Electronic Supplementary Information for

Storage

Yunxia Hu,[a] Shengchang Xiang,[b] Wenwei Zhang,[a,*] Zhuxiu Zhang,[a] Lei Wang,[a] Junfeng Bai,[a,*] and Banglin Chen[b,*]

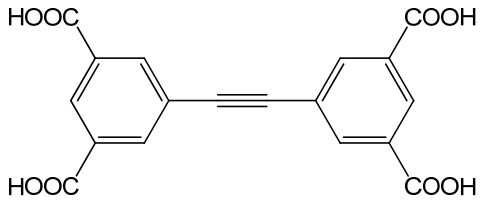
[a] *State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China. E-mail: wwzhang@nju.edu.cn, bjunfeng@nju.edu.cn*
[b] *Department of Chemistry, University of Texas at San Antonio, San Antonio, TX 78249-0698, USA. E-mail: banglin.chen@utsa.edu*,

General Method

Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer. The IR spectra were obtained on a VECTOR TM 22 spectrometer with KBr pellets in the 4000~400 cm^{-1} region. ^1H NMR spectra were recorded on a Bruker DRX-500 spectrometer at ambient temperature with tetramethylsilane as an internal reference. The MS spectra were measured on a Finnigan LCQ electron spray mass spectrometer. TGA-DTA diagrams were recorded by a CA Instruments DTA-TGA 2960 type simultaneous analyzer heating from 293 to 973 K in nitrogen atmosphere at a rate of 20 K/min. Powder X-ray diffraction (PXRD) data were recorded on a Shimadzu XRD-6000 diffractometer with Cu Kα (λ = 1.54056 Å) radiation at room temperature with a scan speed of 5º/min and a step size of 0.02 in 2θ.

Synthesis of H_4EBTC

The organic linker molecule H_4EBTC was prepared according the literatures.[1] It was characterized by IR and MS.



H_4EBTC

Data for **H_4EBTC**: IR (cm^{-1}) :3087~2867(br, m), 2953(m), 2159(w~m), 1707 (vs), 1595 (m), 1446 (s), 1279(vs), 908(m), 755 (m), 690 (m); MS: *m/z* 353.00 $[M-1]^-$ (calcd 353.04).

Derivation of the Isosteric Heats of Adsorption. A virial type expression of the following form was used to fit the combined isotherm data for a given material at 295 and 273 K.

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

Here, P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m, n represent the number of coefficients required to adequately describe the isotherms. The equation was fit using the statistical software package ***SPSS*** 16.0; m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, as determined using the t-test, and the average value of the squared deviations from the experimental values was minimized. The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i \qquad (2)$$

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas

constant.

The parameters a_i and b_i in the Virial type expression after the data fitting

	a0	a1	a2	a3	a4	a5	a6	b0	b1	B2	B3
C2H2	-4265.215±60.907	125.029±2.341	-4.509±0.205	0±0	0±0	0±0	0±0	16.788±0.214	0±0	0±0	0±0

Coefficients[a]

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
3	(Constant)	16.788	.214		78.597	.000
	1/T*N	125.029	2.341	1.716	53.397	.000
	1/T	-4265.215	60.907	-.693	-70.028	.000
	1/T*N^2	-4.509	.205	-.727	-21.972	.000

a. Dependent Variable: LnP-LnN

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
3	.998[c]	.995	.995	.059665604113477

c. Predictors: (Constant), 1/T*N, 1/T, 1/T*N^2

Table S1. Crystal data and structure refinement for $[Cu_2(EBTC)(H_2O)_2]$ (MOF 1)

Identification code	MOF **1**	
Empirical formula	C18 H10 Cu2 O10	
Formula weight	513.34	
Temperature	293K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R-3m	
Unit cell dimensions.	a = 18.6844(11) Å	α = 90°
	b = 18.6844(11) Å	β = 90˚
	c = 32.862(4)	γ =120˚
Volume	9935.3(14) $Å^3$	
Z	9	
Density (calculated)	0.772 Mg/m^3	
Absorption coefficient	0.987 mm^{-1}	
F(000)	2304	
Crystal size	0.26 x 0.26 x 0.24 mm	
Theta range for data collection.	1.77 to 28.33°	
Index ranges	-24<=h<=13, -15<=k<=24, -42<=l<=38	
Reflections collected	20186	
Independent reflections	2954 [R(int) = 0.143]	
Completeness to theta = 28.33°	98.0 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.79 and 0.76	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	2954 / 0 / 76	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2sigma(I)]	R1 = 0.0472, wR2 = 0.1077	
R indices (all data)	R1 = 0.1052, wR2 = 0.1101	
Largest diff. peak and hole	0.543 and -0.300 $e.Å^{-3}$	

Table S2. Selected bond lengths [Å] and angles [°] for MOF 1

Cu(1)-O(2)#1	1.952(3)
Cu(1)-O(2)#2	1.952(3)
Cu(1)-O(1)	1.963(3)
Cu(1)-O(1)#3	1.962(3)
Cu(1)-O(3)	2.149(4)
O(2)-Cu(1)#2	1.952(3)
O(2)#1-Cu(1)-O(2)#2	88.87(18)
O(2)#1-Cu(1)-O(1)	90.59(12)
O(2)#2-Cu(1)-O(1)	168.36(12)
O(2)#1-Cu(1)-O(1)#3	168.36(12)
O(2)#2-Cu(1)-O(1)#3	90.59(12)
O(1)-Cu(1)-O(1)#3	87.59(17)
O(2)#1-Cu(1)-O(3)	94.97(14)
O(2)#2-Cu(1)-O(3)	94.97(14)
O(1)-Cu(1)-O(3)	96.67(14)
O(1)#3-Cu(1)-O(3)	96.66(14)

Symmetry transformations used to generate equivalent atoms:

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

Table S3. Data for the adsorption of C_2H_2 in MOF 1a at 273.2 K

Pressure (Torr)	Adsorption (cm^3/g)	Adsorption (mmol/g)
0.969	4.852	0.217
4.516	20.973	0.936
7.958	31.677	1.414
10.000	36.721	1.639
11.108	40.043	1.788
15.152	47.513	2.121
30.627	66.811	2.983
55.311	85.734	3.827
93.258	104.659	4.672
111.379	111.920	4.996
138.698	121.627	5.430
166.181	130.510	5.826
193.758	138.768	6.195
221.577	146.621	6.546
249.353	154.058	6.878
277.322	161.160	7.195
305.234	167.984	7.499
333.343	174.582	7.794
359.483	180.525	8.059
387.037	186.551	8.328
414.610	192.357	8.587
442.073	197.958	8.837
469.689	203.407	9.081
497.141	208.644	9.315
524.758	213.747	9.542
552.207	218.639	9.761
579.807	223.406	9.974
607.341	227.979	10.178
634.813	232.421	10.376
662.378	236.604	10.563
689.825	240.646	10.743
717.520	244.559	10.918
744.978	248.263	11.083
772.539	251.805	11.241
800.042	255.182	11.392

Table S4. Data for the desorption of C_2H_2 in MOF 1a at 273.2 K

Pressure (Torr)	Adsorption (cm^3/g)	Adsorption (mmol/g)
746.491	249.665	11.146
704.671	244.662	10.922
663.371	239.255	10.681
633.745	235.142	10.497
592.279	229.027	10.224
550.775	222.482	9.932
509.289	215.498	9.621
467.613	208.071	9.289
426.048	200.246	8.939
384.474	191.969	8.570
342.952	183.187	8.178
301.516	173.862	7.762
259.741	163.847	7.315
218.366	153.128	6.836
176.754	141.381	6.312
135.317	128.273	5.727
93.849	112.807	5.036
53.187	92.353	4.123
10.183	45.578	2.034

Table S5. Data for the adsorption of C_2H_2 in MOF 1a at 295.0 K

Pressure (Torr)	Adsorption (cm^3/g)	Adsorption (mmol/g)
1.031	1.872	0.084
4.261	7.528	0.336
8.354	13.785	0.615
9.3457	15.227	0.680
11.673	18.238	0.814
14.931	22.171	0.990
29.7075	36.016	1.608
56.8041	53.029	2.367
79.7431	63.462	2.833
111.413	74.888	3.343
139.020	83.076	3.709
166.735	90.161	4.025
194.575	96.416	4.304
222.253	102.037	4.555
250.041	107.149	4.783
277.957	111.885	4.995
305.925	116.285	5.191
333.464	120.334	5.372
359.400	123.897	5.531
386.919	127.456	5.690
414.620	130.821	5.840
442.172	134.012	5.983
469.674	137.004	6.116
497.247	139.848	6.243
524.668	142.537	6.363
552.263	145.100	6.478
579.749	147.519	6.586
607.373	149.803	6.688
634.898	151.941	6.783
662.414	153.957	6.873
689.948	155.849	6.958
717.480	157.649	7.038
745.092	159.329	7.113
772.555	160.886	7.182
800.110	162.329	7.247

Table S6. Data for the desorption of C_2H_2 in **MOF 1a** at 295.0 K

Pressure (Torr)	Adsorption (cm^3/g)	Adsorption (mmol/g)
745.112	160.057	7.145
703.395	157.974	7.052
661.962	155.591	6.946
633.797	153.813	6.867
592.438	150.921	6.738
550.889	147.679	6.593
509.112	144.07	6.432
467.632	140.142	6.256
426.222	135.806	6.063
384.598	131.015	5.849
342.899	125.729	5.613
301.375	119.908	5.353
260.056	113.418	5.063
218.208	105.954	4.73
176.882	97.3996	4.348
135.31	87.0976	3.888
94.0579	74.182	3.312
52.879	56.3441	2.515
8.18486	19.1635	0.856

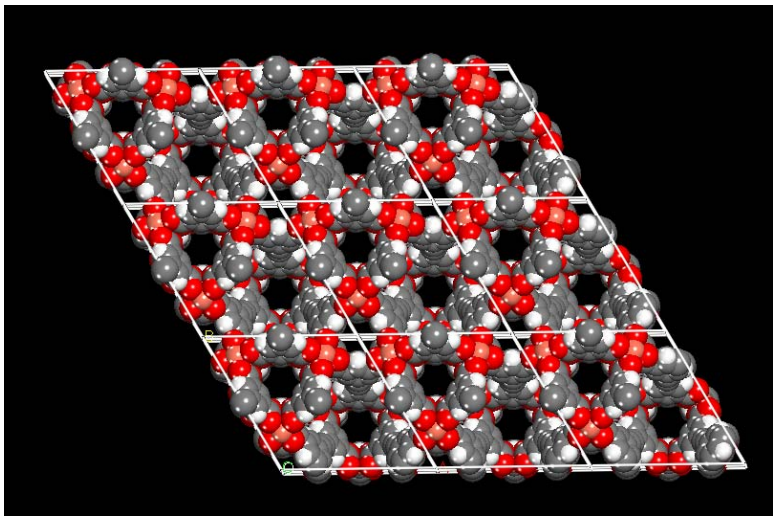


Figure S1. X-ray single crystal structure of $[Cu_2(EBTC)(H_2O)_2]\cdot 8H_2O\cdot DMF\cdot DMSO$ exhibiting 1D pores along *c* axis.

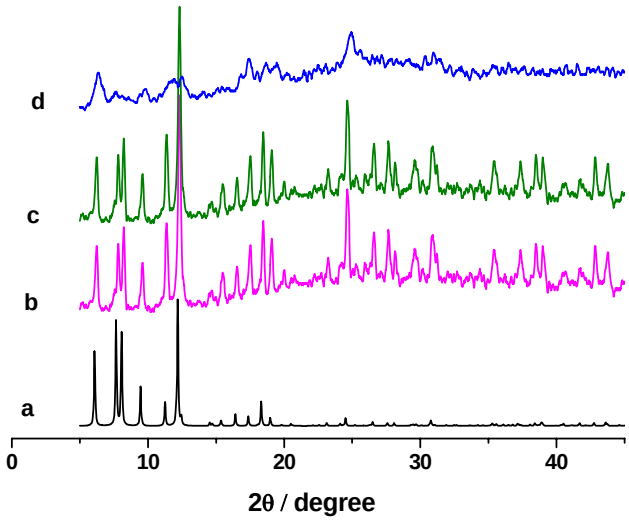


Figure S2. PXRD patterns of MOF **1**: a) simulated pattern based on X-ray single-crystal structure, b) as-synthesized, c) methanol exchanged and d) activated.

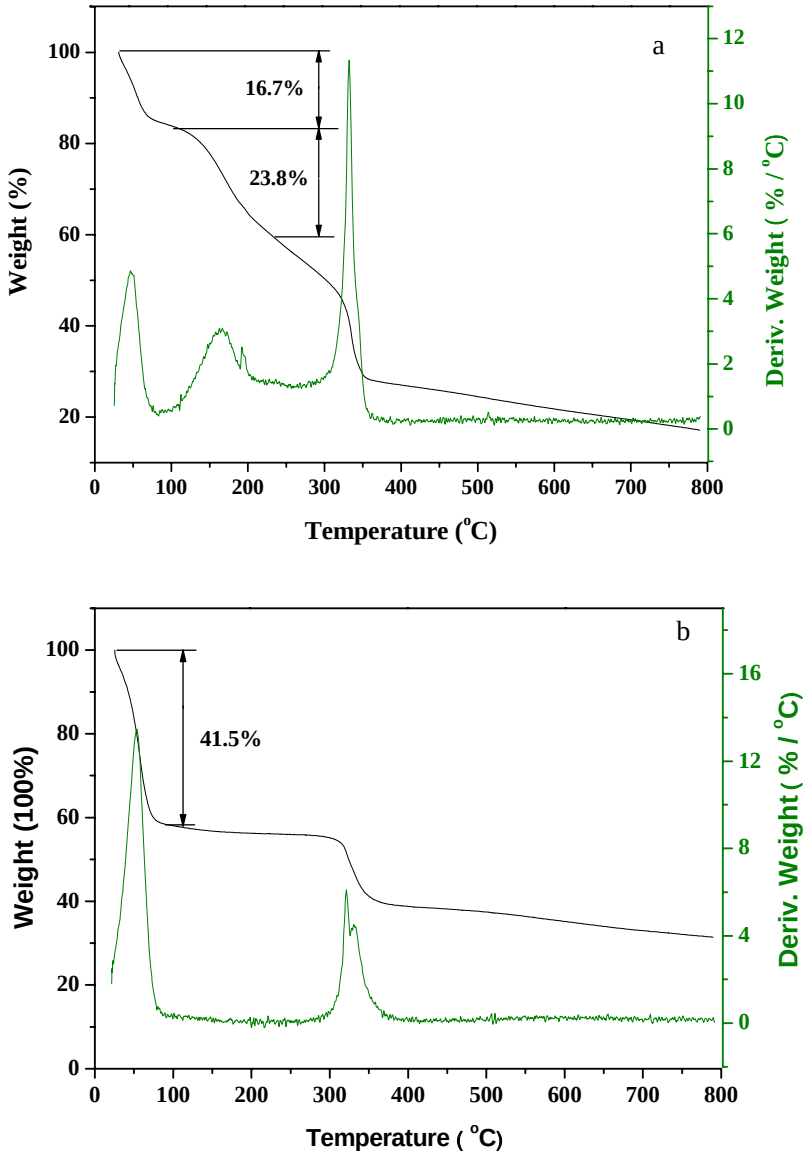


Figure S3. TGA data of MOF **1**: a) as-synthesized and b) methanol exchanged.

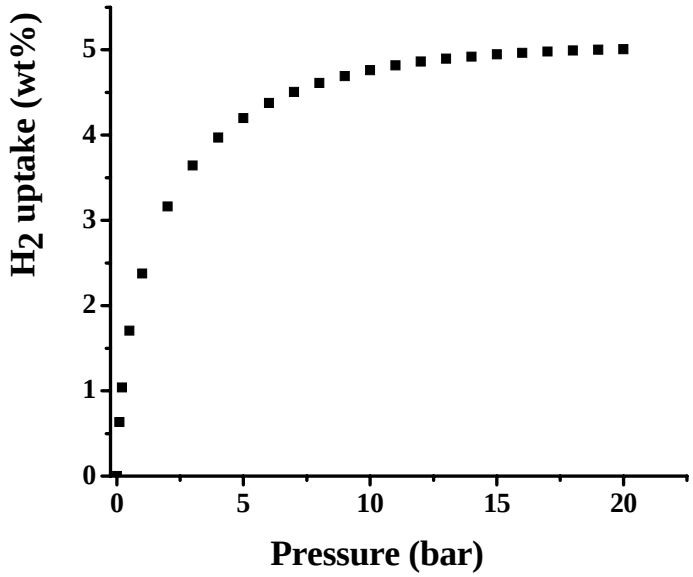


Figure S4. High pressure hydrogen adsorption isotherm of MOF **1a** at 77 K.

References:

1 (a) I. Aujard, J.-P. Baltaze, J.-B. Baudin, E. Cogné, F. Ferrage, L. Jullien, É. Perez, V. Prévost, L. M. Qian and O. Ruel, *J. Am. Chem. Soc.*, 2001,**123**, 8177. (b) G. J. Bodwell, D. O. Miller and R.J. Vermeij, *Org. Lett.*, 2001, ***3***, 2093. (c) H. Zhou, H. Dang, J.-H. Yi, A. Nanci, A. Rochefort and J. D. Wuest, *J. Am. Chem. Soc.*, 2007, **129**, 13774.