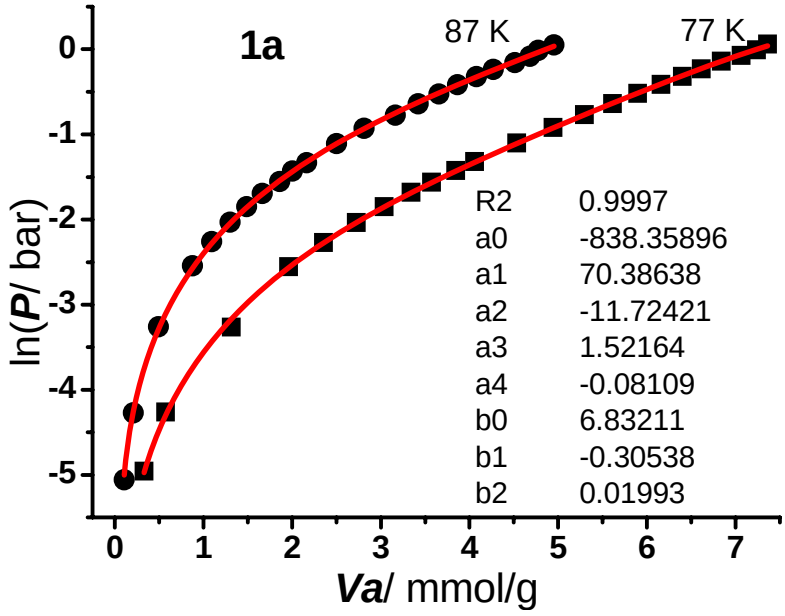

Figure S8. H_2 adsorption isotherms for **1a** fitting by virial method.

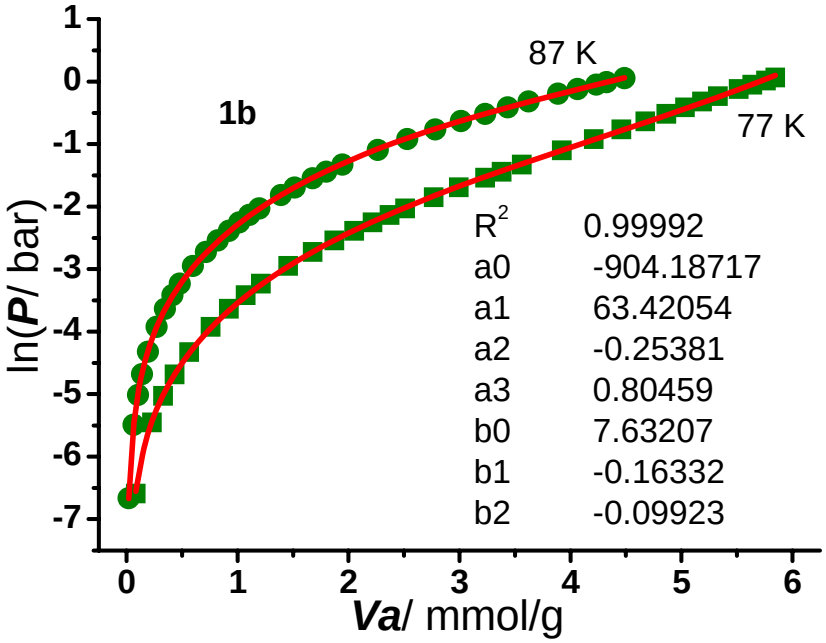

Figure S9. H_2 adsorption isotherms for **1b** fitting by virial method.

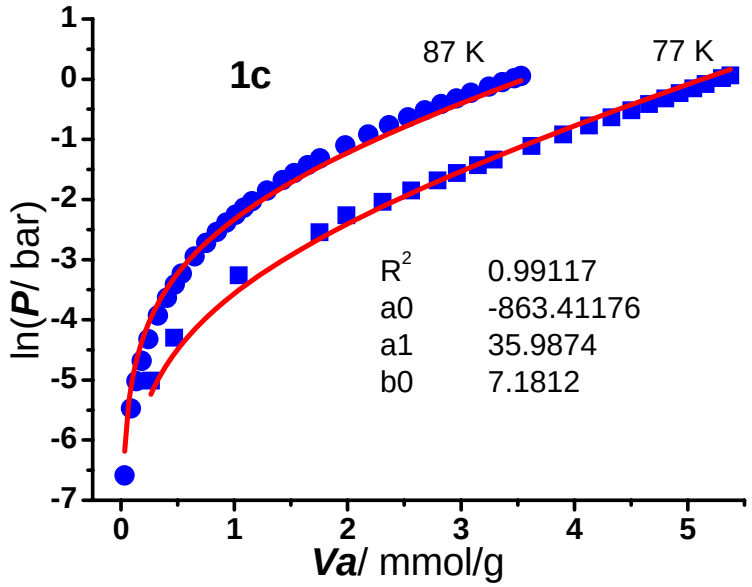

Figure S10. H_2 adsorption isotherms for **1c** fitting by virial method.

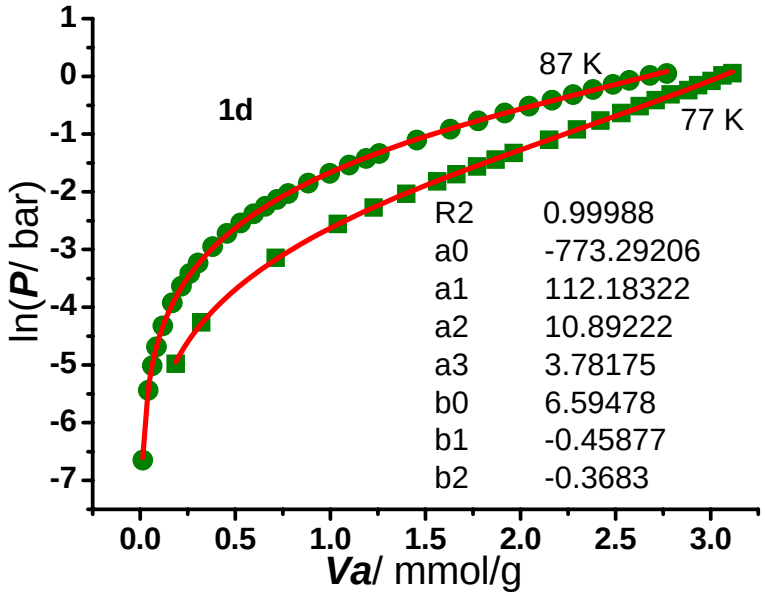

Figure S11. H_2 adsorption isotherms for **1d** fitting by virial method.

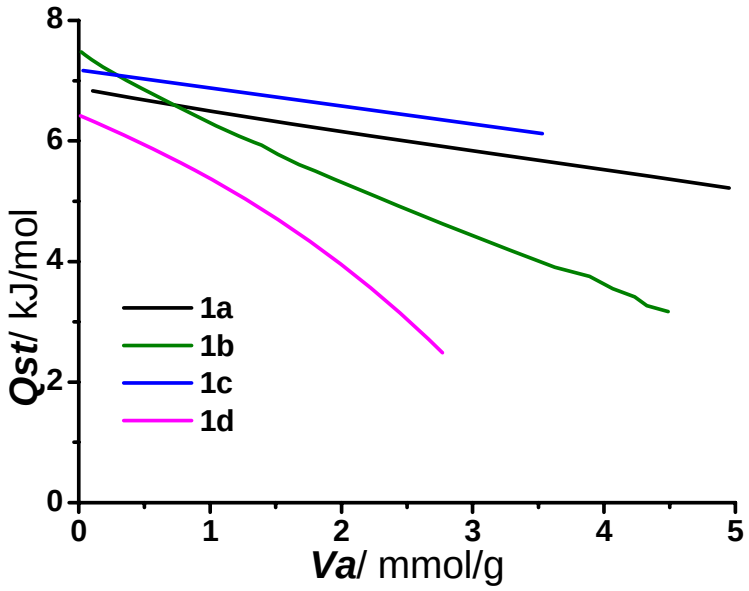

Figure S12 The isosteric heat of H_2 adsorption for **1a-1d** estimated by the virial equation.

Table S1 Summary of porosity measurements, calculations and H_2 adsorption data for materials in this study

material	A_{Lang} (m^2/g)	V_p (cm^3/g)	V_{aH2} (mmol/g)	f_{H2} (%)
IRMOF-2	2544	0.88	12.1	19.4
IRMOF-6	3263	1.14	14.8	18.3
IRMOF-9	2613	0.90	11.7	18.4
IRMOF-13	2100	0.73	17.3	33.5
IRMOF-20	4346	1.53	13.5	12.5
MOF-5	1250	1.19	11.6	13.7
HKUST-1	2715	0.75	25.4	47.8
MOF-74	1132	0.39	17.7	64.1

A_{Lang} is the Langmuir apparent surface areas; V_p is the measured pore volume; N_{H2} is the amount of H_2 adsorbed at 1 atm, 77 K; $f_{H2} = N_{H2}/(1000 \times \rho_{H2} \times Vp)$ is the fraction of the pore volume filled by liquid H_2 (ρ_{H2} = 0.0708 g/cm^3) at 1 bar and 77 K.

Table S2. Bond lengths [A] and angles [deg] for **1**.

Cu(1)-O(1)#1	1.940(3)	O(1)-Cu(1)-O(1)#3	90.8(3)
Cu(1)-O(1)	1.940(3)	O(1)#2-Cu(1)-O(1)#3	85.5(3)
Cu(1)-O(1)#2	1.940(3)	O(1)#1-Cu(1)-Cl(1)	100.34(12)
Cu(1)-O(1)#3	1.940(3)	O(1)-Cu(1)-Cl(1)	100.34(12)
Cu(1)-Cl(1)	2.5227(10)	O(1)#2-Cu(1)-Cl(1)	100.34(12)
Cl(1)-Cu(1)#4	2.5227(10)	O(1)#3-Cu(1)-Cl(1)	100.34(12)
Cl(1)-Cu(1)#5	2.5227(10)	Cu(1)#4-Cl(1)-Cu(1)	90.0
Cl(1)-Cu(1)#6	2.5227(10)	Cu(1)#4-Cl(1)-Cu(1)#5	90.0
O(1)#1-Cu(1)-O(1)	85.5(3)	Cu(1)-Cl(1)-Cu(1)#5	180.0
O(1)#1-Cu(1)-O(1)#2	90.8(3)	Cu(1)#4-Cl(1)-Cu(1)#6	180.0
O(1)-Cu(1)-O(1)#2	159.3(2)	Cu(1)-Cl(1)-Cu(1)#6	90.0
O(1)#1-Cu(1)-O(1)#3	159.3(2)	Cu(1)#5-Cl(1)-Cu(1)#6	90.0

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1,z #2 x,-y+1,-z #3 x,y,-z #4 -y+1,-x+1,z #5 -x+1,-y+1,-z #6 y,x,-z