Electronic Supplementary Information (ESI)

A water stable microporous metal-organic framework based on rod SBUs: synthesis, structure and adsorption properties

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S1. Calculation procedures of selectivity from IAST

The measured experimental data is excess loadings (q^{ex}) of the pure components CO_2, CH_4 and C_2H_6 for compound **1**, which should be converted to absolute loadings (q) firstly.

$$q = q^{ex} + \frac{pV_{pore}}{ZRT}$$

Here Z is the compressibility factor. The Peng-Robinson equation was used to estimate the value of compressibility factor to obtain the absolute loading, while the measure pore volume 0.509 cm^3 g^{-1} is also necessary.

The dual-site Langmuir-Freundlich equation is used for fitting the isotherm data at 298 K.

$$q = q_{m_1} \times \frac{b_1 \times p^{1/n_1}}{1 + b_1 \times p^{1/n_1}} + q_{m_2} \times \frac{b_2 \times p^{1/n_2}}{1 + b_2 \times p^{1/n_2}}$$

Here p is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol kg^{-1}), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol kg-1), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), n_1 and n_2 are the deviations from an ideal homogeneous surface.

The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, perhaps in the presence of other components too, can be formally defined as

$$S = \frac{q_1/q_2}{p_1/p_2}$$

q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

S2. Supporting Figures

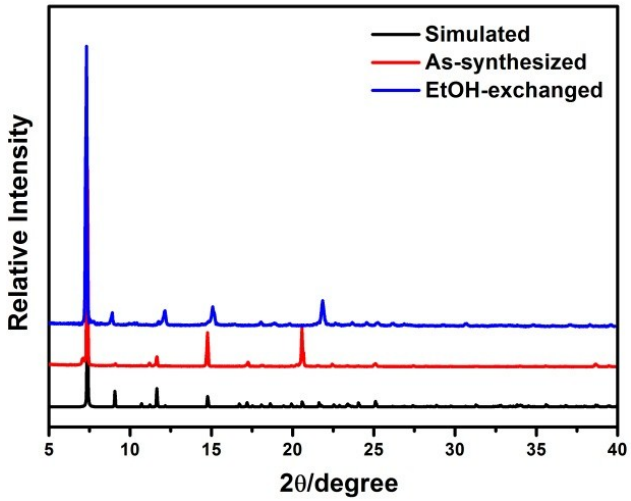

Fig. S1 PXRD patterns of compound **1** for simulated, as-synthesized and EtOH-exchanged samples. The differences in reflection intensity are probably due to preferred orientations in the powder sample.

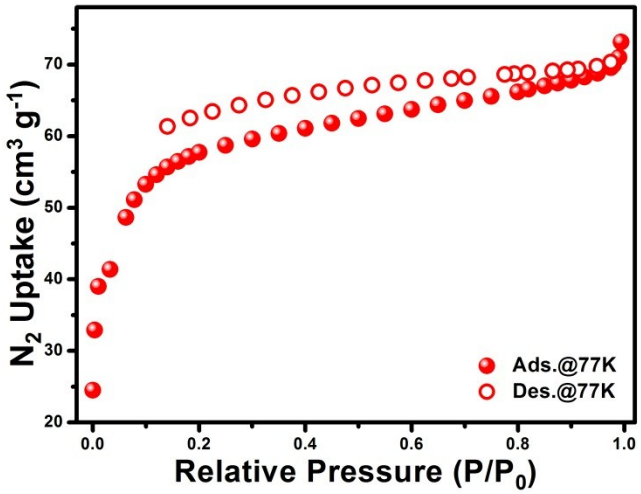

Fig. S2 N_2 isotherms for compound **1** at 77 K under 1 bar.

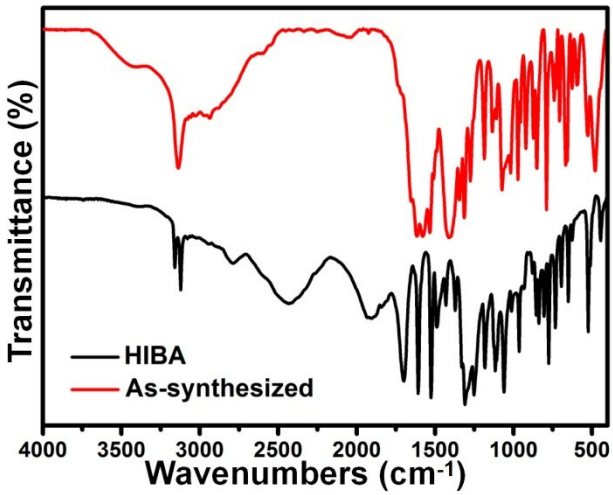

Fig. S3 Infrared spectra for compound **1** and the organic HIBA ligand.

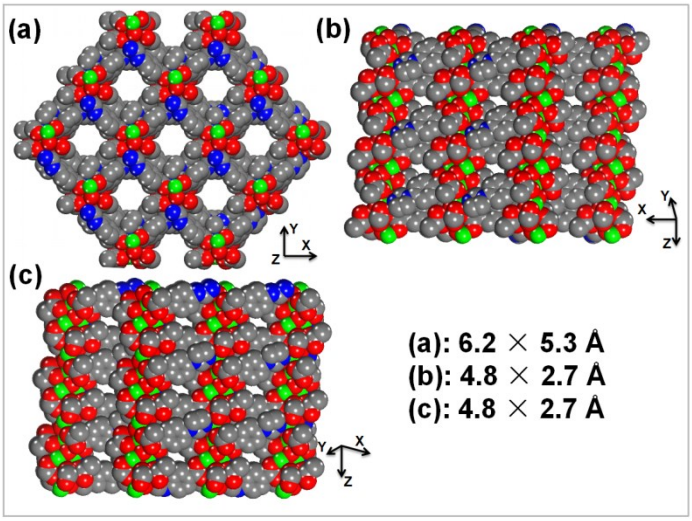

Fig. S4 Space-filling view of the structure of compound **1** showing multiple pores in different directions (regardless of van der Waals radii).

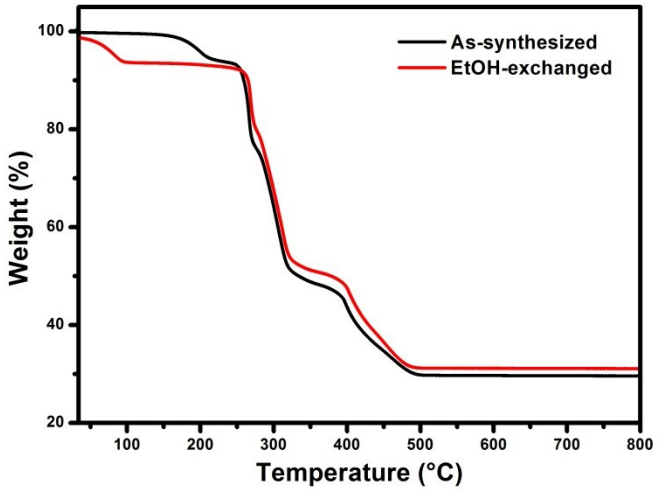

Fig. S5 Thermogravimetric analysis curves of compound **1** for the as-synthesized and EtOH exchanged samples.

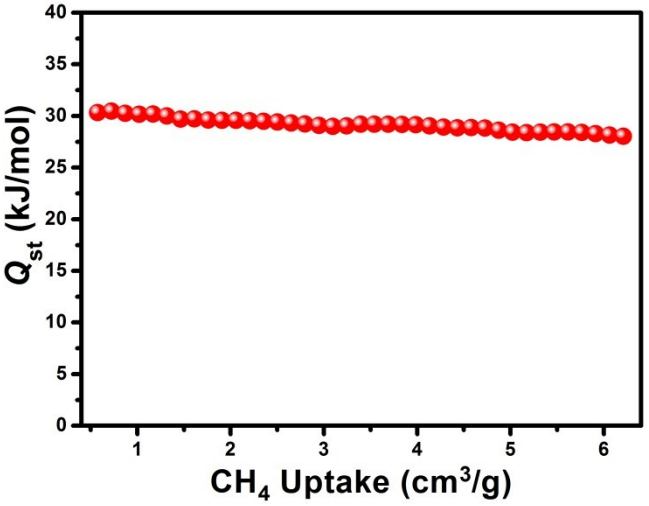

Fig. S6 Q_{st} of CH_4 for compound **1** calculated by MicroActive soft.

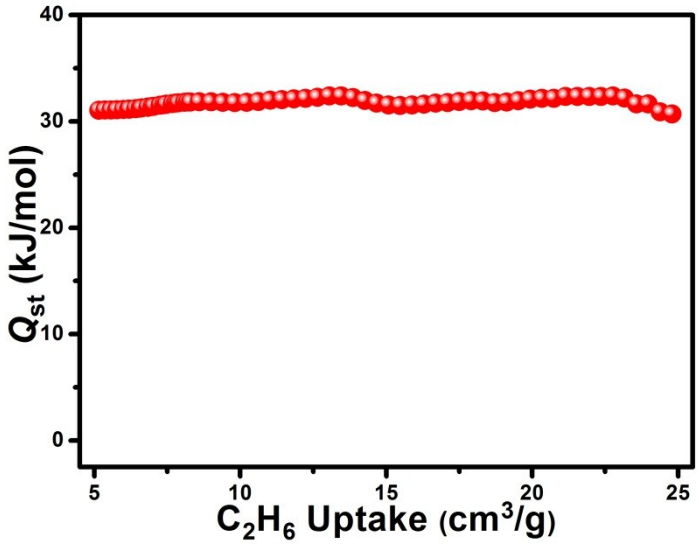

Fig. S7 Q_{st} of C_2H_6 for compound **1** calculated by MicroActive soft.

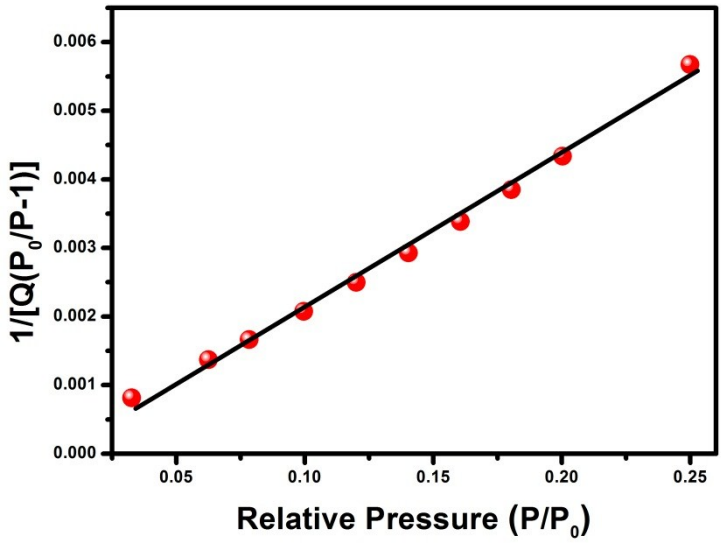

Fig. S8 The linear fitting curve for calculating BET surface areas of compound **1**.

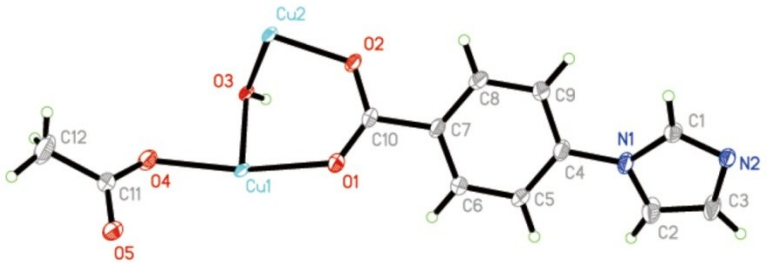

Fig. S9 Thermal ellipsoid (30%) plot of the hydrogen bonded framework of compound **1**.

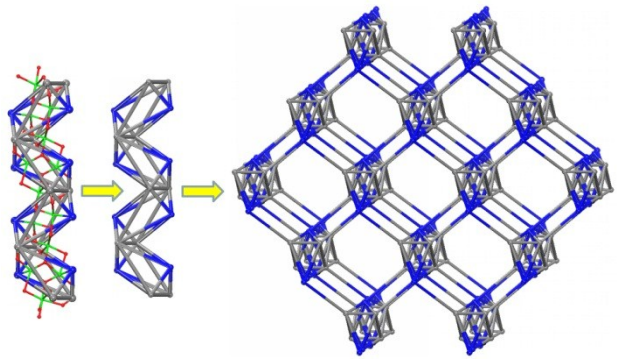

Fig. S10 Topology simplification of compound **1**

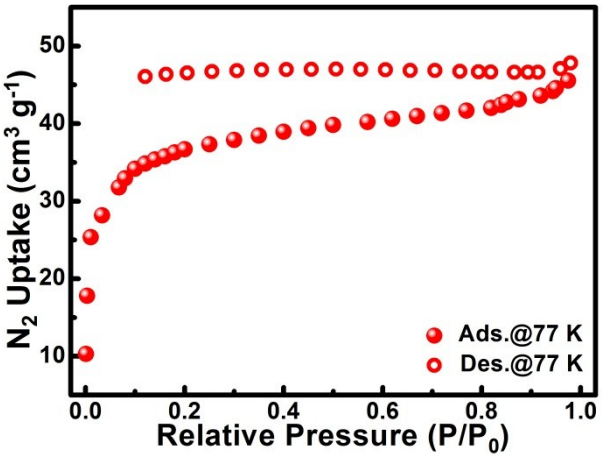

Fig. S11 N_2 isotherms for water-treated compound **1** at 77 K under 1 bar.

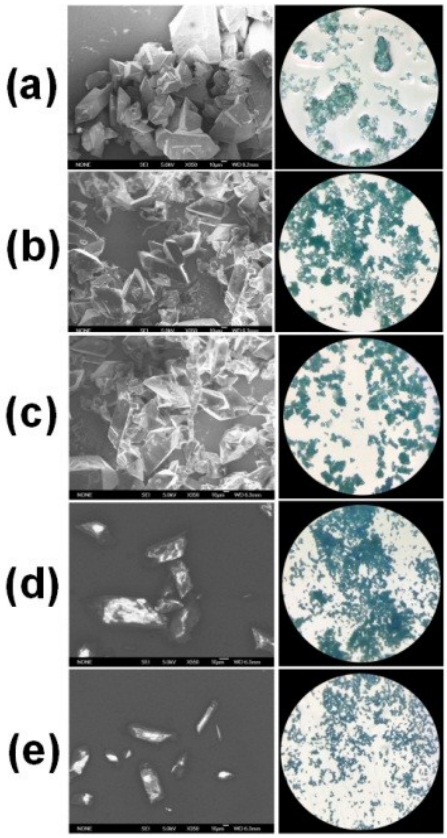

Fig. S12 SEM images (left) and optical photos (right) of compound **1**. From top to bottom is before (a) and after thermal (b), water (c), acid (d) and base treatment (e).

S3. Supporting Tables

Table S1. Crystal data and structure refinements for compound **1**.

Compound	**1**
Formula	$C_{28}H_{34}Cu_3N_6O_{10}$
F_w	805.23
Temp (K)	293(2) K
Crystal system	Monoclinic
Space group	C2/c
a (Å)	15.225(3)
b (Å)	19.518(4)
c (Å)	10.927(2)
α (°)	90
β (°)	93.42(3)
γ (°)	90
V(Å^3)	3241.3(11)
Z	4
D_c (Mg m^{-3})	1.650
Absorption coefficient (mm^{-1})	2.015
F(000)	1644
Reflections collected/unique (R_{int})	10463 / 2952 [R(int) = 0.0236]
Goodness on fit	1.088
Final R indices [I > 2σ(I)]	R1 = 0.0192, wR2 = 0.0522
R indices (all data)	R1 = 0.0217, wR2 = 0.0530

$R_1=\sum||F_o|-|F_c||/\sum|F_o|$. $wR_2=[\sum[\ w\ (F_o^2-F_c^2)^2]\ /\ \sum[\ w\ (F_o^2)^2]]^{1/2}$

Since the highly disordered cations and guest molecules were trapped in the channels of compound 1 and could not be modeled properly, the PLATON/SQUEEZE was applied to remove their diffraction contribution. The final formula of compound **1** was derived from crystallographic data combined with elemental and thermogravimetric analysis data. Thus, there is "Alert level A" about "check chemical formula weight" in the "checkCIF/PLATON report" files for compound **1**.

Table S2. Selected bond lengths [Å] and angles [º] for compound **1**.

Compound 1			
Cu(1)-O(3)#1	1.9471(12)	Cu(1)-O(3)	1.9471(12)
Cu(1)-O(4)	2.1362(13)	Cu(1)-O(4)#1	2.1362(13)
Cu(1)-O(1)#1	2.2043(13)	Cu(1)-O(1)	2.2043(13)
Cu(2)-O(2)	1.9386(11)	Cu(2)-O(3)	1.9749(12)
Cu(2)-N(2)#2	1.9792(14)	Cu(2)-O(3)#3	1.9819(12)
Cu(2)-O(4)#3	2.4148(14)	Cu(2)-Cu(2)#3	3.0407(6)
O(3)-Cu(2)#3	1.9818(12)	O(4)-Cu(2)#3	2.4148(14)
N(2)-Cu(2)#4	1.9792(14)	O(3)#1-Cu(1)-O(3)	179.33(7)
O(3)#1-Cu(1)-O(4)	95.33(5)	O(3)-Cu(1)-O(4)	84.30(5)
O(3)#1-Cu(1)-O(4)#1	84.30(5)	O(3)-Cu(1)-O(4)#1	95.33(5)
O(4)-Cu(1)-O(4)#1	112.91(7)	O(3)#1-Cu(1)-O(1)#1	91.31(5)

O(3)-Cu(1)-O(1)#1	89.18(5)	O(4)-Cu(1)-O(1)#1	81.58(5)
O(4)#1-Cu(1)-O(1)#1	165.15(5)	O(3)#1-Cu(1)-O(1)	89.18(5)
O(3)-Cu(1)-O(1)	91.31(5)	O(4)-Cu(1)-O(1)	165.15(5)
O(4)#1-Cu(1)-O(1)	81.58(5)	O(1)#1-Cu(1)-O(1)	84.18(7)
O(2)-Cu(2)-O(3)	93.84(5)	O(2)-Cu(2)-N(2)#2	89.24(5)
O(3)-Cu(2)-N(2)#2	164.52(5)	O(2)-Cu(2)-O(3)#3	169.52(5)
O(3)-Cu(2)-O(3)#3	79.56(5)	N(2)#2-Cu(2)-O(3)#3	99.29(5)
O(2)-Cu(2)-O(4)#3	98.12(5)	O(3)-Cu(2)-O(4)#3	108.21(5)
N(2)#2-Cu(2)-O(4)#3	86.31(5)	O(3)#3-Cu(2)-O(4)#3	76.53(5)
O(2)-Cu(2)-Cu(2)#3	133.19(4)	O(3)-Cu(2)-Cu(2)#3	39.87(3)
N(2)#2-Cu(2)-Cu(2)#3	136.98(4)	O(3)#3-Cu(2)-Cu(2)#3	39.70(3)
O(4)#3-Cu(2)-Cu(2)#3	92.93(3)	C(10)-O(1)-Cu(1)	128.80(11)
C(10)-O(2)-Cu(2)	125.02(11)	Cu(1)-O(3)-Cu(2)	104.42(5)
Cu(1)-O(3)-Cu(2)#3	109.58(6)	Cu(2)-O(3)-Cu(2)#3	100.44(5)
Cu(1)-O(3)-H(3A)	99.3(18)	Cu(2)-O(3)-H(3A)	118.3(19)
Cu(2)#3-O(3)-H(3A)	123.4(19)	C(11)-O(4)-Cu(1)	121.07(12)
C(11)-O(4)-Cu(2)#3	134.51(12)	Cu(1)-O(4)-Cu(2)#3	89.51(5)
C(1)-N(2)-Cu(2)#4	128.19(12)	C(3)-N(2)-Cu(2)#4	125.86(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2 #2 x-1/2,-y+1/2,z+1/2 #3 -x+1,-y+1,-z+1 #4 x+1/2,-y+1/2,z-1/2

Table S3. The refined parameters for the Dual-site Langmuir-Freundlich equations fit for the pure isotherms of CO_2, CH_4 and C_2H_6 for compound **1** at 298 K.

	q_{m1}	b_1	n_1	q_{m2}	b_2	n_2	R^2
CO_2	0.03951	0.01434	2.54669	1.55648	0.00452	1.36442	0.99996
CH_4	0.00544	5.90407E-5	2.9435	2.85019	0.00101	1.00496	0.99994
C_2H_6	0.96431	0.08232	1.09639	1.45667	0.012	0.57208	0.99999