Electronic Supplementary Information for

An *rht*-type metal-organic framework constructed from an unsymmetrical ligand exhibiting high hydrogen uptake capability

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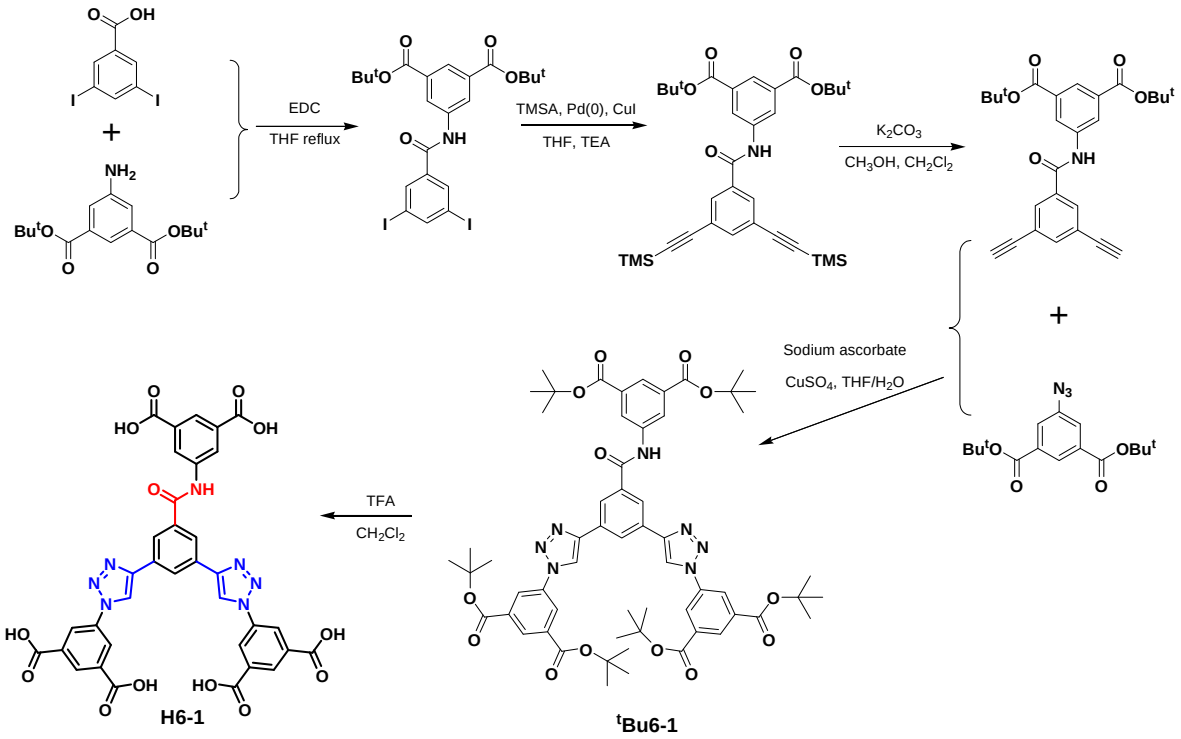


Scheme S1. Synthetic route for ligand **H6-1**. EDC = 1-ethyl-3-(3-dimethyllaminopropyl)carbodiimide; THF = tetrahydrofuran; TMSA = trimethylsilylactylene; TEA = triethylamine; TFA = trifluoracetic acid.

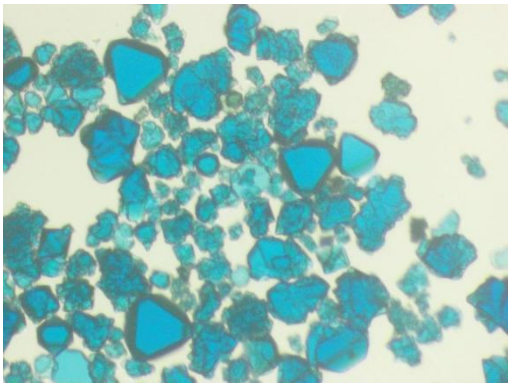


Fig. S1 The photograph of crystals of as-synthesized **Cu-ABTA**, showing they have good and regular morphologies and shapes.

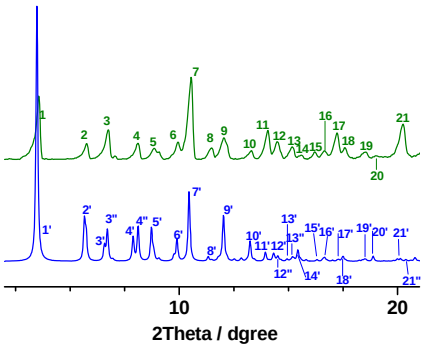


Fig. S2 The zoomed-in comparison of PXRD patterns (2Theta = 2-21°) of as-synthesized MOF **Cu-ABAT** (upper) and simulation from MOF **NTU-105** (bottom) single crystal data. Although some of peaks in **NTU-105** (3' and 3"; 4' and 4"; 12' and 12"; 13' and 13"; 21' and 21") are merged into corresponding one peak in **Cu-ABTA**, mainly due to the different organic ligand in the two MOFs. However, most of the position of main peaks matches very well. This indicates that the overall framework structure of **Cu-ABTA** is the same as that of MOF **NTU-105**.

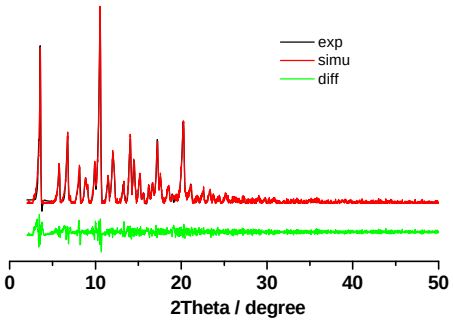


Fig. S3 Experimental (black), calculated (red), and difference (green below observed and calculated patterns) X-ray powder diffraction profiles for **Cu-ABTA**. All diffraction patterns were indexed using DICVOL9113 to obtain lattice parameters that were subsequently refined in a Pawley fit. A modified Thompson-Cox-Hastings pseudo-Voigt profile function with a simple axial correction was used in TOPAS (Topas V3.0: General Profile and Structure Analysis Software for Powder Diffraction Data Bruker AXS Ltd, 2004). The cell parameters are a = 30. 03 Å, b = 30.03 Å, c = 43.11 Å, α = 90°, β = 90°, γ = 90° with a tetragonal space group *I4/m*, which are close to these of **NTU-105**. The results of PXRD measurements and simulation indicate that **Cu-ABTA** still possesses the same (3,24)-connected *rht*-framework as our reported MOF **NTU-105**.

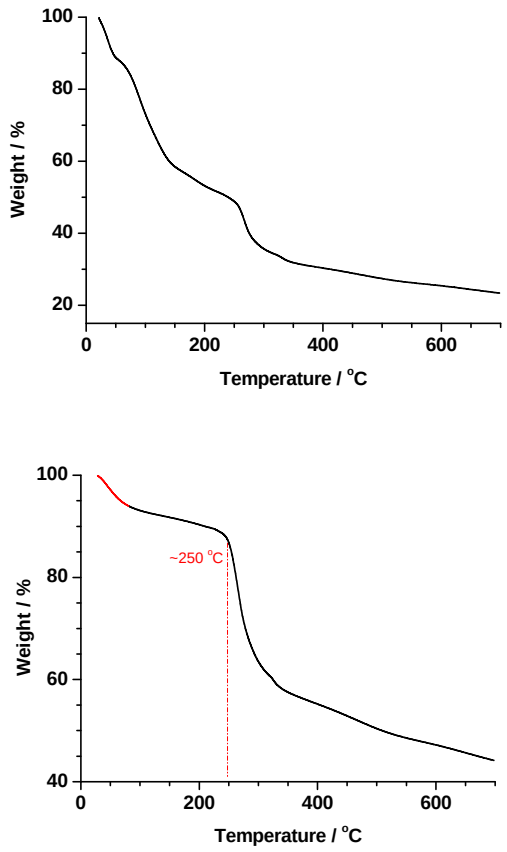


Fig. S4 TGA plot of as-synthesized (upper) and desolvated (bottom) MOF **Cu-ABTA**. The initial weight loss (red line) of activated sample can be attributed to the readsorbed water during sample weighing. This suggests the framework was stable up to ~250 °C, which is similar to **NTU-105**.

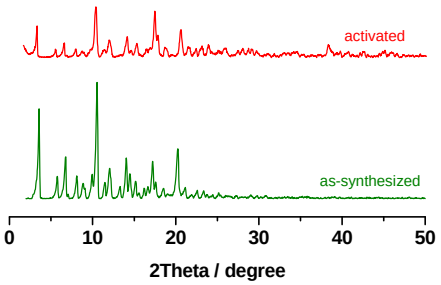


Fig. S5 XRD pattern of desolvated **Cu-ABTA** (indicating the framework was retained well after activation).

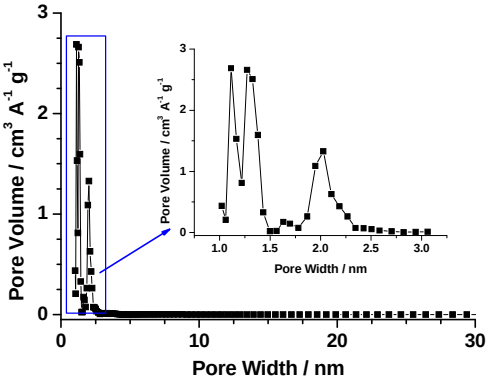


Fig. S6 Pore-size distribution plot for **Cu-ABTA** as calculated from experimental N_2 adsorption isotherm using the nonlocal denity functional theory (NLDFT).

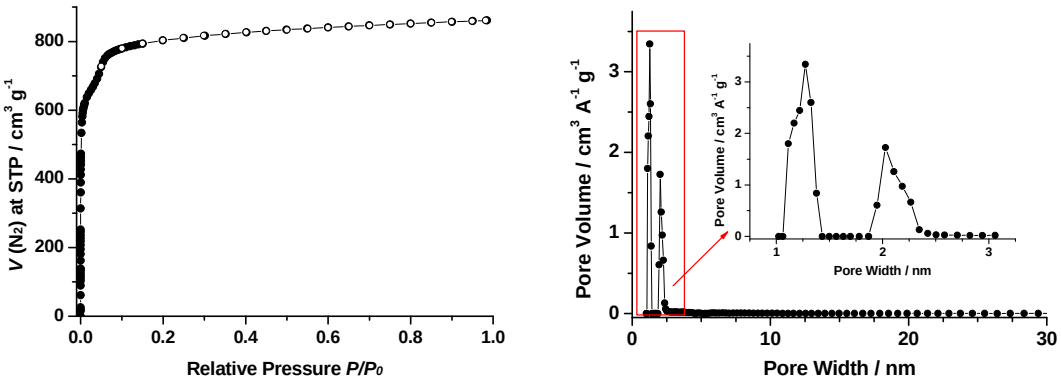


Fig. S7 N_2 sorption isotherm (left) at 77 K and pore-size distribution plot (right) for **NTU-105** as calculated from experimental N_2 adsorption isotherm using the NLDFT.

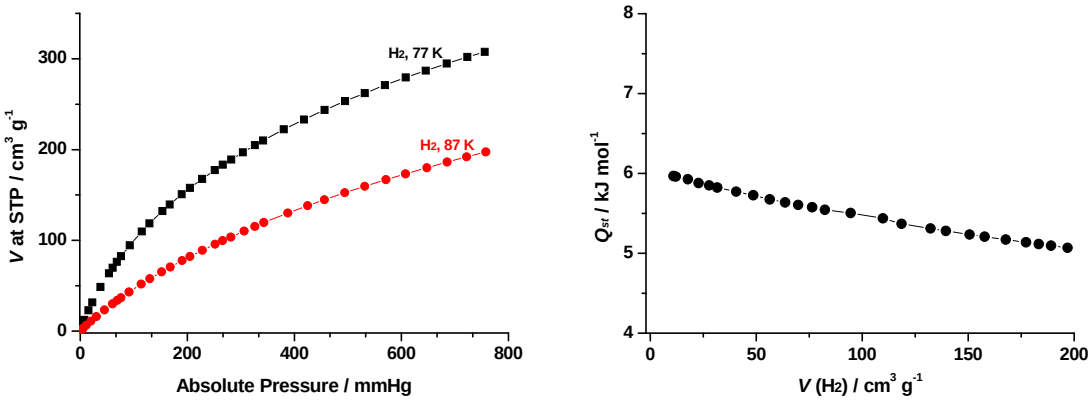


Fig. S8 H_2 adsorption isotherms (left) and isosteric heat of H_2 adsorption (right) for **NTU-105** calculated from the adsorption isotherms at 77 K and 78 K.

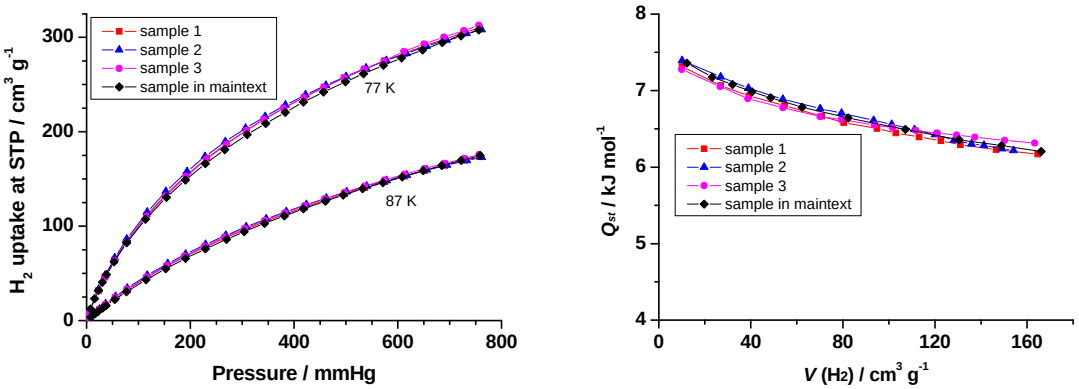


Fig. S9 Another three hydrogen sorption measurements for MOF **Cu-ABTA** (and corresponding Q_{st} calculated from the adsorption isotherms at 77 K and 78 K) by using different samples every time to avoid the accidental error. These indicated the good reproducibility.

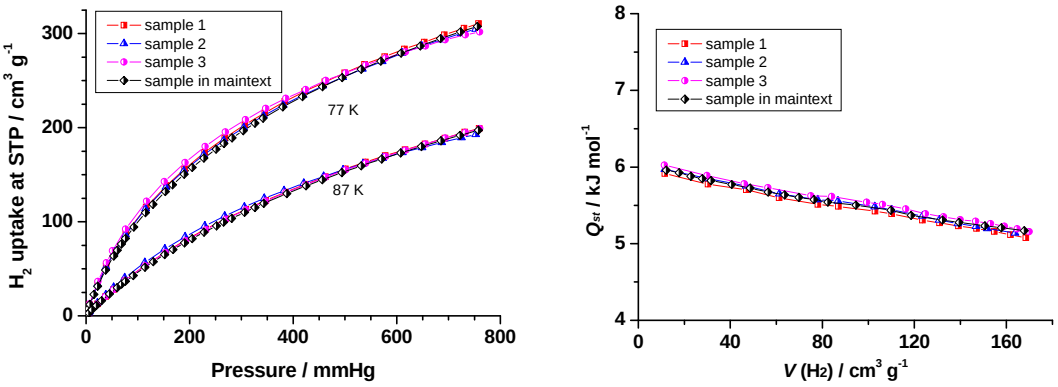


Fig. S10 Another three hydrogen sorption measurements for MOF **NTU-105** (and corresponding Q_{st} calculated from the adsorption isotherms at 77 K and 78 K) by using different samples every time to avoid the accidental error. These indicated the good reproducibility.

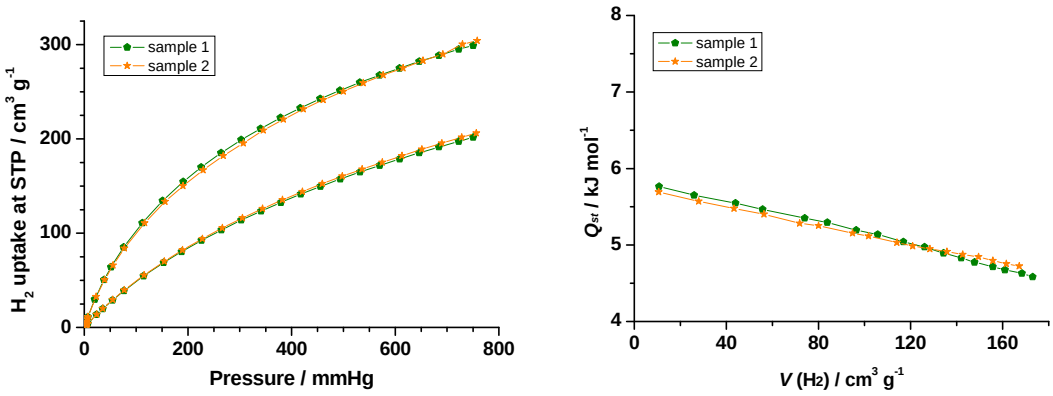


Fig. S11 Two hydrogen sorption measurements for MOF **Cu-TPBTM** (the ligand is connected by three amide groups, *J. Am. Chem. Soc.*, 2011, **133**, 748.) (and corresponding Q_{st} calculated from the adsorption isotherms at 77 K and 78 K) by using two different samples.

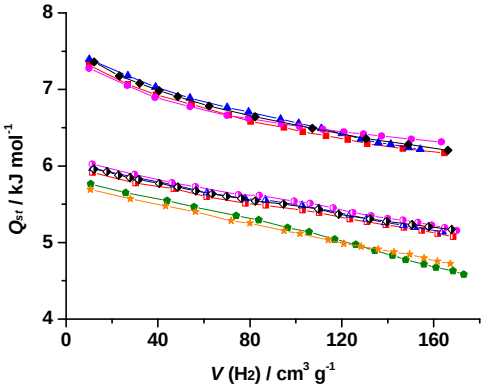


Fig. S12 The comparison of Q_{st} for hydrogen adsorption of MOFs **Cu-ABTA**, **NTU-105** and **Cu-TPBTM**. As shown in **Fig.** S9-12, although there are no huge differences in the amount of hydrogen gas uptake among these three MOFs, however, some differences of the isosteric heat of adsorption (Q_{st}) are presented. The results show that the Q_{st} of our reported MOF **Cu-ABTA** is higher than both of **NTU-105** and **Cu-TPBTM** instead of in between of them (Cu-ABTA > NTU-105 > Cu-TPBTM).

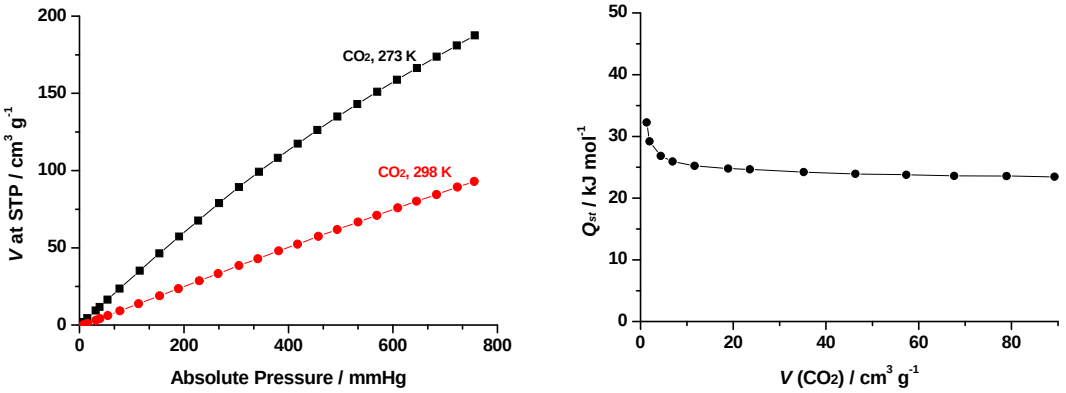


Fig. S13 CO_2 adsorption isotherms (left) and isosteric heat of CO_2 absorption (right) for **NTU-105** calculated from the adsorption isotherms at 273 K and 298 K.

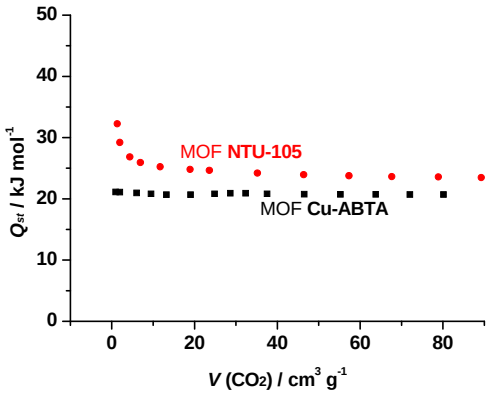
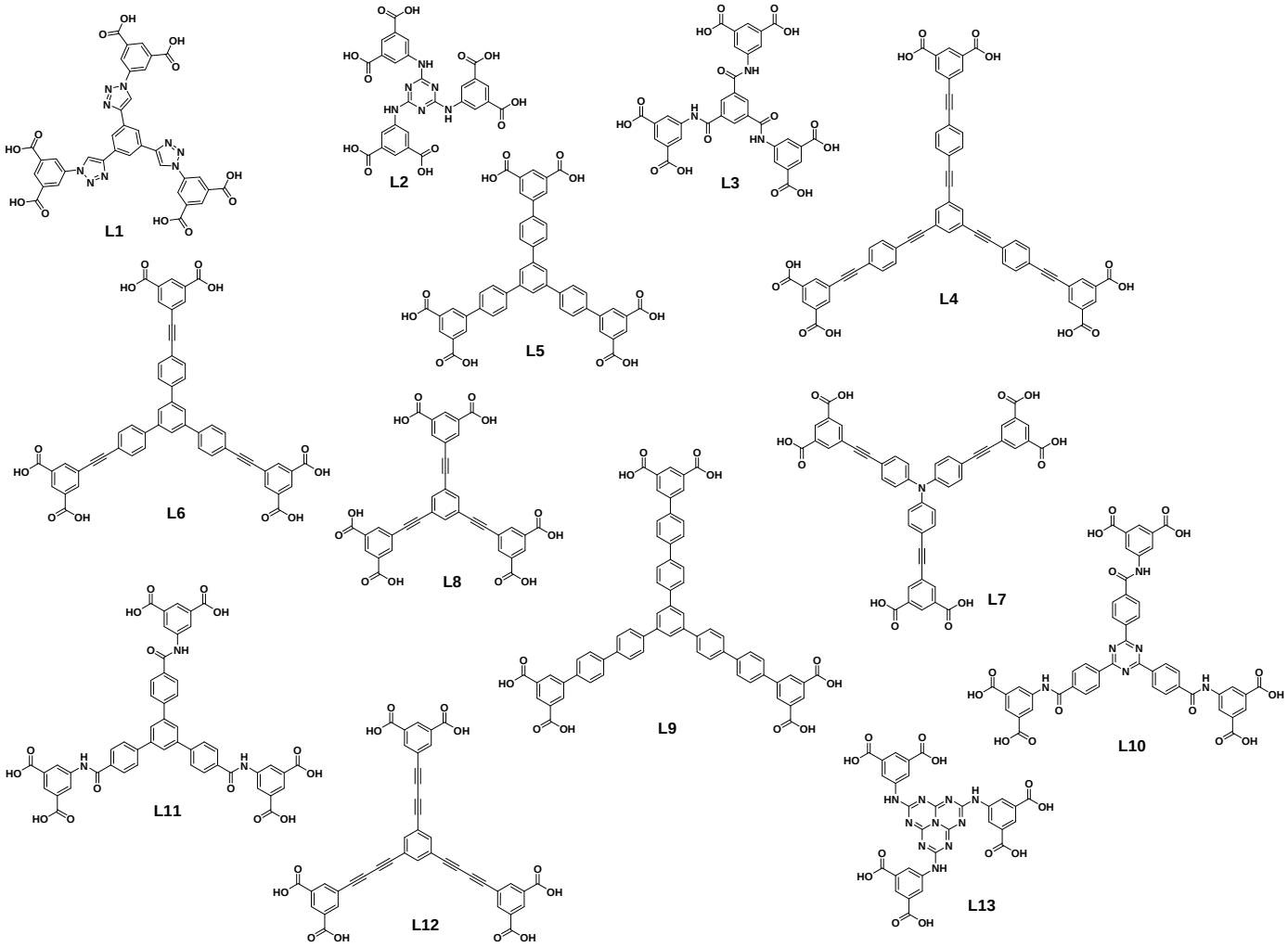


Fig. S14 Comparison of isosteric heat for CO_2 adsorption of MOF **Cu-ABTA** and **NTU-105** under the same uptake amount.



Scheme S2. The chemical structure of reported C_3-symmetric ligands used in constructing *rht*-type MOFs.

Table S1. Summary of the porosities, and gas uptake capacities of various *rth*-type MOFs.

MOF [ligand]	S_{BET} [m^2 g^{-1}][a]	V_{pore} [cm^3 g^{-1}][a]	H_2 uptake [wt%][b]	CO_2 uptake [wt%][c]	ref.
Cu-ABTA [H6-1]	2840	1.19	2.75	30.1	This work
NTU-105[d] [**L1**]	3543	1.33	2.75	36.7	S1
Cu-TDPAT[e] [**L2**]	1938	0.93	2.65	44.5	S2
Cu-TPBTM [**L3**]	3160	1.27	—	42.6	S3
NU-100[f] [**L4**]	6143	2.82	1.82	12.3[g]	S4
NOTT-112 [**L5**]	3800	1.62	2.3	—	S5
PCN-68[h][**L6**]	5109	2.13	1.87	—	S6
PCN-66 [**L7**]	4000	1.63	1.79	—	S6,S7
PCN-61 [**L8**]	3000	1.36	2.25	—	S6,S7
PCN-69[i] [**L9**]	3989	2.17	1.72	—	S8
Cu-TATB [**L10**]	3360	1.91	—	17.3	S9
Cu-BTB [**L11**]	3288	1.77	—	17.2	S9
NU-111 [**L12**]	5000	2.38	2.1	—	S10
rht-MOF-9 [**L13**]	2420[j]	1.01[j]	2.72	25.3	S11

[a]calculated from N_2 isotherms at 77 K; [b]at 77 K, 1 atm; [c]at 273 K, 1 atm; [d]also known as NOTT-122[S12] or NU-125[S13]; [e]also known as rth-MOF-7[S14]; [f]also known as PCN-610[S6]; [g]data at 298 K, 1 atm, due to the absence of the data at 273 K, 1 atm; [h]also known as NOTT-116[S15]; [i]also known as NOTT-119[S16]; [j]calculated from Ar isotherms at 87 K

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